

**VIBRATZ**

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# **VIBRATZ**

## **Version 2.3**

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## Background

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# 2 General Procedure for Input

You should read the section on [Operation - Windows, Menus and Dialogs](#) to become familiar with the basic elements of the VIBRATZ program itself.

The first step is to enter the basic structural data, which is in the dialogs of the [Input](#) menu, or buttons in the [Startup Window](#). There are basically three ways to enter the data, through the **New** or **Import** buttons or options in the [File menu](#); or by modifying an existing file.

The **New** option will step through the dialogs which are usually mandatory for input of new data. This process is described below.

The **Import** option will read data from a file of one sort or another. Crystallographic data files will usually provide most if not all of the information needed in the Input menu, but molecular files may provide only part of the necessary data, namely the atomic coordinates

If you want to enter data for a compound which is closely related to one you have already done, it may be easiest just to change only certain parts of the input, for example the atomic positions and/or symmetry, or perhaps just the atomic weights.

#### [Title/Axes dialog.](#)

*Molecules.* All the **Lattice translation** boxes at the bottom of the dialog must be unchecked for a molecule. Normally the atomic coordinates for a molecule are on Cartesian axes, so axis lengths should be 1.0 and interaxial angles should be 90 degrees. One possible exception might be molecules with trigonal or hexagonal symmetry, for which an interaxial gamma angle of 120 degrees simplifies the symmetry matrices. VIBRATZ uses the gamma angle to distinguish between hexagonal and Cartesian axes and should use the correct symmetry matrices.

*Crystals.* All the **Lattice translation** boxes at the bottom of the dialog must all be checked for a crystal.

Although VIBRATZ will ultimately use only the atoms in the primitive unit cell, you must enter here the axes for the conventional Bravais cell, which may be non-primitive.

In the case of trigonal rhombohedral crystals you can choose either primitive axes or non-primitive hexagonal axes. If you choose rhombohedral axes, VIBRATZ will automatically derive the appropriate [Pre-Calculation Rotations](#) (below) to bring the 3-fold symmetry axis parallel to z, as required for proper symmetry analysis. The choice of rhombohedral/hexagonal axes should agree with the space-group setting in the [Symmetry](#) option. The axes for monoclinic crystals should be consistent with the atomic coordinates, but if the second setting is used (unique axis b), the axes, atoms and symmetry matrices must be rotated so that the unique axis is parallel to z. VIBRATZ detects this setting and automatically enters the correct rotations in the [PreCalculation Rotations](#) dialog (below).

*Polymers.* One or two of the **Lattice translation** boxes at the bottom of the dialog should be checked.

#### [Symmetry dialog.](#)

*Molecules.* Molecules should either have no symmetry or point-group symmetry (not space-group symmetry). The symmetry matrices supplied by VIBRATZ, whether in internal form for crystallographic point groups or in files for non-crystallographic groups, have orientation as



follows. Any unique axis is parallel to z. If "horizontal" two-fold axes perpendicular to the unique (normally high-order) axis are present, one of them is parallel to the x-axis. If there are vertical mirror planes, but no horizontal 2-fold axes, one of the mirror planes is perpendicular to the x-axis. For icosahedral groups, one 5-fold axis is vertical and an adjacent 3-fold axis is in the x-z plane.

If the atomic coordinates for your molecule are not consistent with these orientations, there are two alternatives. First, the atomic coordinates may be rotated around the z-axis with an option in the [Input Atoms](#) dialog. Second, you could supply symmetry matrices consistent with your orientation, reading them in with the **Symmetry from file** option in the [Point-Group Symmetry](#) dialog. This might require different basis functions from the standard ones (see [Making Symmetry Files](#)), or rotations as in the next paragraphs.

*Crystals.* The normal choice of symmetry option is [Space Group](#), but if you have imported a file the option may be [Custom Symmetry](#).

*Polymers.* Polymers should normally use [Space Group](#) or [Custom](#) symmetry. Translations in one or two directions should be disabled in the [Title/Axes dialog](#) dialog. The chosen space group should not have screw-axis, glide-plane or centered-lattice translational components in a non-polymer direction.

#### [Pre-Calculation Rotations.](#)

This is intended primarily for space groups which do not have the standard orientation described above (see [Space Group Symmetry](#)); it rotates both the symmetry matrices and the atoms in order to make the orientation consistent with the basis functions used for symmetry analysis. The proper rotations should usually be determined automatically when space-group symmetry is specified, and this dialog does not normally appear in **New** input. It is not necessary for point groups unless a custom set of symmetry matrices with non-standard orientation is read in with the **Symmetry from file** option in the [Point-Group Symmetry](#) dialog, or if a non-standard orientation is used in the [Custom Symmetry](#) option.

#### [Input Atoms dialog.](#)

VIBRATZ generates all the atoms in a molecule by applying the symmetry matrices to the input atom coordinates, so there is no need to enter all atoms. However, it is possible to enter all atoms, and VIBRATZ should identify those which are unnecessary and delete them with your permission. The **Atom type** for each input atom is typically the atomic number. The [Coordination](#) option can be very valuable in identifying the bonds and angles which may be important as internal coordinates (see **Forces** below) - it lists the bond distances and angles.

#### [Input Atom Types.](#)

The atom types list ties together the atom types assigned to the input atoms with the bond, angle and interaction specifications, and assigns atomic weights. The simplest way to do this in most cases is to use standard atomic numbers, and this is the default list. However, there are times when it may be necessary to assign different type numbers to input atoms of the same chemical species, for example when an element occurs in [Urey-Bradley](#) polyhedra with different

coordination numbers.

### Species dialog.

This dialog lists the species for the selected point/factor group, but before a calculation is made the number of modes in each species is not correct. If the checkbox for a species is not checked at this stage, that species will not be calculated and the number of modes will remain zero. Once a calculation has been made, these numbers are present and are saved in the data file.

### Observed Wavenumbers.

For least-squares adjustment, and general evaluation of the calculation, observed wavenumbers can be entered for each species.

The sequence of dialogs in **New** input may be halted at this point, without entering forces. If this is done, a symmetry analysis may be carried out without entering forces by checking the **Symmetry only** box in the Control Window and clicking on the **Calculate** button. This gives the number of modes in each species only, without information about frequencies or atomic motions.

**Forces.** If the structure is not well known, it may be useful to use the **Coordination** option in the Input Atoms dialog. This can give not only the coordination of each atom, but a sorted list of bonds and angles. Generally the strongest forces involve the chemically strongest bonds, which are usually the shortest. However, some modes are dominated by forces other than bonds and 3-atom angles, and the longer-range forces of this type are not so readily identified. Possible long-range forces included tau torsion angles, psi bond-plane angles and second-nearest neighbor "bonds". It should first be considered whether these more complex forces cannot sometimes be avoided by use of 3-atom angle forces in the direction perpendicular to the plane of the bond (or in two directions for 180 degree angles) - see Angle Force List. Otherwise it may be a good idea to carry out a calculation using only the stronger short-range forces, that is ordinary valence bonds and 3-atom angles, to 1) see what symmetry species are affected by an insufficient number of forces, and 2) study the structure in the Atoms graphics window. No harm is done if there is an insufficient number of force constants (or internal coordinates) overall or for a particular species - some frequencies may simply be calculated as zero or much lower than the true values. It should also be clearly understood that there is no limit to the number of force constants or internal coordinates which may be used - since all forces are converted to Cartesian coordinates, and symmetry analysis and solution of the secular equation are done using the Cartesian coordinates, redundancies among the internal coordinates need not be explicitly considered (but superfluous force constants may cause problems in least-square adjustment).

For crystals, particularly those with a small unit cell, the geometric relationships which call for more complex forces such as tau and psi angles and/or second-nearest neighbor bonds may not always be apparent in the part of the structure (basically one unit cell) which can be shown in the Atoms graphics window. It may be advantageous to examine the structure in a program such as ATOMS which can show larger portions (many unit cells) of the structure.

**Full Calculation.** Having completed the mandatory input in the dialogs of the Input Menu,

with at least some forces specified in the dialogs of the Forces Menu, clicking on the **Calculate** button with the **Symmetry Only** button unchecked will give a full calculation with output of frequencies and information about atomic motions and changes in the bonds and angles (depending somewhat on which output items are selected in the [Listings](#) dialog). In terms of adjusting force constants, the most informative part of the output is probably the parts labeled "En/grp", which is the fraction of the energy of the mode under consideration contributed by all the individual bonds, angle or interactions belonging to each input coordinate or force constant.

**Least-Squares.** In general, least-squares adjustment should not be attempted until the force model is complete, that is until the full number of force constants is specified. Even then, it may be necessary to limit refinement to only a few force constants at a time. The fastest way to change which force constants are refined is through the [Forces List](#) button in the [Control Window](#) - this gives a consolidated list of independent force constants.

Perhaps the main requirement of least-squares is that the assignment of calculated to observed modes be correct, that is the list of calculated modes in order of frequency within each species should correspond to the list of observed modes (of course the assignment of observed modes to species must also be correct). When the full number of modes in a species is not observed, the determination of which particular ones are absent (absent modes are signified in VIBRATZ by entering observed wavenumber 0.0) is extremely critical, especially if higher-frequency modes are absent. Correct assignment and correspondence of modes becomes more difficult, and requires more exact pre-adjustment of force constants, the more frequencies there are in a species and the fewer restrictions there are on the nature of the modes because of symmetry. This consideration being met (not a trivial requirement), the least-squares process is capable of adjusting force constants over a considerable range, especially if only one or a few are done at a time.

Some force constants may only appear in certain species, and both [Species](#) and force constants (most easily with the [Forces List](#) button in the [Control Window](#) ) may be omitted from a least-squares calculation to take advantage of such situations. The force constants or internal coordinates which participate in each species are not directly determined by the symmetry analysis in VIBRATZ (as they would be in a symmetry analysis based on internal coordinates), but the average contribution of each force constant to each species is given in the [Output](#).

### 3 Operation - Windows, Menus

#### Windows

VIBRATZ uses five types of windows; the **Start-up Window**, the **Control Window**, the **Spectra Window**, the **Atoms Window**, and **Text Windows**.

[Start-up Window](#). This window allows entry of a **New** data set, **Opening** an old Vibratz (or VIBRAT) data set, or [Importing](#) structural data from various types of molecular and crystallographic data files. Once a data set is present, this window is not shown - the Control window appears in its place.

[Control Window](#). This window controls the overall operation of VIBRATZ once a data set is

present. It is actually a dialog with standard controls. It is present whenever there is a data set in memory. Among other things, the Control Window determines whether the other main types of windows are present. The [Output](#) window (a Text Window - see below) appears only if the **Window** radio button in the **Output file** group is checked. The Spectra Window and Atoms Window appear after calculation only if the corresponding boxes are checked. The **Calculate** button causes a calculation or re-calculation, and the Spectra, Atoms and Output windows are redrawn.

[Spectra Window](#). This window displays synthetic infrared, Raman and or NRVs spectra. The parameters controlling the calculation of intensities and appearance of the plot are in the [Spectra Plot Parameters](#) dialog in the [Settings](#) menu. This dialog may also be accessed with a button in the [Control Window](#). The Window itself has a Dialog Bar on its upper edge, which allows selection of the spectra shown, i.e. combined or individual components of IR and/or Raman spectra. The infrared spectra are shown in the upper half of the window, with absorption going downward, while Raman spectra are shown in the lower half, with scattering going upward.

[Atoms Window](#). This window displays a drawing of the atoms in the structure with vectors indicating relative motions in the normal modes. The parameters controlling the appearance of the plot are in the [Atoms Plot Parameters](#) dialog in the [Settings](#) menu; this dialog may also be accessed with a button in the [Control Window](#). When this window is active, there is a [Rotation](#) menu present in the menu bar. The Window itself has a Dialog Bar on its left edge, which allows simple rotation, selection of the mode displayed, and changes of certain other parameters.

[Text Windows](#) - [Output Window](#), [Bonds \(Coordination\)](#) window. These windows, which display results of calculations in textual form, are standard text-edit windows. Each displays the contents of a text file, whose name is given in the title bar of the window. The text may be changed, deleted and printed out, using the standard menu commands for text editing. The menu bar which is present when a text window is active is completely different from the menu bar present which is present when the Control, Spectra or Atoms Window is active - the Text Window menu bar only shows commands pertaining to editing the current text file. To restore the menu bar which allows access to the current VIBRATZ data set you must make one of the other windows active by clicking on it, or by selecting it in the [Window](#) menu.

## Menus

Each of the four types of window has a different Menu Bar (which is present in the window itself in MS Windows, and in the full-screen position in Macintosh). The menu bar for the Control window has entries for editing the data; the menu bar for the Spectra and Atoms windows have entries for output and in the case of the Atoms window for special [Rotations](#). The menu bar which is present when a Text window ([Output](#) or [Coordination](#)) is active has entries for editing and changing fonts, etc.

### 3.1 Startup Window

You should see this window only when there is no VIBRATZ data set in memory. To load a data set, use the **New**, [Import](#) or **Open** commands in the file menu, or the buttons with the same names.

The following commands are available in the File Menu:

**New** - This starts a new data set, stepping through the dialogs of the [Input menu](#), and optionally through those of the [Forces menu](#).

**Open** - Open an existing VIBRATZ file, either a current .VBR data file, or a .VIB file from the old VIBRAT program. Also will open .VBD text files giving output from previous runs.

[Import File](#) - Import atomic coordinates and other parameters from a variety of crystallographic and molecular file types.

**Page Setup** - Sets parameters for printout, such as number of copies and page size.

**Exit/Quit** - Quit VIBRATZ.

You can also access dialogs in the [Settings Menu](#).

### 3.2 Control Window

This window controls the overall operation of VIBRATZ. It is similar to a dialog with standard controls, but it cannot be dismissed without closing the current data set. It is present whenever there is a data set in memory. If no Control Window is present, go to the [File menu](#) and select **New**, **Open** or **Import File**.

See the complete list of [Menu](#) options

**Save, SaveAs, Open, Close** buttons. These buttons duplicate some of the standard functions in the [File menu](#). However, these buttons may be more convenient and safer to use than selecting the functions in the [File menu](#). If the [Output Window](#) or another of the Text windows (see [Operation - Windows, Menus, Dialogs](#)) is active, the commands in the [File menu](#) pertain to that text file, not to the VIBRATZ data set and thus it is quite possible to **Save** (for example) a text file when you really mean to **Save** the current VIBRATZ data set. If you click on the **Save** button in the Control Window, it is always the VIBRATZ data set which is saved.

**Calculate** button. This carries out a normal-coordinate calculation, using the data input through the dialogs in the [Input](#) and [Forces](#) menus. This always causes the **Output file** (below) to be rewritten. If no bond and/or angle forces have been entered (Forces menu), the calculation will be carried out as if the **Symmetry only** box (below) were checked.

**Open** button. This will open an existing .VIB or .VBR data file. Since VIBRATZ only does one problem at a time, the current file will be closed (if changes have been made you are asked if you want to save them).

**Output File.** VIBRATZ always writes the results of the calculation to an [Output File](#), named *infile.VBD*, where *infile.VBR* is the name of the data file. This is a standard ASCII text file, which may be read and modified with any word processor. If the **Window** radio button is checked the contents of this file are shown on screen in a Text window, which has its own menu bar with editing options. The **Listings** button brings up the [Listings](#) dialog, allowing selection of what parts of the output are written to the file.

**Symmetry only.** If this box is checked, VIBRATZ does not actually calculate frequencies, but only determines the number of normal modes in each symmetry species. The results are printed in the [Output](#) file, and will also be shown in the [Species Data](#) dialog in the **Input** menu. If the **Atoms plot** box is checked, the atoms (only) will also appear in the [Atoms Window](#).

**Frequencies only.** If this box is checked the calculations of atomic displacements, changes in internal coordinates and intensities are omitted. This can speed up the calculation considerably, especially for smaller structures. However, the time required for these calculations tends to be linearly proportional to the number of modes, whereas the time required for the actual solution for frequencies is proportional to a higher power of the number of modes in each species.

**Spectrum plot.** If this is checked, sythetic spectra will be drawn in the [Spectra Window](#). The **Parameters** button brings up the [Spectra Plotting Parameters](#) dialog in which the various parameters can be set. The selection of infrared and/or Raman components which are shown in the spectra is made with the controls in the Dialog Bar of the [Spectra Window](#) itself after it appears.

**Atoms plot.** If this is checked, the atomic structure will be drawn in the [Atoms Window](#), with vectors representing the atomic motions in the particular normal mode selected. The **Parameters** button brings up the [Atoms Plotting Parameters](#) dialog in which the various parameters can be set. The [Atoms Window](#) itself has a Dialog Bar which allows simple rotations and selection of the particular mode which is shown. The mode may also be selected in the [Select Mode](#) dialog in the **Settings** menu.

You can see the atomic structure before forces are entered by clicking on **Calculate**, after checking the **Symmetry only** box (above). If fact, if there are no bond or angle forces specified the calculation will be carried out as symmetry only, and there will be no atomic displacement or mode information in the plot.

**Motion file (.mot).** If this is checked, a file is written with the atomic displacements in all modes, for use in other programs, such as ATOMS, which can plot the structure in more elaborate ways than VIBRATZ.

**NRVS** check box. This enables the special features of VIBRATZ for Nuclear Resonance Vibrational Spectroscopy. If you do not have NRVS data or wish to model an NRVS spectrum, uncheck this box.

**NRVS Parameters** button. This calls up the [NRVS parameters](#) dialog.

**Spectrum file (.spc).** If this is checked, a file is written with the calculated intensities of all modes. This includes the individual components (x, y and z for infrared and the six cross-



products or combinations thereof for Raman) and the spatial averages.

**Cartesian forces.** VIBRATZ may optionally use Cartesian atomic forces instead of valence forces or internal coordinates. In this case a matrix of Cartesian atomic forces is read in, and any forces entered in the dialogs of the [Forces](#) menu are ignored. The input file is specified in the [Cartesian Atomic Forces from File](#) dialog, called up with the **Cartesian Forces** button.

The **Units for angle forces option**, formerly in this dialog, has been moved to the [Angle Forces](#) dialog.

**Forces List.** Once the specifications for the forces or internal coordinates have been entered in the dialogs of the [Forces](#) menu, the easiest way to change the force-constant values or select which ones are subject to least-squares adjustment is through the [Forces List](#) button. This gives a single list of all the current force constants.

[Mean-Squares](#) button. This will compute the mean-square changes in interatomic distances, for use in calculating EXAFS

[Isotopes](#) button. This controls isotope substitution in up to two configurations beyond the base or non-substituted configuration - see [Isotope Configurations](#)

**Least-squares iteration.** VIBRATZ can do least-squares adjustment of the force constants in three different ways, analytical refinement on frequencies, step-by-step refinement on frequencies, or step-by-step refinement on intensities for NRVs spectra (and also step-by-step refinement on both frequencies and NRVs intensities). Different parameters appear at the bottom of the Control Window depending on which option is selected.

Note that entire species may be omitted from the calculation, and from least-squares, with the [Species](#) dialog in the Input menu. Also, individual modes may be omitted, using the settings in the [Observed](#) dialog in the Input menu.

-----  
**1) Least-Squares - Analytical method.** This assumes that the calculated atomic motions for each mode are correct, and calculates the change in the force constants required to make the calculated potential energy agree with observed (see [Theory and Implementation](#)). This method is not supported for [Isotope Configurations](#).

*Parameters.* The **End criterion** determines when the cycles are terminated. For frequency refinement only, if the improvement in the average squared deviation in wavenumber for all modes is smaller than this value the adjustment is terminated, keeping the new adjusted values. If the average deviation worsens, the iteration is terminated and the force constants revert to their values before the current cycle. This can usually be set quite small, 0.01 or less, unless computation time is a problem. However, if it is too small in comparison to either the **Reduction factor** or the step-by-step **Increment**, the refinement may terminate prematurely. The **Reduction factor** multiplies the calculated change in each force constant - a value less than 1.0 will potentially reduce overshoot, but will give slower conversion.

The observed wavenumbers are entered in the [Observed](#) dialog in the Input menu. The modes

must be entered in decreasing order of wavenumber for each species. If a mode is not observed, it is given a wavenumber of zero.

-----  
**2) Least-Squares - The step-by-step method** (on mode frequencies) simply varies each selected force constant by the given increment until there is no longer any improvement in the squared deviations.

*Parameters.* The **Fcon Increment** is simply added and/or subtracted from the last value of each force constant until there is no improvement. If the **Order** is up-down the increment will be first added, and if there is no improvement the value of the force constant will revert to the original and the increment will be subtracted. If the order is down-up the process will start with subtraction. It may be a good idea to refine from the original values one way, then re-read the file and try the other way. The **End criterion** of earlier versions is no longer used - the increment is added or subtracted until either the sum of squares increases, or the **Maximum change** in each fcon is reached (this condition will be noted in the refinement output).

The step-by-step method does not require that the number of force constants be less than or equal to the number of observations. The force constants will be adjusted in the order given in the Forces menu, or the **Forces List** in this dialog, and thus any redundant or correlated force constants at the bottom of the list will tend to be adjusted less than those at the top. For example, there is a strong correlation between polyhedron angles and the corresponding Urey-Bradley X-X repulsion forces, and the order in the list dictates that angles will be refined first. If it is desired to refine primarily on the X-X forces the angles should be deselected from refinement in preliminary cycles.

Additional [Isotope Configurations](#) may be included using the **Isotopes** button.

-----  
**3) Least-Squares - NRVS intensity.** See [Spectra Window](#) for details of NRVS spectra. This uses the same step-by-step method of varying force constants as the step-by-step method on mode frequencies, but the quantity minimized is the average sum of squared deviations between calculated and observed NRVS intensity for the specified wavelength limits.

*Parameters.* The **Increment**, **Maximum change** and **Order** are the same as for Step-by-Step (frequencies). The **Low frequency limit** and **High frequency limit** are the same as in the [NRVS Parameters dialog](#), where detailed parameters of the NRVS spectra are set. The Refine box determines whether the refinement is on isotopes using the spatial average spectra, or on orientations using the base isotope configuration (see the [NRVS Parameters dialog](#)).

The individual NRVS frequencies used are those of the input data - frequency intervals can no longer be set.

If the **Use frequency deviations also** box is checked, the refinement will be on the sum of a) the average squared NRVS intensity deviations, plus b) the average squared deviation of observed and calculated wavelengths:

$$\text{Sum of squared deviations} = F(\text{nrvs}) * \text{sum}[\text{Dev}(\text{nrvs})^2] / N(\text{nrvs}) + F(\text{frequency}) *$$



$\text{sum}[\text{Dev}(\text{freq})^2] / N(\text{freq})$

Here the F factors are the **Factor for NRVs deviations** and the **Factor for frequency deviations**. VIBRATZ stores the NRVs spectra in units of cm<sup>-1</sup> for frequency and cm for intensity, so the Factor for NRVs deviations should be on the order of 1000 to get results in the single-digit range - the factor for frequency deviations can be around 1.

Additional [Isotope Configurations](#) may be included using the **Isotopes** button.

-----  
*Recommendations for least-squares refinement on frequencies.* For frequency refinement, the step-by-step method, added to VIBRATZ after the analytical method had been in use for some time, seems to be much more powerful. In fact the analytical method may be dropped if it is not found to give better results in at least some cases. With either method least-squares adjustment is not likely to be successful unless the average deviation between calculated and observed at the start is less than the average frequency difference between modes in each species - your model of the forces must be essentially correct (see [Theory and Implementation](#)).

## Errors and Correlations

After Step-by-Step refinement, VIBRATZ can provide some information about the reliability of the calculation. If the Do Errors box is checked, each fcon is stepped away from the minimum until the total deviation is increased by the specified fraction.

If the Do correlations box is checked, to get the correlation between two fcons, one fcon is moved away from its value at the minimum and then the second fcon is adjusted to re-minimize the sum of squared deviations.

These calculations involve repeated complete solutions of the normal equations, so they can be very time-consuming.

### 3.2.1 Forces List

**Dialog Box: Forces List** [[Control](#) window]

This dialog provides a quick way to change force constant values, or to add or remove them from the list of force constants which are being refined by least-squares.

The force constants are listed 10 at a time - to see others, click on the **Last 10** or **Next 10** buttons.

To change the specifications for individual force constants, as opposed to the value of the force constant, you must go to the individual dialogs in the [Forces](#) menu.

The numbers of the force constants correlate with the "Fcon" numbers in the [Output](#) and in the dialog of the [Forces](#) menu. The four numbers under **Type #s** give some information about the specifications for the force constant - if there are more than one specification for a given force

constant, only the first is listed here. For bonds, 3-atom angles, tau angles, psi angles and Urey-Bradley X-X bonds, the numbers are the atom types, exactly as in the specifications (dialogs in the [Forces](#) menu). For Urey Bradley kappa force constants, the numbers are 1) the number of the U-B polyhedron specification in the list in the [Urey-Bradley Data](#) dialog; 2) the coordination number; 3) the type number of the central atom; and 4) the first type number for ligands (which is often the only one).

Note that when Urey-Bradley models 1) or 2) are in effect (see the [Urey-Bradley Data](#) dialog), polyhedra with coordination number other than 4 or 6 do not use kappa. Thus such polyhedra will not have an entry for kappa in this list.

### 3.2.2 Mean Square Amplitude

**Dialog Box: Mean Square Amplitude Determination** [[Control window](#)]

This option is primarily for use in EXAFS calculation. It will list the mean-square changes in bond distances to a specified atom (**Input atom number** from the list of [Input Atoms](#). Use the number in the list, not the atomic number), out to the specified **Maximum distance**, and a given **Temperature** in Kelvin. Screen out zero and dubious frequencies with the **Minimum frequency** value.

Results will be in a separate text window. Atoms are listed by symmetry-equivalent groups, with contributions from each mode.

### 3.3 Spectra Window

This window displays synthetic spectra, either infrared (absorption downward) or Raman and NRVS (scattering upward), or both. It appears or is refreshed after a calculation if the **Spectra Plot** box is checked in the [Control Window](#).

See the complete list of [Menu](#) options

Individual modes are shown as vertical bars. The **Parameters** button brings up the [Spectra Plot Parameters](#) dialog, for setting of several parameters which influence the appearance of the spectra.

The **Isoconfig** ([Isotope Configuration](#)) spin control selects which isotope configuration is being shown in this window - the base configuration (no isotope substitutions) is number 1.

The **Output** combo box allows file or printed output (these options are also in the File menu for the window). The **Print Current** option will print an image of the current spectra; the **Print All** option will print all the polarized components (not the averages) in pairs, in the order listed in the combo boxes. Since the [Print](#) option in the [File](#) menu prints different things depending on which window is active ([Output](#) file Text window; [Spectra](#); [Atoms](#)), using these buttons insures that the Spectra image is printed.

For degenerate species only one of the (identical) allowed components is present. Generally, x is preferred over y and z, xx-yy over xy, and xz over xy and yz.

The **Infrared** and **Raman** combo boxes allow selection of average spectra, individual species and polarization components, or no spectra.

For the Raman spatially averaged spectrum the upper curve represents the parallel polar orientation, and the lower curve the perpendicular polar orientation. The lower curve is simply obtained by multiplying the calculated Raman intensity of each mode by its depolarization ratio (see [Theory and Implementation](#)).

The **NRVS** (nuclear resonant vibrational spectroscopy) spectrum tracks the motions of certain nuclei, especially  $^{57}\text{Fe}$ , which are subject to a certain kind of gamma-ray (or X-ray) absorption. As implemented in VIBRATZ, an NRVS spectrum shows a peak for each vibrational mode in which the  $^{57}\text{Fe}$  atoms move, and the intensity is proportional to the fraction of kinetic energy in the iron atoms. VIBRATZ identifies iron atoms (assumed to be isotope 57) as any atoms with type number 26 mod 100 (26, 126, 226...). The standard atom type number 26 has natural atomic weight, so for very precise results the weight of any atom types involved should be changed to 57. If an NRVS spectrum for any other isotope is necessary, that atom(s) can simply be assigned type number 26 mod 100. Type number 26 should then be given the actual atomic weight for this isotope.

If the **PED** (potential energy distribution) box is checked, the lowermost plot will show as many as four curves, each with the fractional contribution to the energy of modes from an FCON, or group of FCONs. The color of each curve, and the FCONs which are included in each, are set with the [Spectra Plot Parameters](#) dialog, called with the **Parameters** button. The curves may represent raw fractions of the energy at each mode, or the weighted intensity for infrared, Raman or NRVS, as selected with the **Mode** parameter in the [Spectra Plot Parameters](#) dialog.

The maximum positive fraction is printed out on the top line of a legend in the upper left of the PED section of the window - this number may represent raw fractions of the energy at each mode, or the weighted intensity for infrared, Raman or NRVS, as selected with the **Mode** parameter in the [Spectra Plot Parameters](#) dialog. The second and successive lines give in parentheses the FCONs which contribute to each curve.

### 3.4 Atoms Window

This window shows the atomic structure with lines or vectors attached to each atom showing the displacement in the selected vibrational mode. It appears or is refreshed after a calculation if the **Atoms Plot** box is checked in the [Control Window](#).

See the complete list of [Menu](#) options

The dialog bar on the left edge of the Atoms Window allows manipulating the structure image in the window in several ways. For more elaborate ways of rotating the image, see the dialogs in the [Rotation](#) menu.

At the top of the dialog bar is a small sketch of the current orientation of the original structure axes. These are called a, b and c, which are equivalent to x, y and z for a molecule using a Cartesian coordinate system. The letters are attached to the positive ends of the axes, and the end of the axis which points out of the screen (towards the observer) is drawn with a heavy line.

Below this are buttons for instantaneous rotation on the x, y and z Cartesian reference axes, from top to bottom. The amount of rotation, in degrees, is given in the edit box below the buttons. The default angle value can be set in the [Basic Parameters](#) dialog ([Setting](#) menu).

Below this is the scale factor which is applied to atomic displacements. This factor is applied only in this window. Other factors which affect the magnitude of the atomic-motion vectors are set in the [Basic Parameters](#) dialog ([Setting](#) menu). The displacements as printed in the [Output](#) window, and as used to derive the spectral intensities, need to be small to satisfy the assumptions of the calculations, so it is normally necessary to supply a large magnification factor in this Atoms Window, on the order of 50-100.

The **Replot** button is needed after changing the **Scale** or **Parameters** (below).

The **Parameters** button brings up the [Atoms Plot Parameters](#) dialog ([Settings](#) menu), for setting several aspects of the appearance of the plot.

The [Print](#) button causes printing of the Atoms image. Since the [Print](#) option in the [File](#) menu prints different things depending on which window is active ([Output](#) file Text window; [Spectra](#); Atoms), using this button insures that the Atoms image is printed.

The [Mode](#) button brings up a dialog which allows selection of the particular mode which is being viewed. There is an automatic replot when the mode is changed.

Clicking on an atom in the window itself will bring up the [Generated Atom Data](#) dialog or if atoms are superimposed, the [Atoms at Cursor](#) dialog. These dialogs give information about the specific atom.

**Cursor Mode** radio buttons. In **Atom ID** (identification) mode, clicking on the left mouse button will identify atoms - see [Atoms at Cursor](#). The cursor in this mode is a cross. In **Rotation** mode, clicking and dragging rotates the structure. The cursor in this mode is a circular arrow. Clicking and dragging in most of the window will rotate around the y and z Cartesian axes, in the plane of the screen. Clicking and dragging near the left or upper edges will rotate about the z axis, perpendicular to the screen.

The atomic motions shown in this window are those of the main isotope configuration, not any other isotope configurations. To see which modes in isotope configurations correspond to these, it may be necessary to refer to the "Main" column in the mode lists for isotope configurations near the end of the text output, since the order of modes may be different in different isotope configurations.

### 3.5 Text Windows

See also [Output Window](#), [Bonds \(Coordination\)](#).

These windows, which display results of calculations in textual form, are standard text-edit windows. Each displays the contents of a text file, whose name is given in the title bar of the

window. The text may be changed, deleted and printed out, using the standard menu commands for text editing.

Text windows have their own Menu Bar, containing File, Edit, [Window](#) and [Help](#) menus.

## 4 Menus

Not all menus are present in the menu bar for each type of window, and the contents of each (especially the File menu) may vary - see the individual menus for details.

[File](#) - Contains the usual Open, Save, Print, etc. commands, as well as commands for graphics output (metafiles (Window) PICT files (Macintosh) and raster files).

**Edit** - In Text windows, has standard Cut, Copy, Paste and Select All items for manipulating text.

[Input](#) - (Control only) This is for input of basic structural parameters.

[Forces](#) - (Control only) For specification of the various types of bond and angle force.

[Settings](#) - For setting basic operating parameters and aspects of the display in the Spectra and Atoms Windows.

[Rotation](#) - (Atoms) Allows precise rotation and alignment of the structure image.

[Window](#) - Allows selection of the various windows, and selection of the font for Text windows.

[Help](#) - Allows direct access to the Help system.

### 4.1 File Menu

The File menu appears in the menu bar for all types of windows, but not all topics are present for each window. The type of Window in which each topic is present is given in parentheses.

**New** (Start-up, Control) - This starts a new data set, stepping through the dialogs of the [Input menu](#), and optionally through those of the [Forces menu](#).

**Open** (Start-up, Control) - Open an existing VIBRATZ file, either a current .VBR data file, or a .VIB file from the old VIBRAT program. Also will open .VBD text files giving output from previous runs.

**Save** (Control) - Save the current data set.

**Save As** (Control) - Save with a different name.

**Close** (Atoms, Spectra, Text) - Close the current window.

**Open Recent** (Start-up, Control) - Allows **Opening** of recently-used files.

**Import File** (Start-up, Control) - Import atomic coordinates and other parameters from a variety of crystallographic and molecular file types.

**Print** (Spectra, Atoms, Text) - Printouts of various types. What is printed depends on which window is active. When the **Control Window** is active, this item is not available. When the **Atoms Window** is active, the structure image is printed, when the **Spectra Window** is active, the spectra are printed, and when a text window is active, that text is printed.

**Print Preview** - Gives a screen preview of the printed page(s).

**Page Setup** - Sets parameters for printout, such as number of copies and page size.

**Calculate** (Control) - Carries out a calculation, with output to the .VBD file as well as to the **Output** window (if selected in the **Control Window**). It is usually easier to use the **Calculate** button in the **Control Window**.

**Metafile [Windows]** or **PICT [Macintosh]** (Atoms, Spectra) - Writes Windows metafiles, including enhanced (32-bit) files, or Macintosh Pict files of the **Spectra** or **Atoms** Window images.

**Raster File** (Atoms, Spectra) - Writes raster or bitmap files in .BMP, .PCX, .TIF or .PNG format of the **Spectra** or **Atoms** Window images (.PNG only for Macintosh).

**Save Screen** (Atoms, Spectra) - Saves the exact contents of the client area of the current window (excluding borders, menus, etc.) to a bitmap file, .bmp in the case of Windows or PICT in the case of Macintosh, or places the bitmap image in the clipboard, from which it can be Copied to other applications.

**Exit/Quit** - Quit VIBRATZ.

#### 4.1.1 Import Data File

**Dialog Box: Import File** [**File menu** or button in Startup or Control Window]

If there is a data set in memory which has been modified, you are asked if you want to save the changes.

If there is more than one data set or phase in the file, the **Data Sets...in Import File** dialog will present you with a list. The name of the VIBRATZ data file will be taken from the name of the file, and the title (**Title/Axes** dialog in the Input1 Menu) will be taken from the data set or phase. The extension .VBR will be appended to the structure file.

**File Extension.** The three-letter extension (.xxx) which identifies the file type may be specified here - only files of that type will be shown in the **Open File** dialog. To show all files, enter ".\* ".

**Source of symmetry** (some formats lack this option). If you select **Use positions as xyz**, in which symmetry operators are given in the form of positions in the general equipoint as in the *International Tables*, the symmetry option (Input1 Menu) will be [Custom Symmetry](#). After import, you may need to check the [Symmetry](#) option to be sure the centric/acentric choice and the Bravais lattice type are correct (some formats include a center of inversion and/or lattice centerings in the operators and some do not). If you select **Space group symbol**, the [Space Group](#) symmetry option will be used. The Hall symbol, the Hermann-Mauguin symbol, and then the *International Tables* number will be used in that order if present. If you select **Use positions as xyz** and the information on Settingss is not present, the symmetry option will default to **Space group symbol**. The H-M space-group symbol, Hall symbol, and space-group number are always read if present.

**Get atom types from** (some formats lack this option). VIBRATZ will try to assign an atomic number to each input atom either from the first one or two characters of the atom label itself, or from a separate atom type label if that is present. In diffraction refinement file formats, this separate atom type label typically identifies the scattering factor, and it is your choice whether this or the atom label (if either) will identify the element.

**Import As** crystal or molecule. For some file types, such as CCDC, you can import the structure as either molecule(s) or a crystal. The molecule option may give all molecules in the unit cell, not just one.

The following types of file may be imported

----[FREE-FORM \(.INP\)](#) - Files of this type are read and written by ATOMS and CRYSCON (Shape Software). This option can be used to import atomic coordinates from almost any kind of text (ascii) file.

----**CCDC FDAT** - files from the Cambridge Crystallographic Data Centre.

----**SHELX .INS** - files from the program system of Prof. G. Sheldrick.

----**CIF** - Crystallographic Information Files. Some CIF files (with filename extensions .CIF) are "mmCIF" files, containing data for molecules with atomic coordinates on Cartesian axes. See below for possible conversion of these back to fractional crystal coordinates.

----**DBWS/LHPM** - Rietveld input files.

----[ICSD](#) - Inorganic Crystal Structure Database files.

----**ORTEP** - Original or ORTEP II atom information.



----**XTLVIEW** - Drawing program.

----**ATOMS** - Structure drawing program from Shape Software.

----**PDB** - Protein Data Bank files. These files give Cartesian atomic coordinates for molecules, but may have the information required for transformation back to the original fractional crystal coordinates - see below.

----**RIETAN** - Rietveld program files.

----**GSAS** - Data files (.EXP) from the Los Alamos Lab system - may include magnetic vectors.

----**AM MINERAL** - Data files from the American Mineralogist structure data base.

----**FULLPROF** - All-purpose refinement program - may include magnetic vectors.

----**RAVEL ATOMS** - This program is not the same as ATOMS by Shape Software, but is for EXAFS Analysis.

----**WIEN2K** - The program package WIEN2k performs electronic structure calculations of solids using density functional theory (DFT). VIBRATZ will read the .struct input files, but will only recognize file extensions with three characters, so it may be necessary to rename the files, search manually in the File Open dialog (enter \*.struct) or use the "all files" option. Some files may have the space-group number and symbol, but the orientation may be ambiguous and **Use positions as xyz** should normally be selected in the Import File dialog.

---- **IZA (zeolites)** - Files from the International Zeolite Association database ([www.iza-structure.org/databases/](http://www.iza-structure.org/databases/)).

---- **GAUSSIAN.FCH or .LOG** - Formatted checkpoint or log files from the molecular-orbital program. Cartesian forces from this program can be converted to valence forces.

---- **SIESTA** - Files from the DFT program (<http://icmab.cat/leem/siesta/>) Cartesian forces from this program can be converted to valence forces.

*Importing PDB files and mmCIF files as Crystals.* In PDB files, VIBRATZ can use the information in the SCALEn lines (Cartesian to crystal transformation matrix) and the CRYST1 line to recover the fractional coordinates and space-group symmetry for the original crystal. In some cases this information is not present - if it is present you will be asked if you want to input the data as a crystal instead of a molecule. Note that the transformation matrix given in the SCALEn lines is sometimes not sufficiently precise



(because of limitation to 6 places after the decimal point) to recover the original unit-cell parameters (as given in the CRYST1 line) precisely. The cell parameters used in VIBRATZ are those derived from the transformation matrix, not from the CRYST1 line. After importing, you should check the cell parameters in the [Title/Axes](#) dialog and correct the crystal system - because of this problem the cell parameters are always imported as triclinic.

mmCIF files may have the same information, which in these files is in `_atom_sites.fract_transf_matrix` lines, and the importation procedure is the same.

#### 4.1.1.1 Data Sets, Phases or Crystals in Import File

**Dialog Box: Data Sets, Phases or Crystals in Import File** [[Import dialogs](#), [File menu](#)]

If you import a file containing more than one structure this dialog allows you to select among those present.

There is a maximum of 50 data sets for a single file; any beyond this limit will be ignored

#### 4.1.1.2 Import Free-Form File

**Import Free-Form (.inp) File** [[File menu](#) or button in Startup or Control Window]

See the [Import File](#) dialog for general aspects of importing atomic-structure data files.

This type of ASCII or text file may be used in either the [Input Atoms](#) dialog in the Input menu, or the the **Import** option in the **File** menu, to read in atomic coordinates alone, or to supply complete structure information. Such files are written by the program CRYSCON (Shape Software) which can be used to perform various types of crystallographic conversions, such as sub/supercell, change of origin, change of symmetry, etc. Listings of atomic coordinates from almost any source can be used as the basis of a free-form file.

All or part of the parameters for each input atom, namely label, fractional coordinates, type, radius and display colors and pattern numbers, can be read in. You can also supply default values for some parameters, so that the parameters neither need to be present on every line of the file, nor need to be supplied through the dialog.

Except for the **TITL** line, keywords and actual values to be read in should be separated by spaces or commas, and there should be no spaces within keywords or values. There is no need for alignment by column.

The input file may contain two overall types of lines; *General and crystallographic information* lines; and actual data or *atomic parameter lines*.

*General and crystallographic information lines.* These lines should all precede the atomic parameter lines. Each line consists of a keyword followed by one or more values or character constants. The keyword should start in the first column and be followed by at least one space before the actual values. Where more than one value is called for, they are separated by spaces. All of these lines are optional - when a free-form file is used for import (**File** menu), if any lines are absent, default values will be supplied. When a free-form file is read through the [Input Atoms](#) dialog in the Input menu, current values are kept if the corresponding line is absent.

**TITL** line. Up to 76 characters (may contain spaces).

**CELL** line. The unit-cell lengths in Angstroms and the interaxial angles in degrees (6 floating-point values). If the atomic coordinates are Cartesian, the axes should be 1.0 and the angles 90.0.

**SPGP** line. The Hermann-Mauguin or standard International symbol for the space group. There should be no spaces in the symbol, although there may be underscores (which are ignored when the symbol is interpreted).

**HALL** line. The Hall symbol for the space group. There should be no spaces in the symbol, although there may be underscores (which are ignored when the symbol is interpreted). If this line comes after the **SPGP** line (or that line is absent), the Hall symbol will be used in the [Space Group Symmetry](#) option.

**SYMM** lines. These give symmetry operators in "xyz" form, that is in the form in which the coordinates of the general position are listed in the *International Tables for X-Ray Crystallography*. Fractions must be given as integers separated by a slash ("1/2", "2/3"), rather than decimals ("0.5", "0.333"). The x, y and z positions must be separated by commas and there should be no spaces in the operator. There should be one line for each operator. If the space group is centrosymmetric, only half the operators need be given, if the origin is on a center of inversion. If the origin is not on a center, all operators must be given and the space group should be denoted non-centric in the **LATT** line. If these lines come after the **SPGP** and **HALL** lines (if present), the [Custom Symmetry](#) option will be used.

**LATT** line. This gives the Bravais lattice type (single capital character), followed by a space and 0 if the space group is centrosymmetric or 1 if it is non-centric.

**FACTOR** line. A single (floating-point) factor which multiplies all the fractional or atomic coordinates.

*Atomic parameter lines:*

The file should have all the information for each atom, except for temperature factors, on

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a single line with a maximum of 80 characters per line, and the values must be in *fields*, which are set off or delineated with either spaces or commas. There can be no spaces or commas within fields. The names of fields are given in the following in capitals, but in the actual input they may be lower case; all letters are converted to upper case when the line is read in.

**DEFAULT** lines supply values to the parameters, such as colors, which are not read in for each atom. If default values are not entered in this way, default values are obtained from the separate ELEMENTS file, using the chemical symbol of the atom which is assumed to be in the first two characters of the atom label. See the further description of **DEFAULT** lines and the ELEMENTS file below.

**FIELDS** lines. These lines set up the ATOMS input parameters which are to be read from the file, and the order in which they are to be read.. This is followed by the keywords giving the order of the fields. The allowed keywords are as follows (INTEGER fields may not contain a decimal point) - some of these fields are not used by VIBRATZ, but are given here in case they are seen in a file written by another program:

1) **LAB** - (6 characters maximum). Any label for the input atom may be used, but the label normally begins with the chemical symbol for the element. The first two characters may be used to determine default values for some of the parameters, as described below. The characters may be upper or lower case, but they are all converted to upper case after input. This is a required field.

2) **COO** - This actually denotes three floating-point fields giving the fractional atomic coordinates for crystals, or the absolute coordinates for molecules. After input, the coordinates are multiplied by the number in the FACTOR line, if this line is present. These are required fields.

3) **TYP** - This is the type which is used in force specifications - normally the atomic number. INTEGER

4) **RAD** - This is the radius used when the atom is plotted as a sphere. FLOATING-POINT \*\*\*IGNORED in VIBRATZ

5) **RMC** - This is the color for the atom rim or edge, in terms of three RGB components 0-255. 3 INTEGERS \*\*\*IGNORED in VIBRATZ

6) **FLC** - This is the color for the atom fill, in terms of three RGB components 0-255. 3 INTEGERS \*\*\*IGNORED in VIBRATZ

7) **RMP** - This is the pattern number or gray shade used in black-and-white display or output. This number is used only for wide lines. INTEGER \*\*\*IGNORED in VIBRATZ

8) **FLP** - This is the b/w pattern number for fills. This is used only if shading is off or the initial pattern number option is on. INTEGER \*\*\*IGNORED in VIBRATZ

9) **PEN** - This is the pen number used for atom outlines in pen plots. INTEGER \*\*\*IGNORED in VIBRATZ

10) **TFB** - Temperature factors in B or bij (beta) form, types 0 (anisotropic) or 6 (isotropic) in ORTEP. If this keyword is present, the temperature factor(s) are present on a second line for each atom, in up to six fields. The order is 11, 22, 33, 12, 13, 23. If the second value is absent or zero, the temperature factor will be read as isotropic. Note that ATOMS will save temperature factors only if at least one atom has non-zero for the first value or b11. \*\*\*IGNORED in VIBRATZ

11) **TFU** - Temperature factors in U or uij form, for anisotropic type 8 in ORTEP. Similar to TFB. Isotropic U values will be converted to B values (type 6 in ORTEP). \*\*\*IGNORED in VIBRATZ

12) **VEC** - Atomic vectors, e.g. for magnetic spins or vibrational displacements. If this keyword is present, the vector coefficients are present on a second line, in four fields. The first three are the relative components in the structure axes, and the fourth is the length. Vectors and temperature factors may not both be present. \*\*\*IGNORED in VIBRATZ

13) **DUM** - This designates a field (character, integer or floating-point) that exists in the input data line, but should be ignored by ATOMS.

Note that the actual atom data lines do not contain any keywords. The keywords in the FIELDS lines set up the sequence of parameters in each data line.

An example FIELDS line:

FIELDS DUM LAB COO TYP RAD

Some corresponding data lines:

```
1 C1 0.1234 0.2345 0.3456 6 1.2
2 H2 0.4321 0.5432 0.6543 1 0.1
```

Here the first field, which is simply a sequence number, must be ignored by ATOMS, and is designated with a DUM. The last field, RAD, is not used in VIBRATZ - atomic radius is fixed for each atomic type (not for each input atom) and specified in the [Atom Types](#) dialog.

Here is an example of some lines copied from an (old) ATOMS.STR file (spinel):

## FIELDS DUM LAB TYP COO RAD

1 MG1 12 .12500 .12500 .12500 .000

2 AL2 13 .50000 .50000 .50000 .000

3 O3 8 .26200 .26200 .26200 .000

There should normally be a FIELDS line at the beginning of the atomic parameter lines, but additional FIELDS lines can be inserted at any point to redefine the fields. If there is no FIELDS line, the fields are by default; LAB and COO.

In the actual data lines, fields denoted INTEGER above should not be more than 6 characters; the COO and RAD fields (floating-point) should not be more than 20 characters.

**DEFAULT line.** This is used to set particular default values for fields other than LAB or COO. DEFAULT must be the first 7 characters. Then the default values are indicated with the name of the field connected with an equals sign (with no intervening spaces) to an appropriate value. Example default line:

DEFAULT TYP=1 RAD=0.95 FLC=15

**ELEMENTS.DAT** file. This file, in the VIBRATZ folder, gives the default values for atom types as shown in the [Atom Types](#) dialog. These are used for import, or when defaults are selected in the [Atom Types](#) dialog. The first field in each line is the atomic number or other designated type number. The second field consisting of one or two characters, is usually the normal elemental symbol. The remaining fields give the default values for the radius, color (R, G and B values 0-255), a dummy (not used), weight and charge.

### 4.1.1.3 Import ICSD File

**Dialog Box: Import ICSD File** [[File menu](#) or button in Startup or Control Window]

This imports files from the Inorganic Crystal Structure Database. Four types of ICSD file are supported, classified according to source:

1) Files from the current CD-ROM database, accessed by the program **RETRIEVE**. The RETRIEVE files must be written from the DATA window using the PRINT option, not as export files (if there is sufficient demand, export files may be supported). That is, the file should be a copy of what is shown on the screen in the RETRIEVE program.

- 2) Files from the Canadian Scientific Numeric Database System (**CAN/SND**). This service may no longer be available. The files are referred to as CRYSTIN, but are different from original 3) CRYSTIN files.
- 3) Original **CRYSTIN** files, available from the Netherlands CAOS information system, from ETH (Switzerland) and perhaps other sources.
- 4) Files from the the ICSD World Wide Web site (barns.ill.fr/dif/icsd/).

In CAN/SND files, VIBRATZ will use the "NA:" line for the title; in RETRIEVE and original CRYSTIN files, VIBRATZ will use the first "MINR" line if present, otherwise it will use the "NAME" line.

VIBRATZ distinguishes among the four different file types by reading part of the main title or "Collection" line, which gives the ICSD index number:

- 1) RETRIEVE - " COL Collection Code "
- 2) CANSND - "ID: "
- 3) ORIGINAL - " \*\*\*\* COLLECTION CODE COL= "
- 4) WWW - " COL ICSD Collection Code "

In each case the index number follows the above excerpt. Note that in all file types except CANSND there is always a blank character in the first column.

Please contact Shape Software if you have ICSD files which cannot be read by one of these options. The best procedure is to send samples of the files by email or on a floppy diskette.

If there is more than one data set in a file, the [Data Sets...in Import File](#) dialog will appear, and you can select the data set. Each line will show the sequence number in the file, the ICSD number, and the first 24 character of the title as selected above. A maximum of 50 data sets can be listed in each file.

**Symmetry for RETRIEVE.** The crystal symmetry can be taken from the SGR line, which has the space-group symbol -this will result in the [Space-Group Symmetry](#) option; or from SYM lines, each of which contains one equivalent position or symmetry operator in xyz notation - this will result in the [Custom Symmetry option](#). For consistency it is best to use the symbol from the SGR line, but if this gives incorrect results because of a non-standard orientation, try selecting SYM lines. The symbol in the file has "S" added to the end for non-standard settings (i.e. origin not on a center of inversion), and in this case VIBRATZ automatically uses the equivalent positions, leaving the "S" on the end of the symbol. Thus manual selection of the equivalent-position option may seldom if ever be needed.

If there is more than one atom at a single position, only the first will be read in - occupancy factors are ignored.

#### 4.1.1.4 Import GAUSSIAN File

**Dialog Box: Import GAUSSIAN File** [[File menu](#) or button in Startup or Control Window]

This will import either a GAUSSIAN log (.log) file or a formatted checkfile (.fch or .fchk), obtaining the atomic coordinates and the [Cartesian force matrix](#). VIBRATZ will convert the force matrix from Hartrees/Bohr<sup>2</sup> to md/A and write a file named *infile.car* if the GAUSSIAN file is *infile.fch* or *infile.log* and will be set up to use Cartesian forces in this file.

Recent versions of GAUSSIAN can write the required information to a log file - the sections which CRYSCON requires are headed "Input orientation:" and "Force constants in Cartesian coordinates:". For older GAUSSIAN version it may be necessary to use a formatted checkfile - the required sections are "Current cartesian coordinates" and "Cartesian Force Constants"

It is assumed that no symmetry is being used by GAUSSIAN, and that all atoms are present in the input list, even if some are equivalent by symmetry - you can convert to a calculation using symmetry after the conversion is made (see below).

The following procedure can be used to import a GAUSSIAN or other molecular-orbital output file and convert the forces to valence force constants.

- 1) If some other type of molecular-orbital output file is being imported (not among the VIBRATZ-supported types), you can probably import the atomic coordinates using the Free-Form import option (cut-and-paste the coordinate section into a separate .inp file). If the Cartesian force matrix is in lower-diagonal form, it will probably be usable without modification (cut-and-paste into a separate text file with the .car extension). If the units are not md/A, it may be necessary to use a scale factor in the [Cartesian Forces dialog](#).
- 2) If you have some [observed frequencies](#), you can refine the Cartesian scale factor which appears in the [Cartesian Forces dialog](#) (Forces menu). To do this, just select any of the least-squares options and hit the Calculate button in the [Control Window](#). (while Use Cartesian forces is selected in the [Cartesian Forces dialog](#)).
- 3) You must set up a complete valence force field (Urey-Bradley forces are not currently supported for the conversion) in the other dialogs of the Forces menu. You may be able to import part or all of these force specifications using the Read Force File option in the Forces menu - the file must have been previously written by VIBRATZ for the same or a similar structure. The force constant values may be zero or dummies - they are not used in the conversion. However, it is best to insert nominal values, then do a calculation using these valence forces to make sure that there are no zero frequencies, i.e. that the forces are complete.

It is theoretically possible to use the bonds and angles in a [z-matrix](#) to describe the forces in any molecule, since they constitute a complete geometric description. The specifications can be entered with the [Manual Bonds](#), [Manual Angles](#) and [Manual Tau](#) dialogs in the Forces menu. In general, however, the z-matrix is a poor description because it uses torsional forces in place of 3-atom angles or even bonds (in cyclic molecules or parts thereof), and the torsion angles are not always valence angles (the legs are not bonds), and because dummy atoms are sometimes



used. That is, a z-matrix is usually not a good chemical description of a molecule.

4) Now select **Convert Cartesian to Internal** in the Forces menu. The results (new force constants) of a special calculation will be shown in the Output Window, and at your option the old or dummy valence force constants will be replaced with the new values derived from the Cartesian matrix.

5) Change the setting in the **Cartesian Forces** dialog, accessed either from the Control Window or from the Forces menu, to non-Cartesian forces. Now a **Calculation** (Control Window) will use the new valence forces.

6) If desired, you can change the **Symmetry** (Input menu), that is use some point- or space-group rather than no symmetry. This will usually involve deleting some symmetry-equivalent input atoms, and possibly a change of orientation, both of which can be done in the **Input Atoms dialog** (Input menu). If you have used some **Manual Forces** it may be necessary to change atom numbers in these specifications.

There is a tutorial for importing GAUSSIAN files in the folder GAUSSIAN. The explanation is in the file Gaussian\_import.txt.

#### 4.1.1.5 Import IZA file

**Import IZA (International Zeolite Association) File** [[File menu](#)]

See the **Import File** dialog for general aspects of importing atomic-structure data files.

The IZA has an extensive database of natural and synthetic zeolites available on the WWWeb, but does not seem to have an option for export of the data - it will be necessary to cut-and-paste the information into a text file.

Go to the Web page for the Database:

<http://www.iza-structure.org/databases/>

and select "**Collection of Simulated XRD Powder Patterns for Zeolites**". This should show a matrix of structure types by three-letter code - select one of these. You can also access structures in other ways, but you need to end up on a page showing options for X-ray powder diffraction together with the structure data. There should be lines for "Material name" ... "Composition:" ... "Crystal Data:" and others, with the fractional coordinates for the atoms in a table.

Mark the top right part of the page with your mouse, starting with the three-letter code centered at the top, and going below the atomic-coordinates table. Do not include the "Reset" and "Submit" buttons and material below this line. Do not include the column of options on the left of the page. Copy the marked information into the clipboard in the standard way.



Now, in a word processor, open a new text (ascii) file. Paste the clipboard contents into the file. Save the file, giving it a ".iza" extension if possible. Here is a sample (or look in the ZEOLITES subfolder for sample .iza files):

```

-----
LAU
Material name:  Laumontite
Composition:  |Ca4(H2O)18|  [Si16Al8O48]
Refined composition:  |Ca4(H2O)18|  [Si16Al8O48]
Crystal data:  Space group:  C12/m1      (# 12)
  a =  14.8538 Å  b =  13.1695 Å  c =   7.5421 Å
alpha =  90°  beta =  110.323°  gamma =  90°

  X-ray Rietveld refinement, Rwp=0.115, Rp=0.090, RF2=0.046
  Comment: unique axis b, cell choice 1
Reference: Artioli, G. and Ståhl, K.
Zeolites, 17, 249-255, (1993)

Atomic coordinates Atom name Form factor x y z PP B(iso)
CA Ca 0.2601 0.5 0.737 1.0 3.4
SI1 Si 0.2368 0.3838 0.156 1.0 1.89
SI2 Si 0.0763 0.3834 0.325 1.0 2.13
AL1 Al 0.1315 0.3080 0.737 1.0 2.61
O1 O 0.260 0.5 0.219 1.0 0.79
O2 O 0.2084 0.3744 0.919 1.0 1.66
O3 O 0.1384 0.3838 0.552 1.0 0.55
O4 O 0.146 0.3454 0.203 1.0 2.92
O5 O 0.3205 0.3185 0.248 1.0 0.79
O6 O 0.043 0.5 0.267 1.0 0.71
O7 O 0.013 0.3083 0.743 1.0 2.53
H2O1 O2-(H2O) 0.029 0.171 0.0 0.5 2.45
H2O2 O2-(H2O) 0.401 0.5 0.026 1.0 5.92
H2O5 O2-(H2O) 0.5 0.467 0.5 0.5 3.16
H2O8 O2-(H2O) 0.1426 0.129 0.332 1.0 4.03
-----

```

#### 4.1.1.6 Import SIESTA File

**Dialog Box: Import SIESTA File** [[File menu](#) or button in Startup or Control Window]

The SIESTA DFT program can be used to calculate interatomic forces for both molecules and crystals, and the output in the form of a Cartesian force-constant matrix can be read into VIBRATZ. These forces in turn can be converted to valence forces (bond and angle force constants), which can be refined by least-squares to improve agreement of calculated with observed frequencies. The VIBRATZ calculation can use the full symmetry to separate the vibrations into symmetry species, and the valence forces can easily be transferred to similar compounds.

**Setup in VIBRATZ and export to SIESTA.** Because the Cartesian forces must refer to a specific orientation as well as order of the atoms it is usually best to follow a certain procedure if a crystal to be calculated or if symmetry is to be used for a molecule. First the calculation should be set up in VIBRATZ. The full symmetry should be used, since that usually dictates the orientation of the molecule or crystal with respect to the Cartesian axes. It is not absolutely

necessary to supply valence-force specifications at this point, since the orientation can be checked and the symmetry analysis carried out without forces, but if it is intended to convert Cartesian to valence forces it will be necessary to do a valence calculation at some time to verify that the specifications are correct.

Once a calculation has been done in VIBRATZ, select **Export data for SIESTA** in the **Forces** menu. This will write a complete .fdf input file for the SIESTA program; its name by default is *myfile\_siesta.fdf* if the VIBRATZ data file is *myfile.vbr*. The dialog asks for the number of extra unit cells in each axis direction; this is for possible later use of the SIESTA results in VIBRATOR. If you intend to import the SIESTA results back into VIBRATZ, set all these to zero; then all the atoms in the primitive unit cell, and only those atoms (not those in a supercell) will be given in the .fdf file. The part which deals with calculation parameters for SIESTA gives only rudimentary parameters and may need to be modified to give good results. The system label within the .fdf file is simply the name of the VIBRATZ .vbr file plus "\_siesta". Most files generated by SIESTA will use this for a file name.

SIESTA is a Fortran Program and is run in command-line mode, not in a window. The command line

```
siesta < myfile_siesta.fdf
```

will execute the data, but atomic-potential files for each of the input atom types must also be present (not supplied by VIBRATZ).

**Importing SIESTA files into VIBRATZ.** Having completed the above, the results can now be imported back into VIBRATZ. The SIESTA output files which are used by VIBRATZ are *myfile\_siesta.XV*, which gives the crystal axes and atomic coordinates (in bohrs) and *myfile\_siesta.FC*, which gives the values for the Cartesian force matrix. In VIBRATZ, select **Import** and choose SIESTA .XV file type. If importing data for a crystal, check all the **Lattice translation** boxes and if importing data for a molecule check none - these settings should be the same as those in the original VIBRATZ file. The **Read Cartesian force matrix** box must be checked to import forces.

Now you will be asked to locate the .XV and .FC files. The data in the .FC file is converted into a VIBRATZ .car file, which is in a somewhat different format (lower diagonal) with a different scaling from the .FC file (md/A instead of mv/A).

Now the data should be set up for a VIBRATZ calculation using Cartesian forces. Since there is no symmetry all the vibrations will be in the A species.

When you import SIESTA files in this way, VIBRATZ operates in a special fixed-orientation mode, in which the structure coordinate axes remain in exactly the same orientation as in the SIESTA calculation, instead of the standard VIBRATZ orientation (c parallel to z, b in the y-z plane, except for rhombohedral crystals). Any pre-calculation **Rotations** (Input menu) are not applied. This is to guarantee that the orientation is correct for the Cartesian forces. If you have set up the .fdf file as described above the orientation should be the same; after the first calculation it should be verified that the orientation of axes and locations of all atoms are the same as in the original VIBRATZ calculation. The presence of the special fixed-orientation

mode is indicated in the Title/Axes dialog in the Input menu. It may be removed there. Actually any files generated by SIESTA may be imported, even without the setup described above, but the orientation may not be appropriate for a calculation in full symmetry.

If the valence forces (**Forces** menu) have been set up you can just select **Convert Cartesian to internal** in the **Forces** menu to convert forces from Cartesian to bond and angle forces. The number of valence forces must not be larger than the number of independent vibrations, otherwise the conversion is ambiguous (it is done by least-squares). If you get unreasonably large and/or negative values, you should eliminate one or more force-constant specifications, presumably the weakest first, although this depends on geometry.

To calculate using the new valence forces, select the **Set File** button in the **Cartesian forces** group in the **Control Window** and choose "Do not use Cartesian forces". You can restore the original full symmetry in this file, but it will also be necessary to delete non-symmetry-unique input atoms. The fixed-orientation mode can be de-selected in the **Input1/Title-Axes** dialog. It may be easier however, depending on how many symmetry-unique atoms there are, to write a forces file (**Forces** menu) and then read this file into the original full-symmetry data set. This can be done even if the orientation in the SIESTA file was different from that in VIBRATZ. You can also use the Cartesian force file (*myfile-siesta.car*) in this data set if the orientations were the same.

#### 4.1.2 Print Graphics Image

##### Dialog Box: Print Graphics Image [[File Menu](#)]

This dialog is shown when either the [Atoms](#) or [Spectra](#) Window is active; when a Text window is active, there is only a standard system printer dialog (next paragraph).

If the **Standard printer dialog on OK** box is checked, the **Print** dialog supplied by the operating system or the printer driver comes up after you click OK. Use that dialog to set the number of copies or the resolution. The orientation (portrait or landscape) is set in the **Print Setup** dialog in the **File** menu.

If you have a color printer, you may need to make a choice between color and black-and-white printing in one of the printer dialogs as well as with the **Color printing** checkbox in this dialog. This choice may be an option in the standard printer dialog above, or you may need to set in the **Print Setup** option in the [File](#) menu. Background applies only to color printing; for black-and-white printing the background is always white.

See [Frames](#) for details of the frame and frame units.

-----Macintosh Only-----

**Resolutions.** The list box at the bottom of the dialog should show the currently-available resolutions for your printer. The units are pixels per inch. Generally, the highest resolution should be chosen.

### 4.1.3 Page Setup

This allows Setting of the paper type or size, the standard orientation (portrait or landscape) and the paper margins (except Macintosh). Margins will only be used in [Text Windows](#).

---Macintosh only -----

Use the [Page Margins](#) dialog to set margins.

### 4.1.4 Page Margins

-----Macintosh only----

This dialog sets the margins for [Text Windows](#). Use the [Page Setup](#) dialog to choose page size and orientation.

### 4.1.5 Raster (Bitmap) Files

**Dialog Box: Raster (Bitmap) Files** [[File Menu](#)]

This dialog can be called from the [File](#) menu when either the [Spectra](#) window or the [Atoms](#) window is active, and the image which goes into the raster file can thus be either the spectrum or the atoms plot.

Windows/Linux only -----

This command can write files in four different formats (**File type**): Windows device-independent format (.BMP); PC-Paintbrush (.PCX); Tag-image-format (.TIF); or Portable Network Graphics (.PNG).

Macintosh only -----

This option writes raster file in the Portable Network Graphics (.PNG) format. Bitmap files can alternatively be written in the [PICT File](#) format.

-----

The drawing may be either black and white or color. If black and white, the **pixel size** is 1-bit. For color files the pixel size is based on the current screen; 4-bit for standard VGA or other 4-bit display, 8-bit for 256-color display, and 24-bit for 16- or 24-bit display.

The images will look much the same as a screen image, except that for black-and-white files gray shades are always rendered as dot patterns.

If the **Compress** box is checked, .TIF files are compressed with run-length encoding, which is one of the required formats under the TIFF 6.0 standard. However, some applications may not support this type of compression, or may reject TIF files for other reasons. Also, if the

**Compress** box is checked, 4- and 8-bit BMP files are compressed. 1-bit and 24-bit .BMP files are never compressed. Owing to a system bug, compression of 4-bit .BMP files may not work when banding is used (see below). PCX files are always compressed with their own format. For most purposes, PCX files are the best choice. 24-bit .PCX files can compress well, whereas 24-bit .TIF files are only partially compressed (and then only if there are large areas of black, white or grey), and 24-bit .BMP files are not compressed at all. If applications claim to support .PCX, they will almost surely read files written by VIBRATZ, whereas complete support for .TIF files is less certain.

See **Frames** for details of the frame and frame units.

**Maximum memory.** Windows and Mac operating systems both use *virtual memory*, which means that they pretend that a hard disk can be used in place of actual hardware memory chips. For some applications this is useful, but when writing raster files it often results in "disk thrashing", or constant reading and writing of data to the hard disk.

VIBRATZ is capable of imaging and writing raster files in segments or bands to avoid this problem. This requires repeating the entire drawing process for each band, but this usually is much faster than the reading/writing to disk involved in using virtual memory. To do this requires knowing how much actual chip memory is available. Unfortunately, at present the operating system does not provide this information in a usable form. Thus the user may need to determine this by trial and error using the **Maximum memory** parameter.

When the **Maximum memory** parameter is set to zero, VIBRATZ will simply ask the system for a block of memory large enough to image the entire drawing at once. This amount of memory is printed out in the dialog which appears after starting the raster imaging: "nnnn bytes required, mmmm bytes available - will require 1 bands". If this amount of memory is greater than the amount of chip memory available, the system will use virtual memory, which is typically manifested by constant running of the hard disk for long periods. If you change the **Maximum memory** to some amount smaller than nnnn (say half), VIBRATZ will only request this amount of memory from the system, and virtual memory may not come into play. A **Maximum memory** Setting should be good for a given session, regardless of the size of the raster file; larger files will use more bands. However, the amount of memory available may depend on whether other applications are active.

The amount of virtual memory is determined by the available space on the hard disk. If this is insufficient, VIBRATZ will automatically use bands, but since virtual memory is being used, it may still be advantageous to use a **Maximum memory** value which will increase the number of bands.

#### 4.1.6 Metafiles (Windows)

**Dialog Box: Metafiles [Windows only]** [[File Menu](#)]

This dialog can be called from the File menu when either the [Spectra](#) window or the [Atoms](#) window is active, and the image which goes into the metafile can thus be either the spectra or the atoms plot.

Windows metafiles are basically vector images (but including fills) that can be rescaled without necessarily losing resolution. They record the drawing commands that are used for the screen or standard printer output, but the result may depend on the software or device for which they are intended. A metafile image may either be saved in the Clipboard, to be Pasted into another application, or written to a file.

VIBRATZ can write three types of metafiles. The original or **Standard** metafile format has proven inadequate for transmitting scaling information, and many applications do not even accept Standard metafiles. **Placeable** metafiles, a format which was originated by Aldus Corporation, contain scaling information in an additional header. The standard and placeable metafiles have the .WMF extension. WMF or standard files are 16-bit format, i.e. use 2-byte integers. **Enhanced** metafiles are 32-bit format files which also contain scaling information. They are the preferred type of metafile for use in 32-bit Windows systems (Windows NT or Windows 95), but cannot be used in standard 16-bit Windows 3.1 or Win32s.

Original (16-bit or .WMF) metafiles can be written with either of two **Scaling Modes**; Isotropic or Anisotropic. Isotropic supposedly keeps the same proportions. Generally, Isotropic is the best as it allows rescaling while preserving proportions. However, some applications only accept Anisotropic files, and some ignore the scaling mode completely.

When writing to a file, to prevent loss of resolution, VIBRATZ uses a standard scaling of 2540 dots or pixels per inch (1000/cm). However, some drawing applications may not read the scaling correctly (assuming 72 dpi) and it may be necessary to rescale the drawing after importation.

When writing to the clipboard, VIBRATZ uses the current screen resolution, which usually is about 92 dpi. This is because most drawing applications assume screen resolution or 72 dpi. The clipboard image can be either 16-bit (.wmf) or 32-bit (.emf) according to the setting of the **Type** option.

See [Frames](#) for details of the frame and frame units.

*Limitations of Metafiles.* As designed and implemented by Microsoft, the metafile allows recording of all Windows drawing commands, so that a file image can be a copy of what is shown on the screen but rescalable. Unfortunately non-Microsoft drawing applications (e.g. Corel Draw, Adobe Illustrator) sometimes implement metafiles incompletely or incorrectly so that there are some limitations in metafiles written by this option, in order to allow them to work in as many applications as possible. It may be necessary to try many combinations of settings (Destination, Scaling mode, Type of file) to get satisfactory results in an importing program.

1) Resolution for the clipboard is now that of the screen, typically 72-96 dots-per-inch (dpi) - earlier versions of VIBRATZ used 2540 dpi. The lower resolution should not

cause problems except for very complex drawings - if a drawing looks good on the screen, it should look good in a document. If the clipboard is unsatisfactory use a file.

- 2) Bitmap patterns for black-and-white images cannot be used. Fills are transmitted as gray shades which are interpreted by the importing application and/or printer.
- 3) A background is always present, to insure correct scaling. With some care, this drawing element may be removed in importing applications.
- 4) There is no clipping of the image, although some importing applications may use the drawing frame for clipping.
- 5) Transmission of the image in Corel Draw with the Clipboard may require use of Edit/Paste Special rather than a simple Paste.
- 6) Adobe Illustrator generally does not do well with labels - it may be necessary to use an EPS file for Adobe Illustrator. Label backgrounds may not be transmitted in other applications.

If a metafile is not satisfactory, a raster file can be used. PNG raster files are often smaller than metafiles, especially for complex drawings. Also, many drawing programs now support import of EPS (Direct PostScript) files. EPS is usually the preferred type of file for Adobe Illustrator.

#### 4.1.7 PICT Files (Macintosh)

##### **Dialog Box: PICT Files [Macintosh only] [File Menu]**

This dialog can be called from the File menu when either the [Spectra](#) window or the [Atoms](#) window is active, and the image which goes into the PICT file can thus be either the spectra or the atoms plot.

This option can write images either to the Clipboard or to PICT files, in either of two formats: (a) a rescalable 2-dimensional Picture, or (b) a raster image or bitmap.

Macintosh Pictures, as used here, are images containing lines or vectors and fills of regions defined by lines, that can be rescaled without necessarily losing resolution. They record the drawing commands that are used for the screen or standard printer output, but the result may depend on the software or device in which they are used.

Bitmaps or raster images record every pixel, so they are not susceptible to undesirable modification by other software. Although most "painting" software can resize bitmaps, this usually causes a loss of quality, so it is best to save a bitmap in exactly the desired size. Note that you can also save bitmaps in the [PNG file](#) format (File menu), which is superior in some



respects to PICT files.

If color output is selected, the pixel depth of bitmaps will be the same as the current screen.

You can select the nominal dots per inch/centimeter, but note that programs which read the file may ignore this and show the image at 72 dots per inch.

**Background color.** If this option is on, the color selected in the [Atoms Plot Parameters](#) dialog (Settings menu) will be applied in color output only. Background in b/w output is always white.

See [Frames](#) for details of the frame and frame units.

### 4.1.8 PostScript Output

**Dialog Box: Postscript Output** [ [File menu](#) ]

----- Linux only -----

PostScript printing is standard in Linux, so for non-3D output, including diffraction diagrams, printing is routed to this dialog, not the [Print Graphics](#) command in the [File menu](#). Output can be directly to the printer or to an EPS file, as for Windows (below).

---- Windows only ----

This option can be used to write Encapsulated Postscript (EPS) files for transmission of graphics to other software, as well as for direct output to a Postscript printer. This direct output is generally superior to, as well as faster than, the output from the normal [Print Graphics](#) command in the [File menu](#) if your printer is PostScript. The **Destination** option sends output either directly to a printer or to a file in standard EPS (Encapsulated Postscript V3.0) format.

#### Screen Preview.

Most word-processing and publishing software cannot display an EPS file on the screen unless the file has a special bitmap attached, called the screen preview. This is actually a sub-file in the TIFF format. The pixel depth of this file can be set in the [PostScript Settings](#) dialog (**Settings** button). The pixel depth of the preview is set to that of the screen, and the pattern series is set to fine (see [Raster Files](#)).

---- Macintosh only ----

This option can only be used to write Encapsulated Postscript (EPS) files for transmission of graphics to other software. For direct output to a Postscript printer, use the [Print Graphics](#) option.



## Screen Preview.

Most word-processing and publishing software cannot display an EPS file on the screen unless the file has a special attachment, called the screen preview. This is actually a PICT in the resource fork of the file.

---- End Linux/Windows/Macintosh only ----

**Settings** button ([PostScript Settings](#) dialog). On or before first using the **Direct PostScript Output** command, you should set or verify the settings in this dialog, especially the port to which the printer is attached.

*Fonts in PostScript output.* Currently VIBRATZ uses the Times-Roman typeface for all PostScript output (Atoms or Spectra Window).

See [Frames](#) for details of the frame and frame units.

### 4.1.8.1 PostScript Settings

**Dialog Box: PostScript Settings** [ [Postscript Output Dialog](#) ]

The page size, page margins and dots per inch/centimeter should be determined by the actual printer used for final output; if these are not correct, the drawing may not be scaled and/or placed on the page correctly.

The **Transfer Function** is analogous to the PostScript function of the same name. The linear option is standard; modify the function to get lighter or darker shading in PostScript print-out.

**Preview Color.** If you select a screen preview (TIFF bitmap or PICT sub-file) in the [PostScript Output](#) dialog, and if color output is selected, you can specify either a color or black-and-white bitmap. The **Screen** option uses the color depth of the the current screen display. Black-and-white PostScript output always uses a 1-bit or black-and-white screen preview.

**Background color.** If this option is on, the gray background will be applied in color output only. Background in b/w output is always white.

---- Windows only ----

If you are using direct output to a printer you *must* select the **Port**; this will be either "LPTn" or "COMn". Also, if you are using a serial port for the printer, you must set or verify the data transmission parameters, such as baud, parity, etc., even if the port

currently shown is the correct one. This is done in the **Ports** item of the Windows **Control Panel** (not in VIBRATZ).

#### 4.1.8.2 PostScript Transfer Function

**Dialog Box - called from:** [Postscript Settings dialog](#)

The **Transfer Function** is analogous to the PostScript function of the same name. It changes the nominal gray values (0.0-1.0 for black-white) calculated by ATOMS as true illumination to values actually output. (Note that the PostScript gray scale, 0.0-1.0 for black to white, is in the opposite direction to the ATOMS gray scale, 0-15 for white-black; the transfer function applies to the Postscript gray scale.) If your printer gives gray shadings that are too dark (this is common, especially for lighter shades), you can increase the output values. Values in between the listed values are linearly interpolated. The actual gray values output to the printer or EPS file are changed; the transfer function itself is not part of the EPS file. Note that the gray-scale conversion also applies to lines of greater than single-dot width (single-dot lines are always black).

#### 4.1.9 Molekel Files

**Dialog Box: Molekel Files** [[File Menu](#)]

This option is available only the File menu of the [Atoms window](#). It will write a file in the native (.mkl) format for the (free) molecular graphics program Molekel ([www.cscs.ch/molekel](http://www.cscs.ch/molekel)). Among other things, this program will animate the vibrational motion.

It will also write raster files of the animation, although they are not collected into a "movie". Among the raster formats available for the Windows version, TIFF packbits seems to be the only one with compression (avoid JPEG because it is not lossless).

The **Scale:** factor shown in the Dialog Bar on the left is applied to the atomic motions given in the [Output Window](#).

#### 4.1.10 Text File with Spectral Data

**Dialog Box: Text File with Spectral Data** [[File Menu](#)]

This will write a text file with data for the observed and calculated IR, Raman, NRVS or IXS spectra in a form that can be read by Kaleidagraph and other X-Y plotting programs.

Each line will have the frequency, the calculated intensity and the observed intensity (if present).

If **Bars** are selected in the **Mode** radio box, the calculated part will consist of a vertical

(intensity) value of zero at the low-limit frequency; another zero value at the first mode; a point at the maximum for this mode; another zero value, still at the same frequency, and so on. That is, each mode will be represented by three values at the mode frequency; zero, maximum, zero. If Curve is selected, there will be a data point (line in the file) for each frequency **Interval**.

The units on the **Y-axis units** (horizontal scale) can be either meV or cm<sup>-1</sup> - the **Interval** will be in the same units. The calculated intensity data will be redone for each of the points on the Interval, and the observed data will be interpolated.

The Normalization mode for NRVS will be as selected in the [NRVS Parameters](#) dialog (or in the least-squares section of the [Control Window](#)). The choice of **Normalization** in this dialog will then determine whether the output matches the calculated (absolute NRVS fraction or mode composition factor) or the observed.

**File with IXS sequence in zone.** When the **IXS Spectra** box in the [Control Window](#) is checked, there is a special group which will write a file containing calculated intensities for a sequence of Q-points along a central zone in reciprocal space. The calculations will be done at integral points, the indices of which are given by multiplying the **Zone Indices** successively by integers from the **Start order** through the **End order**. In the file itself, there will be a header row with the 2-theta values and another with the indices. The observed intensity, if present, is in the first column (after frequencies). Other parameters are as for the main part of the dialog. This only draws the curves, not bars. The file is written when you click the **Write File** button in the group, not the main **OK** button, and when the file is complete you are returned to this dialog.

## 4.2 Input Menu

This menu (Control Window) contains dialogs which allow input and correction of data on the molecular or crystal structure itself.

[Title/Axes](#) For specifying the type of coordinate axes, or the unit-cell of crystals, and specifying lattice translation in any of the axes (i.e. whether the structure is a crystal, molecule or polymer).

[Symmetry](#) For specifying the point group for molecules or the space group for crystals of polymers - or no symmetry.

[Pre-Calculation Rotations](#) For rotating and aligning the image in the Atoms Windows.

[Input Atoms](#) For entering the label, coordinates and type of the input atoms.

[Atom Types](#) For specifying the type numbers, atomic weights and formal charges of the atoms used. By default, this is a table of the standard atomic numbers and weights of the elements.

[Species](#) This gives information on the symmetry species, including the number of modes, and allows selection of the species for calculation.

[Observed](#) This is for input of the observed wavenumbers in each species, for least-squares

refinement or just for comparison.

**Remove Symmetry.** This option will convert all the atoms generated by symmetry to input atoms, and removes the symmetry specifications. It does not remove lattice translations. This is only possible after a calculation has been carried out.

#### 4.2.1 Title/Axes

**Dialog Box: Title/Axes** [[Input menu](#)]

The title may be any information, up to 80 characters. It is printed on most output.

For a molecule using cartesian coordinates, the a, b and c axes should in most cases be 1.0 and the interaxial angles alpha, beta and gamma should be 90.0. However, molecules with trigonal or hexagonal symmetry can use either Cartesian coordinates and Cartesian axes as just specified, or coordinates on hexagonal axes with a gamma angle of 120 degrees. The symmetry matrices are adjusted for either case depending on whether gamma is 90 or 120 degrees.

The angles should be consistent with the data for the crystal which is entered in the [Symmetry](#) and [Input Atoms](#) dialogs. In particular, for monoclinic crystals in the second setting (b-axis unique), beta (and not gamma) should be non-ninety. VIBRATZ requires a unique axes to be parallel to z, but this orientation should be attained by entering a rotation of 90 degrees on x in the [Pre-Calculation Rotations](#) dialog.

If a trigonal rhombohedral crystal is to use the primitive cell, the a, b and c axes must be equal and the three angles must be equal. You must also select a rhombohedral setting in the Symmetry option.

**Lattice translations** check boxes. These boxes are extremely important because they determine whether the calculation is to be for a crystal if all three boxes are checked; for a molecule if all three are unchecked, and for a polymer if either one (chain) or two (sheet) are checked.

The conversion from crystallographic to Cartesian coordinates is made by setting c parallel to z, and b in the y-z plane (a\* parallel to x). If you use hexagonal axes for a molecule, that is gamma = 120 degrees, the orientation is the same as for a crystal - the a2 or b axis is parallel to y, so that a1 or a is not parallel to x.

The orientation of the reference Cartesian axes in the [Atoms Graphics Window](#) is x pointing directly out of the screen or paper, towards the observer; y horizontal to the observer's right; and z vertical.

#### 4.2.2 Symmetry

**Dialog Box: Symmetry** [[Input menu](#)]

This gives four options for specifying the symmetry. Note that you *must* also set the **Lattice Translation** flags for the three axes in the [Title/Axes](#) dialog.

**Space Group.** This is the normal option for a crystal or polymer, although the **Custom** option can also be used.

**Point Group.** This is the normal option for a molecule, if symmetry is used.

**Custom Point or Space Group.** This option uses symmetry operators in form of the general equipoint in the *International Tables for X-ray Crystallography*. This is used for certain import file formats, and for old VIBRAT files. It is not normally used for new input except in the case of a non-standard space group, for example C( $\bar{4}$ )1.

**Use No Symmetry.** This sets the point group to C1 and the space group to P1 if necessary.

#### 4.2.2.1 Space-Group Symmetry

**Dialog Box: Space-Group Symmetry** [[Symmetry](#) Dialog, [Input](#) menu]

Space-group symmetry is generated using licensed excerpts from the SGInfo program of Ralf Grosse-Kunstleve. You can specify the space group in any of three ways: 1) the Hermann-Mauguin (H-M) or International symbol; 2) the Hall symbol (S.R. Hall: Acta Cryst., A37, 517, 1981); or 3) the number of the group in the *International Tables for X-ray Crystallography*.

*International Tables Volume.* You have the option of using the older version of the *Tables* (called the Second Edition: various revisions and reprints from 1952 to 1979) in which the symmetry information was in Volume I, or the newer version (1983 onwards) in which it is in Volume A. The principal difference between the two versions is that in the older one the unique axis of a monoclinic group is assumed to be the c-axis, whereas in the newer one it is assumed to be the b-axis. Thus entering the symbol P2/m gives two different orientations depending on the volume selected. You can always specify the setting by entering the long form of the symbol, i.e. P<sub>2</sub>/m<sub>1</sub>1, P<sub>1</sub>2/m<sub>1</sub>1 or P<sub>1</sub>12/m. Of course, for the first two of these examples you would have to use the [Pre-Calculation Rotations](#) to attain the standard orientation, which is unique axis parallel to c.

The H-M symbol can be typed into the edit box in either short form or long form, with or without spaces or underscores between positions. However, it is usually safer to select the symbol from the list box at the bottom, which gives the standard-form symbols for all the space-groups. Clicking the **Select** button copies the relevant data to the edit boxes at the top; it does not actually generate the symmetry. Symmetry generation is done after you click OK - this may take a few seconds.

If the space group you select does not appear to be consistent with your choice of axes, a warning box appears, but in most cases consistency is not required. Select the rhombohedral setting for trigonal crystals by adding :R to the end of the symbol in the case of H-M symbols, or asterisk (\*) in the case of Hall symbols. The choice of rhombohedral vs. primitive cell should agree with the type of axes entered in the Title/Axes dialog. If you select the rhombohedral setting and then switch to the **Custom** symmetry option, the lattice type will be P; it will be R if the axes are hexagonal.

**Origin of Coordinates.** The symmetry analysis in VIBRATZ requires that if a space- or point-group is centric (contains a center of inversion), the origin of coordinates must be on that center.

In the *International Tables*, this is usually standard, but for 24 space groups in the orthorhombic, tetragonal and cubic systems, there is a choice of origins. In VIBRATZ, the first choice of origin, which is off the center of inversion, is denoted by adding ":1" to the standard symbol or number, and the second choice, on the center, is denoted with ":2". In Hall symbols, the origin is explicit. If you enter the symbol or number without extension (":1" or ":2"), origin on the center (":2") is assumed.

If your atomic coordinates are for the first setting in one of these space groups, you can either correct the coordinates manually, using the increments x, y and z given in the Tables in the line "Origin at..., at x, y, z from centre" and enter the symbol for the second setting (add extension ":2" to symbol or number), or you can enter the original coordinates and allow VIBRATZ to make the corrections to the atomic coordinates (add extension ":1" to symbol or number).

**Orientation.** Certain orientations of the symmetry elements are required by the basis functions used for symmetry analysis, and some standard space-group settings may not be consistent with these settings. VIBRATZ will usually detect such cases, and supply appropriate rotations for the [Pre-Calculation Rotations](#) dialog.

VIBRATZ requires any unique axis to be the z-axis or crystallographic c-axis, whereas the standard orientation for monoclinic crystals is the unique axis is usually b, which is by default parallel to y. Thus monoclinic crystals in the standard second setting should be rotated 90 degrees on x. If the unique axis is a, a rotation of 90 degrees on y should be entered

Some trigonal, tetragonal and hexagonal space groups have either of two different orientations of the symmetry elements with respect to the axes. In some cases, only one of the orientations is consistent with the basis functions used for symmetry analysis used in VIBRATZ. Specifically, space groups in the point or factor group D<sub>2d</sub>, of the type P4m<sub>2</sub> (where P and m may be replaced by other symbols), must be rotated by 45 degrees. Space groups in the point or factor group D<sub>3h</sub>, of the type P6<sub>2</sub>m, and of the point or factor group C<sub>3v</sub> of the type P3m<sub>1</sub>, must be rotated by 30 degrees. Space groups of the type P4<sub>2</sub>m, P6<sub>2</sub>m and P3<sub>1</sub>m do not require rotation.

Space groups in the point or factor groups D<sub>3</sub> and D<sub>3d</sub> also may take two different orientations, but either orientation is valid without rotation. However, the Raman components which appear in the E species are different depending on the orientation.

See [Orientation](#) for more information about orientations and rotations.

*Non-standard settings.* Often non-standard settings can be attained by selecting a space group, then switching to the [Custom Symmetry](#) option. It is especially easy to change the Bravais lattice type. For example, for the space group C( $\bar{1}$ ), select P( $\bar{1}$ ) then switch to the the [Custom Symmetry](#) option and change the Bravais lattice to C.

#### 4.2.2.2 Point-Group Symmetry

**Dialog Box: Point-Group Symmetry** [[Symmetry](#) dialog, [Input](#) menu]

This dialog allows direct selection of common point groups through the radio buttons, and also input of any other point group through special files.

VIBRATZ uses two methods to supply the data for point group symmetry, one for crystallographic point groups and one for non-crystallographic groups. The 32 crystallographic groups are those with rotation axes of order 6 or less, excluding 5-fold axes, and excluding linear groups. The operators for these groups are generated internally, in the same way as space groups are generated. These groups may be identified in this dialog by the presence of both Schoenflies (chemical) and Hermann-Mauguin (crystallographic) symbols.

The non-crystallographic groups shown in this dialog include the 5-fold, 7-fold and 8-fold axial groups, the icosahedral groups, the linear groups, and the group D4d (which is actually of order 8). The information for the listed non-crystallographic groups is read from files. These files have the extension.SYM and should be in the subdirectory \SYM in the directory containing the VIBRATZ application (VIBRATZ.EXE).

The methods used in symmetry analysis require that the symmetry elements be fixed in orientation, and the atomic coordinates must conform to these orientations - see the [Orientation](#) topic in the Operation - Special Topics section. Usually to make the atoms conform to the required orientation is a matter of rotation about the z-axis (or very rarely other axes), which can be done in the [Input Atoms](#) dialog in the Input menu.

In all cases, VIBRATZ uses polynomial basis functions to generate the representations that are used in symmetry analysis. These are taken up to 8th order if necessary, which is adequate for all but one species among the listed groups - xxx of D8h. However, the non-optically-active species of the icosahedral groups have not yet been worked out.

The **Read Symmetry from file** option reads a file in the same format as the non-crystallographic groups represented by the other radio buttons. See [Making Symmetry Files](#) for how to prepare a file for use in VIBRATZ. It is possible to generate a file including the optically active species for any point group for which a character table is available, since the first- and second order infrared and Raman active components are normally given in such tables and these components are the first- and second-order basis functions for the active species.

#### 4.2.2.3 Custom Symmetry

**Dialog Box: Custom Symmetry** [[Symmetry](#) dialog, [Input](#) menu]

Note that proper use of this option absolutely depends on identification of the point or factor group, and possibly applying [Pre-Calculation Rotations](#) to bring the atoms and symmetry into standard orientation; both requirements are described below.

This option is used for old VIBRAT files (which should already have the correct factor group number), or for certain import file formats. It is intended primarily for space groups, but can also be used for crystallographic point groups. It cannot be used for non-crystallographic point groups. The symmetry is entered and stored in the form of general positions as given in the *International Tables for X-ray Crystallography*. These are sometimes given in reports on crystal structures (e.g. Wyckoff, Crystal Structures). Note however that often only the operations for special positions are given: VIBRATZ needs all the operations for the general position.

If you specify **Centric**, rather than **acentric**, and the **Operations include center** box is not



checked, only half the symmetry operations should be entered. If the origin of coordinates is not on an inversion center, the **Operations include center** box must be checked and all the operations must be present. However, symmetry analysis will not generally be successful if the origin is not on a center, and the coordinates must be corrected; see below under **Origin of Coordinates**.

The **Space-group symbol** is for your reference only - it is not used directly by VIBRATZ. However, if you click on the **Get Space Group Symbol** button VIBRATZ will analyze the given operations and try to provide a valid space-group symbol. When you click on the **Change Symmetry Option** button, this will also cause an attempt to provide the correct space-group symbol.

The **Point/factor group number** *must* be correct for proper symmetry analysis. This number, as well as the point group symbol (which is for your reference only), may be filled in with the **Get Space Group Symbol** button, but this will succeed only if the current operations constitute a valid space group. If this fails, the number must be entered using the values from the table below.

Note also that the orientation of the symmetry operators must be consistent with the basis functions. For a number of space groups in their standard orientation, this is not the case, and it is necessary to apply [Pre-Calculation Rotations](#) to both input atoms and symmetry matrices. If you select a space-group with the [Space-Group Symmetry](#) option, the proper values are automatically entered in the [Pre-Calculation Rotations](#) dialog if necessary. You must enter these rotations manually, if needed, for the Custom Symmetry option. See the [Space-Group Symmetry](#) dialog for which space groups need rotation.

The **Bravais lattice** is in most cases the capital letter which begins the space-group symbol. However, VIBRATZ uses a somewhat different convention from the standard for trigonal crystals: if you are using hexagonal axes for a rhombohedral crystal (whose standard space group symbol will always begin with "R"), enter "R" - if you are using the primitive rhombohedral axes, enter "P". Enter "P" for a molecule.

In the **Operations** list, you must enter all the "symmetry operations" for the most general position in the structure, with one operator per line. "X, Y, Z;" will always be the first operator. Click on the **Add Line** button to add a line, or **Revise** to change a line, either of which will call up the [Edit Symmetry Operation Line](#) dialog.

**Origin of Coordinates.** The symmetry analysis in VIBRATZ requires that if a space- or point-group is centric (contains a center of inversion), the origin of coordinates must be on that center. In the *International Tables*, this is usually standard, but for 24 space groups in the orthorhombic, tetragonal and cubic systems, there is a choice of origins. In VIBRATZ, the first choice of origin, which is off the center of inversion, is denoted by adding ":1" to the standard symbol or number, and the second choice, on the center, is denoted with ":2". In Hall symbols, the origin is explicit. If you enter the symbol or number without extension ( ":1" or ":2" ), origin on the center (":2") is assumed.

When you use **Custom** symmetry, the choice of origin is not obvious, and if your atomic coordinates are for the first setting in one of these space groups you must correct the coordinates



and symmetry in either of two ways. If you are using one of these settings, the **Centric** radio button should be selected, and the **Operations include center** box should be checked.

First, you can correct coordinates manually, using the increments x, y and z given in the Tables in the line "Origin at..., at x, y, z from centre". The symmetry operations entered in this dialog must also be completely changed - they must be taken from the second setting instead of the first.

Second, you can allow VIBRATZ to make the corrections. This must be done in an indirect way. After entering the original atomic coordinates and symmetry operations for the off-center setting in the Custom symmetry dialog, click the **Change Symmetry Option** button, and change to **Space-Group** symmetry. This should convert your symmetry Settings to a standard space-group symbol (first setting), then correct both the symbols and the atomic coordinates to the second setting. If you click on the **Get Space-Group Symbol** button, the symbols, Settings and atomic coordinates will be corrected, but the Custom symmetry option will be retained. Of course these conversions depend on your data being for the standard off-center (first) setting of one of the 24 space groups of this type in the *Tables*. Any non-standard off-center settings will have to be corrected manually.

### Point/Factor group numbers

1. C1 - 1	9. D3 - 32	17. C3h - 6	25. D3d - 3m
2. Ci - 1	10. D4 - 422	18. C4h - 4/m	26. S4 - 4
3. Cs - m	11. D6 - 622	19. C6h - 6/m	27. S6 - 3
4. C2 - 2	12. C2v - mm2	20. D2h - mmm	28. T - 23
5. C3 - 3	13. C3v - 3m	21. D3h - 6m2	29. Th - m3
6. C4 - 4	14. C4v - 4mm	22. D4h - 4/mmm	30. Td - 43m
7. C6 - 6	15. C6v - 6mm	23. D6h - 6/mmm	31. O - 432
8. D2 - 222	16. C2h - 2/m	24. D2d - 42m	32. Oh - m3m

1. C1 - 1	9. D3 - 32	17. C3h - 6	25. D3d - 3m
2. Ci - 1	10. D4 - 422	18. C4h - 4/m	26. S4 - 4
3. Cs - m	11. D6 - 622	19. C6h - 6/m	27. S6 - 3
4. C2 - 2	12. C2v - mm2	20. D2h - mmm	28. T - 23
5. C3 - 3	13. C3v - 3m	21. D3h - 6m2	29. Th - m3
6. C4 - 4	14. C4v - 4mm	22. D4h - 4/mmm	30. Td - 43m
7. C6 - 6	15. C6v - 6mm	23. D6h - 6/mmm	31. O - 432
8. D2 - 222	16. C2h - 2/m	24. D2d - 42m	32. Oh - m3m

#### 4.2.2.3.1 Edit Symmetry Operation Line

**Dialog Box: Edit Symmetry Operation Line** [[Custom Symmetry](#) dialog, [Input](#) menu]

The individual positions or operations are separated in the *International Tables* by semicolons. Semicolons at the end of each line are optional. Only one operation is allowed per line. The identity operation x, y, z must be present.

### 4.2.3 Pre-Calculation Rotations

**Dialog Box: Pre-Calculation Rotations** [[Input](#) Menu]

The rotations in this dialog are those required to bring both the structure and the symmetry matrices (together) into proper orientation for symmetry analysis. This is required normally only for certain space groups (crystals). If you select the [Space-Group Symmetry](#) option, VIBRATZ usually detects such situations and supplies the appropriate rotations, but for space groups using the [Custom Symmetry](#) option it is necessary to enter the rotations manually.

VIBRATZ requires any unique axis to be the z-axis or crystallographic c-axis, whereas the standard orientation for monoclinic crystals is the unique axis is usually b, which is by default parallel to y. Thus monoclinic crystals in the standard second setting should be rotated 90 degrees on x.

Some trigonal, tetragonal and hexagonal space groups have either of two different orientations of the symmetry elements with respect to the axes. In some cases, only one of the orientations is consistent with the basis functions used for symmetry analysis used in VIBRATZ. Specifically, space groups in the point or factor group D<sub>2d</sub>, of the type P4m2 (where P and m may be replaced by other lattice and symmetry plane symbols respectively), must be rotated by 45 degrees. Space groups in the point or factor group D<sub>3h</sub>, of the type P6m2, and of the point or factor group C<sub>3v</sub> of the type P3m1, must be rotated by 30 degrees. Space groups of the type P42m, P6m2 and P31m do not require rotation. See [Orientation](#) for more information about orientations and rotations.

Space groups in the point or factor groups D<sub>3</sub> and D<sub>3d</sub> also may take two different orientations, but either orientation is valid without rotation. However, the Raman components which appear in the E species are different depending on the orientation.

**Rotate lattice translation flags (polymers).** If the lattice translation check boxes in the [Title/Axes](#) dialog refer to the original orientation of the axes entered in that dialog, if only some boxes are checked (i.e. the structure is a polymer and not a molecule or crystal) and if pre-calculation rotations are then applied, these indicators or flags may also need to be rotated appropriately. This is most likely with monoclinic space groups in which the unique axis is not c. For example if the unique axis is b and the polymer or lattice translation is c, then the 90 degree rotation on x would change the lattice translation direction to b or y. It is also possible to leave the **Rotate lattice translation flags** box in this dialog unchecked, and to select the lattice translation directions in the [Title/Axes](#) dialog as they are after the pre-calculation rotations. In the above example, this would mean checking the b-axis box as the polymer or translation direction.

Note that this option does not change the orientation of the atom coordinates relative to the symmetry matrices; rather it changes both of these, so that they are consistent with the Cartesian polynomial basis functions used for symmetry analysis. To rotate the input atom coordinates with respect to the symmetry elements, use the **Rotate all atoms** option in the [Input Atoms](#) dialog (Input menu).

#### 4.2.4 Input Atoms

##### Dialog Box: Input Atoms [[Input menu](#)]

This gives a list of input atoms. The data for each one is in a single line in the scrolling list or spreadsheet. To add a new entry, press the down arrow key while the focus is on the last row, or click the **Add** button.

The **Label** may be up to 6 characters. There should be no embedded blanks.

The **Type** refers to the [Atom Types](#) list. By default, type numbers are standard atomic numbers, although it is also possible to assign different type numbers to particular atoms to assist in defining bonds and angles. In fact, it is frequently necessary to assign different type numbers to specific input atoms to differentiate bonds and angles. It is usually best to use atomic numbers modulo 100, for example 6, 106, 206, etc. for carbon atoms, as the structure display program ATOMS, which can animate the vibrational motions, will read these all as type 6 (carbon) when importing VIBRATZ files.

In the **x**, **y** and **z** boxes, enter the coordinates, fractional in the case of crystals, or absolute in the case of molecules. For polymers, coordinates could be part fractional and part absolute. Coordinates should be given to the 5th decimal place where necessary - for example, a coordinate which is  $2/3$  by symmetry should be entered as 0.66667, not 0.667.

*Note.* If Urey-Bradley forces are used, and if an element occurs as central atom in CX<sub>n</sub> polyhedra in different coordinations (that is, if n is not always the same), each occurrence must be given a different type number.

VIBRATZ expects to use the specified symmetry on the entered atoms to generate all the atoms in the unit cell or molecule. However, it is possible to enter all the atoms, including some or all symmetry equivalents. VIBRATZ will then identify those which are redundant, and will delete them with your permission.

The **Read Atoms from File** button calls the [Read Atom List from File](#) dialog, to read a text file containing atom labels and coordinates.

The **Coordination** button calls up the [Coordination of Atoms](#) dialog which shows the bonding environment (bonds and angles) of any or all atoms. This option can give sorted lists of bonds and angles which can be an important aid in assigning force constants.

**Z-Matrix.** This allows construction of a molecule from a z-matrix or table of bond lengths and angles instead of using Cartesian coordinates.

**Rotate all input atoms on axis.** This option is primarily for molecules, in case the atomic

coordinates are for a setting of the symmetry elements which is different from that used by VIBRATZ. The standard VIBRATZ orientation is as follows: In Cnv groups a vertical mirror plane is perpendicular to the x axis (not the y axis if there is a difference). In groups which have horizontal 2-fold axes with or without vertical mirror planes, a 2-fold axis is oriented parallel to the x axis and mirror planes are oriented accordingly. The icosahedral groups are oriented with a 5-fold axis parallel to z, and an adjacent 3-fold axis in the x-z plane.

The rotation is permanent, but can be reversed by entering the negative of the angle (see [Orientation](#))

#### 4.2.4.1 Coordination of Atoms

**Dialog Box: Coordination of Atoms** [[Input Atoms](#) dialog, [Input](#) menu]

This dialog sets parameters for a print-out of interatomic bond distances and angles. The results are presented in two ways; 1) all bonds and angles involving the selected input atom, or each input atom in turn; and 2) lists of all bonds and angles, sorted according to bond lengths.

The results are written to a file name BONDS.VBD, and they also appear in a Text window (see [Operation - Windows, Menus](#)). This window has its own menu bar, which is different from the standard VIBRATZ menu bar. The Text window menu bar has standard commands for editing and printing out text. In order to access dialogs in the VIBRATZ menu bar, click on the [Control](#) window or select the [Control](#) window in the **View** or **Windows** menus.

If you check the **All atoms** radio button, each input atom will be analyzed in turn; if you check the **Selected atom only** button, results will be given only for the input atom previously selected in [Input Atoms](#) dialog - return to that dialog with the **Cancel** button.

The **Distance limit - central-ligand** applies to all bonds from the current input atom to surrounding atoms.

The **Distance limit - ligand-ligand** applies to the distances between the atoms surrounding the current input atom. This is normally the way that undesired angles are screened out. For example for octahedral coordination around a central atom, only the ~90 degree angles involving adjacent ligands are usually selected, not the ~180 degree angles involving opposite ligands. This is done by setting this distance limit to just larger than the maximum ligand-ligand distance.

The **Distance limit for angles** (which also applies to ligand-ligand distances), is a test which is applied to the central-ligand distance of both legs of an angle. This allows consideration of next-nearest neighbors for bonds, but not for angles.

If the **Do angles and ligand-ligand distances** box is not checked, only central-ligand bond distances will be calculated.

When the structure is complex and all input atoms are computed at once, the **Use radii to screen sorted lists** allows exclusion of chemically unrealistic bonds and angles. If this is used,

the overall distance limits above should be large enough for all interatomic distances. This option requires suitable atomic radii to be present in the [Atom Types](#) list ([Input](#) menu). The calculated bond lengths will be compared with the sum of the atomic radii, multiplied by the factor in the **Factor for sum of radii** box. A factor of about 1.2-1.3 is usually appropriate. The default radii, obtained from the ELEMENTS.DAT file (see [Types of Files](#)) are standard covalent radii, with some adjustments.

Note that values for individual bonds and angles can be obtained in the [Atoms](#) window by clicking successively on the atoms involved.

#### 4.2.4.2 Read Atom List from File

**Dialog Box: Read Atom List from File** [[Input Atoms](#) dialog, [Input](#) menu]

This dialog specifies parameters for reading a list of atom labels and coordinates from a text file. Such files normally have one atom per line, although actually there could be any number of entries per line. There must be a constant number of fields for each atom entry. A field is a group of letters or numbers with no embedded spaces, separated by spaces or commas. There should be no lines other than atomic parameter lines in the file. VIBRATZ will keep reading lines until the end of the file.

The **Field string** determines how each input line is interpreted. The field string may contain up to 20 tokens or keywords - LAB, COO, TYP or DUM, separated by spaces. DUM is the only token which can be repeated - the others should appear only once

LAB indicates an atomic label. Labels may have up to 6 characters and may not contain embedded spaces. COO indicates three numbers giving the x, y and z coordinates of the atom. These two fields are mandatory. TYP is optional and gives an atomic type number, which may or may not be the standard atomic number. If there is no TYP field, VIBRATZ will attempt to assign standard atomic numbers using the first one or two letters of the label. DUM indicates a field that is to be skipped.

**Example.** The field string

DUM LAB COO

would be used to read in lines of the form

```
1 C1 1.3456 2.4323 5.6432
2 C2 2.1233 3.6367 5.4524
3 H1 8.3445 1.2344 3.1233
```

and so on.

If you know the full path of the file, you can type it into the edit box and use the **Read Named File** button. Otherwise you can locate the file with the **Browse** button.

#### 4.2.4.3 Construct Molecule from Z-Matrix

##### Dialog Box: Construct Molecule from Z-Matrix [ [Revise Atom Dialog](#) ]

With this dialog you can construct a molecule or structure fragment from a table of bond length and angles. The table, called a z-matrix, is widely used in molecular science, and you can read files from other sources or write files for use in other software.

##### *Action button section*

The buttons at the top of the dialog indicate actions to be taken after the z-matrix at the bottom is filled out

**Add** will add the new generated atoms to the atoms already in the [Atoms \(Input\)](#) list. If the structure axes are not already Cartesian they are changed to Cartesian.

**Replace** will remove all the old atoms from the [Atoms \(Input\)](#) list and insert the new generated atoms.

Add and Replace will change the structure axes to Cartesian, since all calculations with z-matrices assume Cartesian coordinates, but most other settings, such as symmetry, boundary option and others in the Input1 menu, will not be changed

**Read** will reading a file containing a z-matrix and insert the contents into this dialog. There should be no title or other extraneous lines, and each line, for each atom should contain the fields Label, Bond Connect, Bond Distance, Angle Connect, Bond Angle, Dihedral Connect and Dihedral Angle. Note that atom Type is not in this sequence, but the atom type or atomic number may be on the end of the line. The fields should be separated by spaces, commas, colons or semicolons.

**Write** will write a file as described in the previous paragraph, with one line for each atom, and with the type number at the end of the line. The Orientation (below) will be added after the atoms.

**Show** will do a conversion from z-matrix to Cartesian coordinates and display the z-matrix and the results in a [Text window](#).

You can cut-and-paste blocks of atom lines in the z-matrix by using the **Read**, **Write** and **Show** buttons - for example you can save a file from the Text window (**Show**) after suitable editing, then **Read** it back.

##### *Orientation section*

The **Orientation** section allows the molecule or fragment to be located and oriented in any desirable way. It always refers to the first three atoms in the z-matrix list. Coordinates are always Cartesian.

The **Position** gives the x, y and z coordinates of the first atom. By default they are 0,0,0.

The **Atoms 1-2 vector** gives the vector from the first to the second atom. By default it is 1,0,0, which puts the second atom on the x-axis at the given bond distance from the first atom.

The **Atoms 1-2-3 plane** gives the normal to the plane containing the first three atoms. The vector from atom 2 to atom 1, the vector from atom 2 to atom 3, and this normal form a right-

handed system. By default this normal is 0,0,-1 which puts the third atom in the x-y plane with a positive angle giving a positive y-coordinate for atom 3 (assuming standard placement and orientation for atoms 1 and 2).

The vectors need not be normalized; they will be normalized during the transformation.

#### *Z-Matrix section*

Each line in the matrix below refers to an atom. You can select each atom by clicking on the number to the left, and the entries are acted upon by the **Move Up**, **Move Down** (move the line within the list), **Insert** and **Delete** buttons. The up and down arrows to the right scroll the entire list up or down if there are more atoms than the list can hold at once.

The atoms are positioned with respect to other atoms in the list. The first three atoms are oriented and positioned as described above in Orientation, and all other atoms are placed with respect to these three.

Each line describes the positioning of a new atom (1) with respect to up to 3 atoms already in the list (2, 3, and 4).

The **Label** and **Type** give the VIBRATZ label and type; the type is normally the atomic number. If the type is 0, VIBRATZ will attempt to determine the atomic number (or other type number) from the first two characters of the label.

**Bond Connect:** the number in this list of the atom (2) to which the new atom (1) is directly bonded.

**Bond Distance:** distance in Angstroms from 1 to 2.

**Angle Connect:** the number in this list of an atom forming an ordinary angle 1-2-3.

**Bond Angle:** the value of the angle 1-2-3 in degrees.

**Dihedral Connect:** the number in this list of an atom forming a dihedral (tau) angle 1-2-3-4. The dihedral angle is the angle between the normals to the plane 1-2-3 and the plane 2-3-4. This angle is conventionally given values from 0 to 180 and 0 to -180 degrees, and the sign is positive if, viewing the angle along the bond 2-3, with 2 nearer the observer than 3, the angle from the projection of 2-1 to the projection of 3-4 is traced in the clockwise sense (definition from Wilson, Decius and Cross, Molecular Vibrations, 1955, p 60).

**Dihedral Angle:** the value of the (tau) angle between the normals to the plane 1-2-3 and the plane 2-3-4 in degrees.

## 4.2.5 Atom Types

**Dialog Box: Atom Types** [[Input menu](#)]

This lists the atom types which are used in the definitions of force constants ([Forces menu](#)).

The atom type list also specifies the atomic weights, which must be accurate for proper calculation of frequencies. The data for each type is in a single line in the scrolling list or spreadsheet. To add a new entry, press the down arrow key while the focus is on the last row, or



click the **Add** button.

The **Type** number is the number which is used in the bond and angle specifications ([Forces](#) menu). It is typically the atomic number, but see below.

The **Mass** is the atomic weight - see below under ELEMENTS.DAT file for different default values.

The **Charge** is used to calculate the dipole moment, changes in which determine the infrared intensities.

If the **Use** (charge) button is not checked, this atom type is assigned the charge necessary to neutralize the molecule or unit cell. This assumes that at least some other atoms are assigned charges. This option is intended for radicals, such as CO<sub>3</sub>, SiO<sub>4</sub>, etc.

The **Radius** is optionally used in the [Coordinates](#) option (called from [the Input Atoms](#) dialog, Input menu), to help in screening bond lengths. It is not used in the [Atoms](#) graphics window, where all atoms have a constant radius ([Atom Plot Parameters](#)).

The **Color**, which is shown on the button, is selected graphically with a standard system color dialog which comes up when the button is clicked.

**Shade.** Gray shades, which are used in black-and-white display, printing and other output, are numbers ranging from 0 (white) to 15 (black).

**Used.** After a calculation, this column will indicate whether each type is actually used by the current data set. When saving a data set, if not all atom types are used by the [Input Atoms](#) you are given the option of deleting the unused types.

The **Clear** button entirely removes the current list. The **Defaults** button restores the standard atomic numbers and atomic weights. The default atom type list contains standard atomic numbers and mean atomic weights for the natural isotope mixture of each element, which is adequate for many purposes. Of course if the compound under consideration has isotopic substitution, you must correct the atomic weight. See below under ELEMENTS.DAT file.

*Type numbers.* It may be necessary to use more than one type for a given element, in order to more easily differentiate bond and angle force constants. The main alternative to using standard atomic numbers, or in other words chemical species, as type numbers is to use symmetrically distinct input atoms. This may be necessary in some cases, for example when using Urey-Bradley forces involving a single element in different coordinations, but generally should be avoided as it often leads to an excessive number of force constants. Defining bonds and angles using chemical species (atomic numbers) and bond-length and angle limits allows easy transference of specifications from one compound to another. In fact, files containing such specifications may be written and read (**Read** and **Write** file options in the [Forces](#) menu). When assigning different type numbers to the same chemical element, it is usually best to use atomic numbers modulo 100, for example 6, 106, 206, etc. for carbon atoms, as the structure display program ATOMS, which can animate the vibrational motions, will read these all as type 6 (carbon) when importing VIBRATZ files.

If you are studying compounds which are isostructural or even very similar, it may be



advantageous to retain all the force specifications using constant type numbers, and just change the atomic weights. Certainly isotopic substitutions can be handled this way, if the substitution is complete. Also, for example, substitution of one transition metal for another, or one rare-earth element for another, may not require any changes in the force constant specifications, and even the force constant values may be close enough for initial trials.

**ELEMENTS.DAT file.** See [Types of Files](#). The default data for atom types are in this file, which can be modified with a word processor. On each line are listed the atomic number; the standard chemical symbol; the effective (covalent) radius; the red, green and blue components of the color on a scale of 1-255; the gray-scale "color" (for black-and-white output) on a scale of 0 for white to 15 for black; the atomic weight; and the normal ionic charge. The standard version of this file has the atomic weight for the most abundant isotope (if this is known - otherwise the average natural weight is used). An alternate version of the file, called ELEMAY.DAT, has the average natural atomic weight. If you prefer to use this version, it should be renamed ELEMENTS.DAT. The backup for the most-common-isotope version is called ELEMAY.DAT.

#### 4.2.6 Species Data

**Dialog Box: Species Data** [[Input menu](#)]

This dialog gives information about the symmetry species for the current point or factor group. The species labels, infrared (IR) and Raman polarization components are not dependent on the particular structure.

The total number of modes, at the top of the dialog, and the number of modes in each species are not determined until the structure is calculated. This information is thereafter saved in the data file.

The **Observed** button brings up the [Observed Wavenumbers](#) dialog, for entry or correction of the observed wavenumbers, which are not necessary for a single calculation but are necessary for least-squares adjustment. The radio buttons on the right will determine which species is first shown in the [Observed Wavenumbers](#) dialog, but the **Last/Next** buttons in that dialog allow changing between species.

All the infrared and Raman components are listed for each species, but for T and E species, not all will appear in the calculated atomic motions or atomic spectra. That is, the calculated modes will show one of two for E species and one of three for T species.

#### 4.2.7 Observed Wavenumbers

**Dialog Box: Observed Wavenumbers** [[Input menu](#); [Species dialog](#)]

This dialog allows input of observed wavenumbers, for least-square adjustment or just for comparison. You must know, or be able to guess, the assignment of frequencies to species.

**Isotope Configurations** spin control. You can enter wavenumbers for up to three [Isotope Configurations](#). The base configuration is number 1. If most frequencies are identical to those of the main configuration you can write a file (which contains all frequencies) and read

it back for the other configuration(s), then change individual frequencies as necessary.

Individual modes can be omitted from any least-squares adjustment of forces. Modes with zero frequency, either observed or calculated, are never included in least-squares.

The observed wavenumbers are entered in descending order within each species. If a mode is not observed, its place must be taken by a value of 0.0 - the number of observed frequencies entered for each species should correspond with the theoretical number. This number should appear at the top of the dialog, but it will be valid only if a calculation has already been carried out. This can be done with the **Symmetry only** box in the [Control](#) window checked. The number of modes in each species appears in the [Output](#) window, and also can be seen in the [Species](#) dialog (Input menu).

The **Act on Selected Row** group allows you to insert or delete rows (observed values) and move them up or down, keeping the other observed values.

The All and None buttons after Least-squares turn all the least-squares flags, for this species only, on or off.

You can read the observed values from a text file. In this file, each wavenumber must be preceded by the species number (species in the sequence as in the [Species](#) dialog, Input menu). This is best done with a species number and a wavenumber on each line, although line breaks are ignored in the file. The wavenumbers must be given in decreasing order for each species, and with 0.0 in the place of any missing frequencies.

#### 4.2.8 Isotopes

**Dialog Box: Isotopes** [[Input](#) menu; [Control](#) Window; [Atom Types](#) dialog]

This dialog allows you to specify isotope substitutions in up to two configurations beyond the base configuration, which is number 1.

The base configuration uses the atomic weights listed in the [Atom Types](#) dialog. For spectra 2 and 3, you specify the type numbers of all atoms whose atomic weights are to be changed. For example if S atoms with type 16 are to have atomic weight 36 instead of 32, you would enter 16 and 36.0. If more than one atomic type is substituted, for example types 16 and 116 for sulfur, both must be given.

If the Calculate box is not checked, the 2nd and 3rd spectra will be skipped.

See [Isotope Configurations](#) for complete information on isotope substitutions.

### 4.3 Forces Menu

This menu is for specification of the valence forces.

Bonds, valence angles, and tau and psi four-atom angles, the first four items, are implicitly **automatic** forces - that is they are specified by giving the atoms types (usually atomic numbers) with distance and angle limits. All bonds and angles with the given specifications are then

located automatically by VIBRATZ.

The same types of bonds and angles may be specified as **manual**, in the **Manual Forces** group. With this method, each individual bond or angle in a set is specified by giving the sequence numbers of the generated atoms involved. These sequence numbers are not generally the same as the input atoms numbers (unless there is no symmetry). This method is not applicable to crystals or polymers. This method is more direct, and may be easier to apply for simple structures, but may lead to certain types of error, such as not specifying a complete set, or specifying sets which are not consistent with symmetry.

Bonds For specifying true valence bonds with atom types and distance limits.

Angles For specifying 3-atom valence angles with atom types and distance/angle limits.

Tau (Torsion) Angles For specifying 4-atom torsion angles with atom types and distance/angle limits.

Psi (Bond-Plane) Angles For specifying 4-atom torsion angles with atom types and distance/angle limits.

#### Manual Forces

Manual Bonds For specifying individual true valence bonds with generated atom numbers.

Manual Angles For specifying individual valence angles with generated atom numbers.

Manual Tau For specifying individual 4-atom torsion angles with generated atom numbers.

Manual Psi For specifying individual 4-atom torsion angles with generated atom numbers.

Urey-Bradley For specifying forces derived from X-X interaction in CX<sub>n</sub> coordination polyhedra.

Interactions - Automatic For interactions between bonds and 3-atom angles, with at least one common atom.

Interactions - Manual For interactions involving 4-atom angles, or for pairs with no atoms in common.

**Write Force File** Writes a file containing specifications from the above dialogs.

**Read Force File** Reads a file containing valence force specifications, replacing all current forces.

Use Cartesian Forces Specifies the file for reading a Cartesian atomic force matrix.

**Write Cartesian File** Writes a file containing forces converted to the basis of x, y and z Cartesian coordinates of each atom.

### 4.3.1 Bond Force List

#### Dialog Box: Bond Force List [[Forces](#) menu]

This is for "automatic" bond location - VIBRATZ searches the structure for bonds using the specified atom types (usually atomic numbers) and distance limits. For "manual" bond location, using sequence numbers of specific generated atoms, or by point-and-click, see [Manual Bonds](#).

The upper list gives a list of the valence bond forces. The data for each one is in a single line in the scrolling list or spreadsheet. To add a new entry, press the down arrow key while the focus is on the last row, or click the **Add** button. The lower list gives the specifications for each force constant in terms of atom types - an unlimited number of specifications is allowed (there must be at least one).

This is for entering the specifications for standard valence bonds (not Urey-Bradley ligand-ligand contacts - see the [Urey-Bradley Data](#) dialog).

**No.** (number). Since bonds are always first in the overall force constant list, this number is the same as the **fcon** number used in specifying [interactions](#).

**Force.** The force constant, in md/Å.

The **Polarizability** determines the contribution of the specified bond to the Raman intensity (see [Theory and Implementation](#)). Generally a value of 1.0 should be given to the most polarizable bonds.

**Nspc.** Number of atom type specifications for this bond (lower list).

**LstSq.** If this box is checked, this force constant will be refined by least squares.

**Show.** If this box is checked, the bond will be shown in the [Atoms Window](#).

**DMin/Dmax.** Bond-length minimum and maximum. If the maximum is zero, it will be reset to the default value. This default value is fixed in the [Basic Parameters](#) dialog.

The **Atom types** in the specifications in the lower list or spreadsheet should key to entries in the [Input Atoms](#) list - normally the atomic number is used. However, bonds may be differentiated by assigning different atom types ([Atom Types](#) dialog, [Input](#) menu) to structurally or chemically distinct atoms of the same element, as well as by using bond lengths.

Once specifications have been entered, the force-constant values and least-squares flags for bonds may be changed in the overall [Forces List](#), accessible from the [Control](#) Window.

**Badger's rule.** Using this relationship can avoid having to specify different force constants for different bond lengths, and may cut down drastically on the number of force constants required when bond lengths are variable. The general form used is

$$F = 1.86 / (d-d_0)^3$$

Badger used this equation to relate distances and force constants in different diatomic molecules, and  $d_0$  was a constant characteristic of certain combinations of rows in the periodic table, but it is used in VIBRATZ to relate the force constants for individual bonds of a given type to the different individual distances. Thus in VIBRATZ  $d_0$  is derived by solving the above equation when  $F$  is the overall force constant (the **FCON** entered in this dialog) and  $d$  is the average bond distance for this bond type. Then for individual bonds in this group,  $F$  is derived from the individual  $d$ . The entry "Badger" in the output gives the ratio of the force constant for the individual bond to the overall force constant.

*Note:* The first releases of VIBRATZ V2.0 used an incorrect equation as "Badger's rule" for valence bonds

$$F'' = F (d_0/d)^n$$

This is actually the equation for variation of [Urey-Bradley](#) repulsion forces. If you selected "Badger's rule" variation previously, the corrected form will now be used, and the exponent and base distance value (if used) entered previously will be ignored.

### 4.3.2 Angle Force List

**Dialog Box: Angle Force List** [[Forces](#) menu]

This is for "automatic" valence angle location - VIBRATZ searches the structure for angles using the specified atom types (usually atomic numbers) and distance and angle limits. For "manual" angle location, using sequence numbers of specific generated atoms, or by point-and-click, see [Manual Angles](#).

The upper list gives the current 3-atom valence angle coordinates. The data for each one is in a single line in the scrolling list or spreadsheet. To add a new entry, press the down arrow key while the focus is on the last row, or click the **Add** button. The lower list gives the specifications for each force constant in terms of atom types - an unlimited number of specifications is allowed (there must be at least one).

**No.** This is the number in the angle list. Do not use this number for specifying automatic interactions.

**Fcon** This is the number in the overall force constant list. Use this number for specifying automatic interactions.

**Force.** Note that angle forces may be specified in either in md-A or in md/Å. This choice is made in the [Control](#) window or the [Basic Parameters](#) dialog (**Settings menu**).

**Nspc.** Number of atom type specifications for this angle (lower list).

**Lst Sq.** If this box is checked, this force constant will be included in least-squares refinement.

**Type.** Calculations based on internal coordinates for highly symmetric molecules typically do not need to consider angle-bending in more than one plane and there may be only one internal coordinate or force constant per angle. When using Cartesian coordinates, especially in cases of lower symmetry, it is often necessary or convenient to include the complete force field, requiring two internal coordinates.

VIBRATZ supports three types of force constants for 3-atom valence angles - standard in-plane forces or internal coordinates, forces perpendicular to the plane of the bond, and forces in two perpendicular directions but with the same force constant. Standard in-plane forces are appropriate in situations in which it is not necessary to consider out-of-plane bending - for example in small molecules like H<sub>2</sub>O, in which out-of-plane bending can be resolved into in-plane bending and rotation of the molecule; or in cases in which bending is symmetrically degenerate and only one of the two directions is calculated. In-plane forces alone are also conventionally used where there is a redundancy of angle coordinates, such as X-C-X angles in non-planar CX<sub>n</sub> polyhedra with more than 3 X ligands. The second and third radio buttons in this group are for situations in which it is necessary to consider forces in more than one plane, which indeed is the general case in large molecules and crystals. Out-of-plane 3-atom angle bending may be used in many situations in place of psi (bond-plane) angles (see the CO<sub>3</sub>A example). If a given angle is not 180 degrees and out-of-plane forces are to be considered, the force constants for in-plane and out-of-plane bending are presumably different and two separate angle coordinates should normally be defined. The third option, which generates forces in two perpendicular directions, is primarily for 180 degree angles - i.e. linear configurations of three atoms (see the Ni(CO)<sub>4</sub> and Fe(CO)<sub>5</sub> examples). If the angle is 180 degrees, the actual displacement directions are arbitrary. This option will generate two coordinates for each angle. See below for definitions of the displacement or s-vectors for in-plane and out-of-plane coordinates and [Forces - General Considerations](#) for further discussion of the selection of force-constant models.

Again, the out-of-plane angle forces used in VIBRATZ may in some cases take the place of tau and/or psi forces used in calculations on molecules with internal coordinates.

**DMax1/DMax2.** The maximum distance for each of the two legs of the angle. If a value is zero it will be reset to the default maximum ( [Basic Parameters](#) dialog.).

**AngMin/AngMax.** The minimum and maximum values for the angle itself, in degrees. Angle limit values of zero will skip angle tests.

The atom types in the lower **Specifications** list should key to entries in the [Atom Types](#) list - normally the atomic number is used. Types must be given for the Central atom, and for the two legs.

Multiple specifications in terms of atom types are typically used for isotopic substitution. For example, if you are calculating deuterium substituted hydrocarbons and define deuterium as atom type 101 (see [Atom Types](#)), the type specifications (6, 1, 1), (6, 1, 101) and (6, 101, 101) would cover all possible combinations of isotopes for H-C-H.

Note that for [Urey-Bradley](#) forces, angles involving adjacent ligands for the relevant polyhedra (X-C-X angles) must be defined in this dialog, even if there are not considered to be any true

valence bending forces. That is, the force constants for these angles specified in this dialog may be zero.

Once specifications have been entered, the force-constant values and least-squares flags for angles may be changed in the overall [Forces List](#), accessible from the [Control Window](#).

**Urey-Bradley forces.** If you are going to use [Urey-Bradley](#) forces for one or more types of polyhedron, the list of angles should be complete for each polyhedron, including the atom types involved in all ligand-central-ligand angles which correspond to ligand-ligand contact, and excluding angles which do not correspond to ligand-ligand contact. In an octahedron, for example, the 90 degree angles should be included, but the 180 degree angles should not.

The **Units for angle forces** radio buttons determine the units of force constants and the way they are interpreted. Force constants for bonds are always in md/A (millidynes per Angstrom), but those involving angles may be expressed in either of two ways - in md-A (per radian squared) or in md/A. Published values may be given either way, and it is absolutely necessary to choose the appropriate option if such values are to be used or compared. See the [Basic Parameters](#) dialog ([Setting](#) menu) for more details.

*Orientation of coordinates for 180-degree angles and definition of in-plane and out-of-plane coordinates.* Angles in the equilibrium position are always 0 to 180 degrees. In the case of 180 degree angles it is necessary to specify arbitrarily the direction of the displacement or s-vectors (see WDC, p. 54). For in-plane coordinates the s-vectors are obtained from the cross-product of the bond vectors and the y-axis, or the cross-product of the bond vectors and the z-axis if the bond vectors are nearly parallel to y. This ensures that there is a component of displacement in the x-direction, which may be the only direction calculated for many degenerate species (this is the default direction selected by the basis functions in most cases). Since the non-central atoms of 3-atom angles are considered to be interchangeable (and these atoms are often of the same type or chemical species), the sign of the s-vectors must also be specified arbitrarily. If the s-vectors of the outer atoms (which are identical for 180 degree angles) have a significant z component, this is made to be positive; if the z component is very small, then x is made to be positive, and if the s-vectors are nearly parallel to y, then the y-component is made to be positive.

For the out-of-plane coordinates of 180 degree angles, the s-vectors are perpendicular to the in-plane s-vectors and the bond vectors. The same procedure is used to determine sign as for the in-plane coordinates.

In the case of non-180-degree angles, the s-vectors for in-plane coordinates are obtained in the standard way (WDC, p. 56), and the s-vectors for out-of-plane coordinates are perpendicular to the plane of the angle. The sign is determined as above.

After the solution of the secular equation and determination of atomic motions, it is necessary to resolve the atomic motions into in-plane and out-of-plane angle bending, for partitioning of the potential energy. In practice the displaced atom coordinates are projected onto two planes, one of which is the original plane of the angle (if the angle is not 180 degrees), and the other of which is a plane perpendicular to the plane of the angle, passing through the two non-central atoms. These two projections give the in-plane and out-of-plane angle changes, respectively.



Interactions involving out-of-plane angle coordinates or either type of coordinate for 180 degree angles may be questionable because of the arbitrary direction and/or sign of the displacements. Of course this depends on the particular geometry and symmetry.

Once specifications have been entered, the force-constant values and least-squares flags may be changed in the overall [Forces List](#), accessible from the [Control](#) Window.

### 4.3.3 Tau (Torsion) Angle Force List

**Dialog Box: Tau (Torsion) Angle Force List** [[Forces menu](#)]

This is for "automatic" torsion angle location - VIBRATZ searches the structure for torsion angles using the specified atom types (usually atomic numbers) and distance and angle limits. For "manual" torsion angle location, using sequence numbers of specific generated atoms, or by point-and-click, see [Manual Tau](#).

The upper list gives the current 4-atom tau angle forces. The data for each one is in a single line in the scrolling list or spreadsheet. To add a new entry, press the down arrow key while the focus is on the last row, or click the **Add** button. The lower list gives the specifications for each force constant in terms of atom types - an unlimited number of specifications is allowed (there must be at least one).

**No.** This is the number in the angle list.

**Fcon** This is the number in the overall force constant list.

**Force.** Note that angle forces may be specified in either in md-A or in md/A. This choice is made in the [Control](#) window or the [Basic Parameters](#) dialog (**Settings menu**).

**Nspc.** Number of atom type specifications for this angle (lower list).

**Lst Sq.** If this box is checked, this force constant will be included in least-squares refinement.

**Dmax12/Dmax23/Dmax34.** These are the maximum bond distances for each of the three legs. If a value is zero it will be reset to the default maximum ( [Basic Parameters](#) dialog).

**Dmin23.** This is the minimum distance for the middle leg. The two middle atoms in a torsion angle need not be connected to each other with an actual chemical bond. In the example ALLENE the second and third atoms are taken to be the two end atoms of a linear C-C-C configuration, while the central C atom is ignored. DMin23 is required to exclude the two shorter C-C bonds.

**TauMin/Taumax.** The angle limits are applied to the absolute value of the tau angle. Tau angles assume the sign convention as defined by WDC, p. 60; the angle is positive if, viewing the atoms along the bond 2-3 with 2 nearer the observer than 3, the angle from the projection 2-1 to the projection of 3-4 is traced in the clockwise sense. The dog-leg configuration in the diagram in the dialog shows a tau angle near 180; an angle near 0 would give a U-shaped



pattern. Thus using the absolute limits assumes that it is more important to distinguish between dog-leg and U configurations than between left- and right-handed intermediate configurations. Angle limit values of zero will skip angle tests.

The atom types in the lower specification list should key to entries in the [Atom Types](#) list - normally the atomic number is used. Types must be given for each of the four atoms involved in the sequence shown in the diagram to the right.

Once specifications have been entered, the force-constant values and least-squares flags may be changed in the overall [Forces List](#), accessible from the [Control](#) Window.

### 4.3.4 Psi (Bond-Plane) Angle Force List

**Dialog Box: Psi (Bond-Plane) Angle Force List** [[Forces](#) menu]

This is for "automatic" psi bond-plane angle location - VIBRATZ searches the structure for psi angles using the specified atom types (usually atomic numbers) and distance and angle limits. For "manual" psi angle location, using sequence numbers of specific generated atoms, or by point-and-click, see [Manual Psi](#).

The upper list gives the current 4-atom psi (bond-plane) angle forces. The data for each one is in a single line in the scrolling list or spreadsheet. To add a new entry, press the down arrow key while the focus is on the last row, or click the **Add** button. The lower list gives the specifications for each force constant in terms of atom types - an unlimited number of specifications is allowed (there must be at least one).

**No.** This is the number in the angle list.

**Fcon** This is the number in the overall force constant list.

**Force.** Note that angle forces may be specified in either in md-A or in md/A. This choice is made in the [Control](#) window or the [Basic Parameters](#) dialog (**Settings menu**).

**Nspc.** Number of atom type specifications for this angle (lower list).

**Lst Sq.** If this box is checked, this force constant will be included in least-squares refinement.

**Dmax12/Dmax23/Dmax34.** These are the maximum bond distances for each of the three legs.

**PsiMin/Psimax.** Minimum and maximum values for the psi angle. The psi angle itself is the complement of the angle between bond vector 1-2 and the perpendicular to the plane 2-3-4. The angle is zero if all four atoms lie in a plane. Psi angles assume the following sign convention. Viewing the plane defined by atoms 2, 3 and 4 down the 3-4 vector (atom 3 nearest), the psi angle is positive if the projection of the 2-1 vector is traced in a clockwise direction from the extension of the 2-3-4 plane. However, if atoms 3 and 4 are the same type or chemical species, it would be a matter of chance which one is taken first, and therefore whether the psi angle is positive or negative. Thus if the psi angle is other than zero it is taken to be positive and the

number 3 and 4 atoms are switched if necessary to be consistent with this choice. The displacement or s-vectors have direction such as to increase the value of the psi angle. If the psi angle is zero, the s-vector of the central or number 2 atom is given direction (sign) so that its z-component is positive; or if z is near zero, so that the x-component is positive; or if the s-vector is nearly parallel to y, so that the y-component is positive.

For these reasons, negative values for the angle limits have no meaning. Angle limit values of zero will skip angle tests..

**One only.** If this box is checked, one psi coordinate will be located for each central atom (atom 2). This should be used for a configuration such as CO<sub>3</sub>, for example. In this case, assuming all the O atoms are equivalent and are the same type, three psi coordinates will be located if this box is not checked. Indeed, occasions when more than one psi coordinate is needed for a given central atom must be rare, if they exist at all.

Once specifications have been entered, the force-constant values and least-squares flags may be changed in the overall [Forces List](#), accessible from the [Control](#) Window.

### 4.3.5 Manual Forces

This group of input dialogs is for locating sets of bonds using individual generated atoms rather than overall specifications based on type (atomic number) and length limits. For "automatic" bond specification of the latter type, see [Bond Force List](#). This type of bond is not applicable to crystals or polymers.

Using this type of forces when entering a new structure can be done graphically as follows:

- 1) Use the File/New or Import options to enter data up to the point of entering forces, but do not enter forces.
- 2) Click on the **Calculate** button. If there are no bond and angle forces specified a full calculation will not be carried out - the calculation will be to locate atoms and do a symmetry analysis only. If the Atoms plot box in the Control Window is checked, a drawing with atoms, but without bonds, will appear. You can click on atoms successively to specify manual bonds and angle, or you can use the type numbers of the atoms to enter the information in the Manual Forces dialogs. To see the generated atom numbers in the plot, go to the Atoms Plot Parameters dialog (Params button in the dialog bar of the Atoms window, or in the Settings menu) and select Numbers in the Labels group.

#### 4.3.5.1 Manual Bonds

**Dialog Box: Manual Bond Force List** [[Forces](#) menu]

This is for locating sets of bonds using individual generated atoms rather than overall specifications based on type (atomic number) and length limits. For "automatic" bond specification of the latter type, see [Bond Force List](#). This type of bond is not applicable to crystals or polymers.

The upper list gives a list of the valence bond forces. The data for each one is in a single line in

the scrolling list or spreadsheet. To add a new entry, press the down arrow key while the focus is on the last row, or click the **Add** button. The lower list gives the specifications for each force constant in terms of atom types - an unlimited number of specifications is allowed (there must be at least one).

Each entry in the upper list is an "fcon" or force constant - this pertains to a set of actual bonds, specified by the list of pairs of atom numbers in the lower list. This set may or may not be equivalent by symmetry, and whether or not a set of bonds conforms with symmetry is up to you, when you specify the individual atom pairs (automatic bonds specified in the [Bond Force List](#) always conform with symmetry). All members of a symmetry-equivalent set should be included in one manual bond in this list, but one manual bond is not limited to a single symmetry-equivalent set - there may be several chemically similar bonds included.

This is for entering the specifications for standard valence bonds (not Urey-Bradley ligand-ligand contacts - see the [Urey-Bradley Data](#) dialog).

**No.** (number). Since bonds are always first in the overall force constant list, this number is the same as the **fcon** number used in specifying [interactions](#).

**Force.** The force constant, in md/A.

The **Polarizability** determines the contribution of the specified bond to the Raman intensity (see [Theory and Implementation](#)). Generally a value of 1.0 should be given to the most polarizable bonds.

**Nspc.** Number of atom type specifications for this bond (lower list).

**LstSq.** If this box is checked, this force constant will be refined by least squares.

**Show.** If this box is checked, the bond will be shown in the [Atoms Window](#).

The **Atom numbers** in the specifications in the lower list or spreadsheet must be the numbers of actual generated atoms in the molecule. These are best obtained from the [Atoms Window](#) - in fact you can select bonds involving atoms which have been clicked in succession with the mouse. This process, after a query (), will bring up this dialog. Generated atom numbers with coordinates can also be obtained from the [Output Window](#). The numbers entered here are *not* necessarily the [Input Atoms](#) as entered in the Input menu, although the lists of input and generated atoms will be the same if there is no symmetry. If there is symmetry, there will be more generated atoms than input atoms.

Once specifications have been entered, the force-constant values and least-squares flags for bonds may be changed in the overall [Forces List](#), accessible from the [Control](#) Window.

**Badger's rule.** Using this relationship can avoid having to specify different force constants for different bond lengths, and may cut down drastically on the number of force constants required when bond lengths are variable. The general form used is

$$F = 1.86 / (d-d_0)^3$$

Badger used this equation to relate distances and force constants in different diatomic molecules, and  $d_0$  was a constant characteristic of certain combinations of rows in the periodic table, but it is used in VIBRATZ to relate the force constants for individual bonds of a given type to the different individual distances. Thus in VIBRATZ  $d_0$  is derived by solving the above equation when  $F$  is the overall force constant (the FCON entered in this dialog) and  $d$  is the average bond distance for this bond type. Then for individual bonds in this group,  $F$  is derived from the individual  $d$ . The entry "Badger" in the output gives the ratio of the force constant for the individual bond to the overall force constant.

*Note:* The first releases of VIBRATZ V2.0 used an incorrect equation as "Badger's rule" for valence bonds

$$F'' = F (d_0/d)^n$$

This is actually the equation for variation of [Urey-Bradley](#) ligand-ligand repulsion forces. If you selected "Badger's rule" variation previously, the corrected form will now be used, and the exponent and base distance value (if used) entered previously will be ignored.

#### 4.3.5.2 Manual Angles

**Dialog Box: Manual Angle Force List** [[Forces](#) menu]

This is for locating sets of angles using individual generated atoms rather than overall specifications based on type (atomic number) and length limits. For "automatic" angle specification of the latter type, see [Angles](#). This type of angle is not applicable to crystals or polymers.

The upper list gives the current 3-atom valence angle coordinates. The data for each one is in a single line in the scrolling list or spreadsheet. To add a new entry, press the down arrow key while the focus is on the last row, or click the **Add** button. The lower list gives the specifications for each force constant in terms of atom types - an unlimited number of specifications is allowed (there must be at least one).

Each entry in the upper list is an "fcon" or force constant - this pertains to a set of actual angles, specified by the list of triplets of atom numbers in the lower list. This set may or may not be equivalent by symmetry, and whether or not a set of angles conforms with symmetry is up to you, when you specify the individual atom triplets (automatic angles specified in the [Angles](#) dialog always conform with symmetry). All members of a symmetry-equivalent set should be included in one manual angle in this list, but one manual angle is not limited to a single symmetry-equivalent set - there may be several chemically similar angles included.

**No.** This is the number in the angle list. Do not use this number for specifying automatic interactions.

**Fcon** This is the number in the overall force constant list. Use this number for specifying automatic interactions.

**Force.** Note that angle forces may be specified in either in md-A or in md/A. This choice is made with the **Units for angle forces** radio box (below).

**Nspc.** Number of atom type specifications for this angle (lower list).

**Lst Sq.** If this box is checked, this force constant will be included in least-squares refinement.

**Type.** Calculations based on internal coordinates for highly symmetric molecules typically do not need to consider angle-bending in more than one plane and there may be only one internal coordinate or force constant per angle. When using Cartesian coordinates, especially in cases of lower symmetry, it is often necessary or convenient to include the complete force field, requiring two internal coordinates.

VIBRATZ supports three types of force constants for 3-atom valence angles - standard in-plane forces or internal coordinates, forces perpendicular to the plane of the bond, and forces in two perpendicular directions but with the same force constant. Standard in-plane forces are appropriate in situations in which it is not necessary to consider out-of-plane bending - for example in small molecules like H<sub>2</sub>O, in which out-of-plane bending can be resolved into in-plane bending and rotation of the molecule; or in cases in which bending is symmetrically degenerate and only one of the two directions is calculated. In-plane forces alone are also conventionally used where there is a redundancy of angle coordinates, such as X-C-X angles in non-planar CX<sub>n</sub> polyhedra with more than 3 X ligands. The second and third radio buttons in this group are for situations in which it is necessary to consider forces in more than one plane, which indeed is the general case in large molecules and crystals. Out-of-plane 3-atom angle bending may be used in many situations in place of psi (bond-plane) angles (see the CO<sub>3</sub>A example). If a given angle is not 180 degrees and out-of-plane forces are to be considered, the force constants for in-plane and out-of-plane bending are presumably different and two separate angle coordinates should normally be defined. The third option, which generates forces in two perpendicular directions, is primarily for 180 degree angles - i.e. linear configurations of three atoms (see the Ni(CO)<sub>4</sub> and Fe(CO)<sub>5</sub> examples). If the angle is 180 degrees, the actual displacement directions are arbitrary. This option will generate two coordinates for each angle. See below for definitions of the displacement or s-vectors for in-plane and out-of-plane coordinates and [Forces - General Considerations](#) for further discussion of the selection of force-constant models.

Again, the out-of-plane angle forces used in VIBRATZ may in some cases take the place of tau and/or psi forces used in calculations on molecules with internal coordinates.

The **Atom numbers** in the specifications in the lower list or spreadsheet must be the numbers of actual generated atoms in the molecule. These are best obtained from the [Atoms Window](#) - in fact you can select bonds involving atoms which have been clicked in succession with the mouse. Note that when you click on three atoms defining an angle the central atom is second, but in this list the central atom is first. This process, after a query (), will bring up this dialog. Generated atom numbers with coordinates can also be obtained from the [Output Window](#). The numbers entered here are *not* necessarily the [Input Atoms](#) as entered in the Input menu, although the lists of input and generated atoms will be the same if there is no symmetry. If there is symmetry, there will be more generated atoms than input atoms.

Note that for [Urey-Bradley](#) forces, angles involving adjacent ligands for the relevant polyhedra (X-C-X angles) must be defined in this dialog, even if there are not considered to be any true valence bending forces. That is, the force constants for these angles specified in this dialog may be zero.

Once specifications have been entered, the force-constant values and least-squares flags for angles may be changed in the overall [Forces List](#), accessible from the [Control Window](#).

The **Units for angle forces** radio buttons determine the units of force constants and the way they are interpreted. Force constants for bonds are always in md/A (millidynes per Angstrom), but those involving angles may be expressed in either of two ways - in md-A (per radian squared) or in md/A. Published values may be given either way, and it is absolutely necessary to choose the appropriate option if such values are to be used or compared. See the [Basic Parameters](#) dialog ([Setting](#) menu) for more details.

*Orientation of coordinates for 180-degree angles and definition of in-plane and out-of-plane coordinates.* Angles in the equilibrium position are always 0 to 180 degrees. In the case of 180 degree angles it is necessary to specify arbitrarily the direction of the displacement or s-vectors (see WDC, p. 54). For in-plane coordinates the s-vectors are obtained from the cross-product of the bond vectors and the y-axis, or the cross-product of the bond vectors and the z-axis if the bond vectors are nearly parallel to y. This ensures that there is a component of displacement in the x-direction, which may be the only direction calculated for many degenerate species (this is the default direction selected by the basis functions in most cases). Since the non-central atoms of 3-atom angles are considered to be interchangeable (and these atoms are often of the same type or chemical species), the sign of the s-vectors must also be specified arbitrarily. If the s-vectors of the outer atoms (which are identical for 180 degree angles) have a significant z component, this is made to be positive; if the z component is very small, then x is made to be positive, and if the s-vectors are nearly parallel to y, then the y-component is made to be positive.

For the out-of-plane coordinates of 180 degree angles, the s-vectors are perpendicular to the in-plane s-vectors and the bond vectors. The same procedure is used to determine sign as for the in-plane coordinates.

In the case of non-180-degree angles, the s-vectors for in-plane coordinates are obtained in the standard way (WDC, p. 56), and the s-vectors for out-of-plane coordinates are perpendicular to the plane of the angle. The sign is determined as above.

After the solution of the secular equation and determination of atomic motions, it is necessary to resolve the atomic motions into in-plane and out-of-plane angle bending, for partitioning of the potential energy. In practice the displaced atom coordinates are projected onto two planes, one of which is the original plane of the angle (if the angle is not 180 degrees), and the other of which is a plane perpendicular to the plane of the angle, passing through the two non-central atoms. These two projections give the in-plane and out-of-plane angle changes, respectively.

Interactions involving out-of-plane angle coordinates or either type of coordinate for 180 degree angles may be questionable because of the arbitrary direction and/or sign of the displacements. Of course this depends on the particular geometry and symmetry.

Once specifications have been entered, the force-constant values and least-squares flags may be changed in the overall [Forces List](#), accessible from the [Control](#) Window.

### 4.3.5.3 Manual Tau

#### Dialog Box: Manual Tau (Torsion) Angle Force List [[Forces menu](#)]

This is for locating sets of tau angles using individual generated atoms rather than overall specifications based on type (atomic number) and length limits. For "automatic" tau specification of the latter type, see [Tau \(Torsion\) Angles](#). The manual type of tau angle is not applicable to crystals or polymers.

The upper list gives the current 4-atom tau angle forces. The data for each one is in a single line in the scrolling list or spreadsheet. To add a new entry, press the down arrow key while the focus is on the last row, or click the **Add** button. The lower list gives the specifications for each force constant in terms of atom types - an unlimited number of specifications is allowed (there must be at least one).

Each entry in the upper list is an "fcon" or force constant - this pertains to a set of actual tau angles, specified by the list of quadruplets of atom numbers in the lower list. This set may or may not be equivalent by symmetry, and whether or not a set of tau angles conforms with symmetry is up to you, when you specify the individual atom quadruplets (automatic tau angles specified in the [Tau \(Torsion\) Angles](#) dialog always conform with symmetry). All members of a symmetry-equivalent set should be included in one manual tau angle in this list, but one manual tau angle is not limited to a single symmetry-equivalent set - there may be several chemically similar angles included.

**No.** This is the number in the angle list.

**Fcon** This is the number in the overall force constant list.

**Force.** Note that angle forces may be specified in either in md-A or in md/A. This choice is made in the [Control](#) window or the [Basic Parameters](#) dialog (**Settings menu**).

**Nspc.** Number of atom type specifications for this angle (lower list).

**Lst Sq.** If this box is checked, this force constant will be included in least-squares refinement.

The **Atom numbers** in the specifications in the lower list or spreadsheet must be the numbers of actual generated atoms in the molecule. These are best obtained from the [Atoms Window](#) - in fact you can select bonds involving atoms which have been clicked in succession with the mouse. This process, after a query (), will bring up this dialog. Generated atom numbers with coordinates can also be obtained from the [Output Window](#). The numbers entered here are *not* necessarily the [Input Atoms](#) as entered in the Input menu, although the lists of input and generated atoms will be the same if there is no symmetry. If there is symmetry, there will be more generated atoms than input atoms.

The sequence of atom numbers may be reversed - that is 1-2-3-4 is equivalent to 4-3-2-1.



Once specifications have been entered, the force-constant values and least-squares flags may be changed in the overall [Forces List](#), accessible from the [Control](#) Window.

#### 4.3.5.4 Manual Psi

##### Dialog Box: Manual Psi (Bond-Plane) Angle Force List [[Forces](#) menu]

This is for locating sets of psi angles using individual generated atoms rather than overall specifications based on type (atomic number) and length limits. For "automatic" psi specification of the latter type, see [Psi \(Bond-Plane\) Angles](#). The manual type of psi angle is not applicable to crystals or polymers.

The upper list gives the current 4-atom psi (bond-plane) angle forces. The data for each one is in a single line in the scrolling list or spreadsheet. To add a new entry, press the down arrow key while the focus is on the last row, or click the **Add** button. The lower list gives the specifications for each force constant in terms of atom types - an unlimited number of specifications is allowed (there must be at least one).

Each entry in the upper list is an "fcon" or force constant - this pertains to a set of actual psi angles, specified by the list of quadruplets of atom numbers in the lower list. This set may or may not be equivalent by symmetry, and whether or not a set of psi angles conforms with symmetry is up to you, when you specify the individual atom quadruplets (automatic psi angles specified in the [Psi \(Bond-Plane\) Angles](#) dialog always conform with symmetry). All members of a symmetry-equivalent set should be included in one manual psi angle in this list, but one manual psi angle is not limited to a single symmetry-equivalent set - there may be several chemically similar angles included.

**No.** This is the number in the psi angle list.

**Fcon** This is the number in the overall force constant list.

**Force.** Note that angle forces may be specified in either in md-A or in md/A. This choice is made in the [Control](#) window or the [Basic Parameters](#) dialog (**Settings menu**).

**Nspc.** Number of atom type specifications for this angle (lower list).

**Lst Sq.** If this box is checked, this force constant will be included in least-squares refinement.

The **Atom numbers** in the specifications in the lower list or spreadsheet must be the numbers of actual generated atoms in the molecule. These are best obtained from the [Atoms Window](#) - in fact you can select bonds involving atoms which have been clicked in succession with the mouse. This process, after a query (), will bring up this dialog. Generated atom numbers with coordinates can also be obtained from the [Output Window](#). The numbers entered here are *not* necessarily the [Input Atoms](#) as entered in the Input menu, although the lists of input and generated atoms will be the same if there is no symmetry. If there is symmetry, there will be more generated atoms than input atoms.



The sequence of atoms in the list (and as selected with the mouse) must be 1) outer atom defining the "bond" of the bond-plane; 2) central atom; and 3) and 4) other atoms defining, with 2), the plane. Atoms 3) and 4) are interchangeable in sequence.

Once specifications have been entered, the force-constant values and least-squares flags may be changed in the overall [Forces List](#), accessible from the [Control](#) Window.

### 4.3.6 Urey Bradley Data

#### Dialog Box: Urey Bradley Data [[Forces](#) menu]

This dialog gives some overall specifications for the [Urey-Bradley](#) model and provides access to the data for individual polyhedron type and ligand-ligand pseudo-bond specifications.

Currently all Urey-Bradley information is automatic, not manual, that is specifications are in terms of atom types and bond distance limits, rather than in terms of individual generated atoms.

Use of Urey-Bradley forces requires entering data in four separate places.

- 1) All central-ligand (C-X) bonds must be defined in the [Bonds](#) dialog.
- 2) The ligand-central-ligand (X-C-X) angles corresponding to each ligand-ligand "contact" in each U-B polyhedron must be defined in the [Angles](#) dialog. This is true even if there are considered to be no valence angle forces apart from those which are derived from the U-B ligand-ligand bonds, since there are always derived U-B angle forces and these must be added to any valence angle forces. Thus the list of angles should be complete, including the atom types involved in all X-C-X angles which correspond to X-X contact, and excluding angles which do not correspond to X-X contact. In an octahedron, for example, the 90 degree angles should be included, but the 180 degree angles should not.
- 3) The U-B polyhedra themselves must be defined in the [Urey-Bradley Polyhedron Specification](#) dialog, accessible from this dialog (upper list).
- 4) The U-B ligand-ligand (X-X) "bonds" must be defined in the [Urey-Bradley Ligand-Ligand Bond Specification](#) dialog, accessible from this dialog (lower list). These are defined throughout the structure (all U-B polyhedra), not just for individual polyhedra.

Once you have specified the U-B polyhedra as in 3) above, you may select the **Derive from Angles** button - this will derive all the U-B ligand-ligand (X-X) "bonds" as in 4) from the list of valence [angles](#) as in 2) above. The list of X-X "bonds" will need to be edited, if only to insert the proper force values - distance limits may also need to be revised. The upper distance limit is just calculated from the upper limits in the angle specification.

The three radio buttons at the top of the dialog specify the way the "internal tension"  $\kappa$  and the linear force constants  $F'$  and  $H'$  are handled.

- (a) If the **F' derived from  $\kappa$**  option is selected,  $H'$  force constants are set to zero and the

values of the  $F'$  force constants are calculated from the formula for kappa. (b) If the **Use given  $F'$**  option is selected, the values for  $F'$  are entered along with values for  $F$  in the [Urey-Bradley Ligand-Ligand Bonds](#) dialog. In this case, or if (c) the  **$F' = -0.1 F$**  option is selected, the  $H'$  values are derived from kappa and  $F'$  using the formula for kappa. See [Urey-Bradley Forces - Theory](#) for more explanation of these options.

**Print out derived valence forces.** Those forces in the Urey-Bradley/Shimanouchi model which are not of the conventional quadratic nature (namely  $F'$  and  $H'$ ) must be converted to quadratic pseudo-valence forces. This results in additions to the C-X bond forces, X-C-X angle forces and C-X bond-bond, bond-angle and angle/angle interactions. These are added to any forces of these types which may be defined independently of the Urey-Bradley forces (Urey-Bradley forces are those arising from the interactions of the ligands with each other). If this box is checked, there will be a printout in the [Output](#) file (and the output window if selected) of the relevant forces. If these forces are then added to any true valence forces, and explicit Urey-Bradley forces are removed, the results should be exactly the same.

#### 4.3.6.1 Urey-Bradley Polyhedron Specification

**Dialog Box: Urey-Bradley Polyhedron Specification** [[Urey-Bradley Data](#) dialog, [Forces](#) menu]

This dialog gives the definition of each type of Urey-Bradley polyhedron. The central-ligand bonds must be defined in the [Bonds](#) dialog, and the ligand-central-ligand angles corresponding to each ligand-ligand "contact" must be defined in the [Angles](#) dialog. The ligand-ligand "contacts" or "bonds" are defined in the [Ligand-Ligand Bond](#) dialog, accessible from the main [Urey-Bradley Data](#) dialog.

The same **Central atom type number** should not be used for more than one polyhedron specification, even if coordination numbers are different. Thus it may be necessary to define more than one atom type ([Atom Types](#) dialog in the [Input Menu](#)) for a given chemical element. For example, aluminum in silicates often occurs in both tetrahedral and octahedral coordination, and carbon may occur in various coordinations in moderately complex molecules. Type numbers such as 13 and 113 for aluminum, and 6, 106 etc. for carbon can be assigned in such cases.

**Coordination number** may range from 2 to 8.

The **Ligand atom types** list does not require a type for each individual ligand, only the types necessary to include all ligands. For example, if all ligands are of type 8, the number 8 should be entered only once and other boxes should be blank.

The **Kappa value** is that in the approximation of Urey-Bradley forces by Shimanouchi. Once specifications have been entered, the force-constant value and least-squares flag for kappa may be changed in the overall [Forces List](#), accessible from the [Control](#) Window. Kappa is used only for 4- and 6- coordinated polyhedra, which are assumed to be at least approximately tetrahedral and octahedral, respectively. If you are dealing with a 4- or 6- coordinated polyhedron which is not approximately tetrahedral or octahedral respectively (for example tetragonal planar), kappa should normally be set to zero. Setting kappa equal zero is equivalent to using a first-order approximation to the angular redundancies in the polyhedron, instead of second-order. Note,

however, that in planar configurations the second-order terms vanish anyway.

**Maximum distance.** Any atoms bonded to the central atom at greater than the specified distance will not be included in U-B forces. If the value is 0.0, no test will be applied.

See [Urey-Bradley Forces - Theory](#) for more details on the implementation.

#### 4.3.6.2 Urey-Bradley Ligand-Ligand Bond Specifications

**Dialog Box: Urey-Bradley Ligand-Ligand Bond Specifications** [[Urey-Bradley Data](#) dialog, [Forces](#) menu]

Specifications for Urey-Bradley ligand-ligand "bonds" are similar to those for valence bonds (Bonds dialog) except for the secondary force constant  $f'$ . This value is used only if the second model (Use given  $f'$ ) in the main [Urey-Bradley Data](#) dialog is selected.

The specifications given in this dialog apply throughout the structure, and not to any specific U-B polyhedron type. For example, in the silicate garnet crystal structure in which there are three different cations, with coordination numbers of 4, 6 and 8, but only one anion, oxygen, a single U-B bond oxygen-oxygen specification could conceivably be applied to all three polyhedra. However, the O-O distances differ greatly and it is probably advisable to assign different force constants to different ligand-ligand distances.

Once specifications have been entered, the force-constant values and least-squares flags may be changed in the overall [Forces List](#), accessible from the [Control](#) Window.

**Distance dependence.** Using this option can avoid having to specify different force constants for different ligand-ligand bond lengths, and may cut down drastically on the number of force constants required when bond lengths are variable. According to this rule, the repulsion force constants involving two specific types of atoms tend to be related according to

$$F' = F (d_0/d)^n$$

where  $d$  is the actual bond distance,  $d_0$  is a reference distance, typically the average distance for this type of bond, and  $n$  is the exponent, usually about 9. In VIBRATZ, the force constant  $F$  is specified in this dialog and may be subject to least-square refinement, and  $F'$  is applied to a particular bond. The reference distance  $d_0$  may be the average for this particular bond specification (determined at run time), or it may be a fixed value which you enter. Neither the exponent nor the fixed reference distance are subject to least-squares refinement. The correction factor ( $F'/F$ ) applied for each ligand-ligand "bond" is given in the output in the column under "d-factor".

This relationship is applied to the main UB ligand-ligand "bond" force, that is  $F = f$ . If the secondary UB force  $f'$  is dependent on the main force  $f$ , as specified in the main [Urey-Bradley Data](#) dialog, it is derived from the adjusted value of  $f$ . If the secondary UB force  $f'$  is independent, it is not subject to adjustment.

This distance dependence was incorrectly referred to in initial releases of VIBRATZ V2.0 as "Badger's rule" - see [Bonds](#) and [Manual Bonds](#) for Badger's rule as applied to valence bonds.

See [Urey-Bradley Forces - Theory](#) for more details on the implementation.

### 4.3.7 Interactions - Manual

**Dialog Box: Interactions - Manual** [[Forces](#) menu]

This dialog is for specifying interactions involving tau (torsion) or psi (bond-plane) angles, or involving bonds or 3-atom angles which do not share atoms. The index number of each individual generated coordinate (bond or atom) must be known, which can only be done by carrying out a preliminary calculation and obtaining the numbers from the [printout](#). Again, this option specifies interactions between individual specific generated bonds and angles (including tau and psi), rather than types, as in the Interactions - Automatic option. Of course if the specifications of the primary force constants are changed so that the numbers change, the Manual Interactions may be invalid.

For interactions involving bonds and 3-atoms angles which share atoms, it is usually easier to use the [Interactions - Automatic](#) option.

The upper list gives the interaction forces. The data for each one is in a single line in the scrolling list or spreadsheet. To add a new entry, press the down arrow key while the focus is on the last row, or click the **Add** button. The lower list gives the specifications for each force constant in terms of pairs of primary coordinates - an unlimited number of specifications is allowed (there must be at least one).

**No.** This is the number in the automatic interaction list.

**Fcon** This is the number in the overall force constant list.

**Force.** The force constants for interactions may be entered either in variable units (md/A for bond/bond; md for bond/angle and md-A for angle/angle interactions) or in constant md/A. The choice between the two types of force is made in the [Control](#) window or the [Basic Parameters](#) dialog in the [Setting](#) menu. See that dialog for the details of calculation using the two types of units, and formulas for interconversion of force constants.

**Nspc.** Number of atom type specifications for this interaction (lower list).

**Lst Sq.** If this box is checked, this force constant will be included in least-squares refinement.

**Specifications** (lower list). In the fields labeled **Coor1** and **Coor2** you must enter the numbers of two generated coordinates (bonds and angles) - *not* coordinate types or fcons as listed in the dialogs of the Forces menu. The generated coordinate numbers must be obtained from the [printout](#) of a preliminary calculation - these numbers are in the sections below "Internal Coordinates Generated".

*Note :* there is currently a limit of 50 coordinate pairs per force constant.

For examples of this type of interaction specification, see the sample files BENZ.VBR and NI(CO)4.VBR

Certain types of interactions may be questionable because of the arbitrary direction and/or sign of the displacements. This includes: 1) out-of-plane coordinates for non-180-degree 3-atom angles; 2) either in-plane or out-of-plane coordinates for 180-degree 3-atom angles; and/or 3) psi angles for planar configurations (psi angle = 0). Of course this may depend on the particular geometry and symmetry.

Once specifications have been entered, the force-constant values and least-squares flags may be changed in the overall [Forces List](#), accessible from the [Control](#) Window.

### 4.3.8 Interactions - Automatic

**Dialog Box: Interactions - Automatic** [[Forces](#) menu]

This option will automatically locate interactions involving bonds and 3-atom valence angles sharing one or two atoms. It cannot be used for interactions involving tau or psi 4-atom angles, or bonds and 3-atom angles which do not share atoms. For these other types of interaction, use the [Interactions - Manual](#) option.

The left upper list gives the interaction forces. The data for each one is in a single line in the scrolling list or spreadsheet. To add a new entry, press the down arrow key while the focus is on the last row, or click the **Add** button. The right upper list gives the specifications for each force constant in terms of atom types - an unlimited number of specifications is allowed (there must be at least one).

**No.** This is the number in the automatic interaction list.

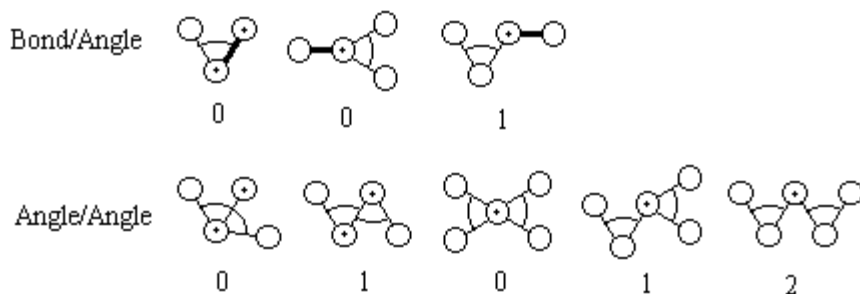
**Fcon** This is the number in the overall force constant list.

**Force.** The force constants for interactions may be entered either in variable units (md/A for bond/bond; md for bond/angle and md-A for angle/angle interactions) or in constant md/A. The choice between the two types of force is made in the [Control](#) window or the [Basic Parameters](#) dialog in the [Setting](#) menu. See that dialog for the details of calculation using the two types of units, and formulas for interconversion of force constants.

**Nspc.** Number of atom type specifications for this interaction (lower list).

**Lst Sq.** If this box is checked, this force constant will be included in least-squares refinement.

**Type.** The type, or **Sharing code** specifies which atoms are shared, according to the diagrams below. The small dot denotes atoms which are shared. Note that the number of atoms shared, either one or two, distinguishes among several type of configuration, and that the code number increases as the sharing becomes more "remote" and presumably less important. The most common types of interactions have code zero (the default), and thus it is seldom necessary to actually specify this number.



**AngMin/AngMax.** The minimum and maximum angle limits apply in only two (common) cases - bond/bond interactions and angle/angle interactions with a shared leg (same central atom). The angle is between the non-shared legs. These limits may be needed, for example, in distinguishing different types of interaction in octahedra. They do not apply to angle/angle interactions with only the central atom shared. If the limits are zero there will be no testing of angle values.

**Specifications** (right upper list). The numbers of the two primary force constants or types of internal coordinates (bonds or 3-atom angles) must be entered in the **Prim1** and **Prim2** edit boxes at the left. The bonds or angles of the primary coordinates may share either one or two atoms, whose types must be given in the second two boxes (**Com1** and **Com2**). When only one atom is shared, the second number must be zero. The types are those given in the [Atom Types](#) list, which are typically atomic numbers, not the sequence numbers of the [Input Atoms](#).

The list box at the bottom of the dialog gives the fcon number, atom types and force constant for the current bond and 3-atom angle force constants. The **Prim1** and **Prim2** entries in the the interaction specifications must be taken from the fcon numbers, and the **Com1** and **Com2** entries must be taken from the corresponding atom types in this list.

Interactions involving 1) out-of-plane coordinates for non-180 degree angles; or 2) either in-plane or out-of-plane coordinates for 180 degree angles, may be questionable because of the arbitrary direction and/or sign of the displacements (see

Once specifications have been entered, the force-constant values and least-squares flags may be changed in the overall [Forces List](#), accessible from the [Control](#) Window.

#### 4.3.9 Read/Write force file

This option allows reading and writing the force specifications in a file. This is mainly for transferring forces from one structure (.vbr file) to another.

#### 4.3.10 Cartesian Atomic Forces from File

**Dialog Box: Cartesian Forces from File** [[Control](#) window: [Forces](#) menu]

VIBRATZ can use either valence forces, or Cartesian atomic forces. If one of the **Use Cartesian forces** radio buttons is checked, a matrix of Cartesian atomic forces is read in, and

any forces entered in the dialogs of the [Forces](#) menu are ignored. This matrix must contain x, y and z entries for each atom listed in the "All Atoms in Unit-Cell/Molecule" section of the output; that is, all atoms, not just a symmetry-unique set, must be included. The matrix should be in lower-diagonal form, and the number of entries per line in the file is not important. The total number of entries should be  $3n*(3n+1)/2$ .

The Raman intensities are based entirely on changes in bond lengths using the bond polarizabilities assigned in the [Bonds](#) dialog ([Forces](#) menu). Thus the **Use Cartesian forces with bonds** radio button must be selected if Raman intensities are to be calculated, and appropriate bonds must be defined in the [Bonds](#) dialog of the [Forces](#) menu. The force constants entered for bonds are ignored in this case, i.e. the bond forces are not used at all.

**Factor to apply.** This multiplies every element of the Cartesian force matrix prior to the calculation. If the Cartesian matrix is in units other than md/A, this can be the scaling factor (e.g. 15.56914 to convert from Hartrees/Bohr<sup>2</sup>). If the Cartesian matrix is from a molecular orbital calculation (e.g. GAUSSIAN) there may be an overall bias, which can be counteracted with this factor.

The scale factor will be refined in a Calculation by the step-by-step least-squares method if any least-squares option is chosen when one of the Use Cartesian Forces option is selected in this dialog. This is all that will be refined in that case. Of course you must have [observed frequencies](#) to do this.

#### 4.3.11 Write Cartesian File

**Dialog Box: Write Cartesian File** [[Control](#) window: [Forces](#) menu]

This writes the current forces in the form of a matrix, exactly as required in the previous dialog ([Cartesian Atomic Forces from File](#)).

#### 4.3.12 Convert Cartesian to Internal

**Dialog Box: Convert Cartesian to Internal** [[Control](#) window: [Forces](#) menu]

This option converts the forces in a Cartesian matrix, from a file specified in the [Cartesian Forces from File](#) dialog, to valence forces as specified in other dialogs in the **Forces** menu. When the conversion is completed, you have the option of replacing the current valence force constants with the derived values, and the results will be printed at the end of the output in the [Output Window](#).

The order of atoms in the Cartesian force matrix must correspond to the generated atoms which are printed in the output. If you intend to use the Cartesian force output from a molecular-orbital program, it may be necessary to use the atoms generated by VIBRATZ as input to that program, as the sequence of generated atoms in VIBRATZ is dictated by symmetry.

This conversion will be valid only to the extent that you have specified a complete set of forces in the other dialogs of the Forces menu. The actual force constants entered in these dialogs will not be used in the conversion; any such values will be replaced at the end of the calculation, at your option. However, it is probably best to do a preliminary frequency calculation using the



valence forces with nominal force-constant values, just to be sure that there are no non-zero frequencies (if there are, the forces are incomplete). Also, you can test that VIBRATZ that the conversion is correctly functioning by writing a Cartesian force file, and using that as input.

See the Import GAUSSIAN File dialog for a step-by-step example of the procedure for importing and converting a molecular-orbital file.

Using a Urey-Bradley force field for conversion is valid, but may lead to anomalous results. The strong correlation between angle and ligand-ligand forces may result in negative force constants for either.

#### 4.3.13 Export File for SIESTA or VIBRATOR

This dialog is used when exporting data either for SIESTA, the DFT program for calculating forces by molecular-orbital methods, or its auxiliary program VIBRATOR which can use force output from VIBRATZ as well as SIESTA to calculate crystal vibrational dispersion relationships (not just  $\kappa=0$  or gamma-point vibrations).

The export of data when setting up a SIESTA calculation is covered in the section on [importing SIESTA files](#). Briefly, this export option writes a .fdf file which contains the unit cell and atom locations, but usually the SIESTA calculation parameters will have to be edited in that file.

The remainder of this section describes the output for VIBRATOR, for complete dispersion calculations on crystals.

The VIBRATOR auxiliary program in the SIESTA package can calculate frequencies for all phonons, not just optical vibrations at  $\kappa=0$  (the gamma point), but it does not do symmetry. VIBRATZ can set up supercells and calculate a Cartesian force-constant matrix for input into VIBRATOR. This is done with the **Export files for VIBRATOR** option in the **Forces** menu. The output will be a .fdf file for input into VIBRATOR as well as a .FC (Cartesian forces) file with the same name. VIBRATOR inputs a .fdf with most of the same parameters as required for SIESTA, but with some additions. You must specify in the **Export files for VIBRATOR** dialog the number of unit cells to be added in each crystal or polymer axis direction. Adding one unit cell in all three directions will give 27 total unit cells; adding two will give 125 total cells, etc. The file name by default is *myfile\_vibra.fdf*. The .fdf file will have an arbitrary or sample "%block BandLines" section which specifies the points or lines in reciprocal- or k-space to be calculated. These will likely not be appropriate for your particular problem and will have to be modified - this can be done with a word-processor. Other modifications to the .fdf file may be necessary.

VIBRATZ can also export a .fdf file with supercell specifications for calculation by SIESTA of the forces (.FC file) for later use in VIBRATOR. For this you must specify the **Export data for SIESTA** option and give the number of extra unit cells in each axis direction. The resulting .fdf file will work in SIESTA, but will need to be modified for use in VIBRATOR.



## 4.4 Settings Menu

This has to do with various operational parameters, and what and how derived data are printed out or displayed in the various windows

[Basic Parameters](#) This specifies some general operating parameters.

[Listing](#) This specifies which particular results of each calculation are printed in the [Output](#) file and window. This dialog is also accessible from the [Control Window](#).

[Select Mode](#) This selects which vibrational mode is shown in the [Atoms Window](#). This dialog is also accessible from the dialog bar of the [Atoms Window](#).

[Atom Plot Parameters](#) This specifies parameters for the [Atoms Window](#) for graphics display of the structure.

[Spectrum Plot Parameters](#) This specifies parameters for the [Spectra Window](#).

**Save Defaults** This saves most of the optional parameters specific to individual structures.

**Read Defaults** This reads the file containing the optional parameters specific to individual structures.

**Cursor Mode** In the [Atoms Window](#), this switches between the Atom Identification mode, and the Rotate mode. In **Atom ID** (identification) mode, clicking on the left mouse button will identify atoms - see **Atoms at Cursor**. In **Rotation** mode, clicking and dragging rotates the structure. In most of the window, rotation will be around the y and z Cartesian axes, in the plane of the screen. Clicking and dragging near the left or upper edges will rotate about the z axis, perpendicular to the screen.

### 4.4.1 Basic Parameters

**Dialog Box: Basic Parameters** [[Settings menu](#)]

The **Force constants** radio buttons determine the units of force constants and the way they are interpreted. Force constants for bonds are always in md/A (millidynes per Angstrom), but those involving angles may be expressed in either of two ways - in md-A (per radian squared) or in md/A. Published values may be given either way, and it is absolutely necessary to choose the appropriate option if such values are to be used or compared.

Using md-A is the more "natural" in terms of the calculations - to use md/A everywhere it is necessary during calculation to multiply the angle force constants entered by two bond lengths. In the case of 3-atom valence angles this is straightforward - the two bond lengths are simply the two legs of the angle. However, for tau and psi angles there are three bond lengths, and for interactions involving these angles as many as six bond lengths could be involved. Selection of two bond lengths from among all the possibilities would be arbitrary. Therefore the approach taken in VIBRATZ when the universal md/A option is chosen is to multiply together all n bond lengths in all angles involved, take the nth root, and multiply the s-vectors for the angle

coordinate by this factor. When the internal coordinates are converted to Cartesian forces, these s-vectors are multiplied together. Thus the result is to multiply the entered force constants by the following factors:

$$f(\text{angle}) = \text{square root}(d_1 * d_2 * d_1 * d_2) = d_1 * d_2$$

$$f(\text{angle/angle}) = \text{square root}(d_1 * d_2 * d_3 * d_4)$$

$$f(\text{bond/angle}) = \text{square root}(d_1 * d_2)$$

$$f(\text{tau or psi}) = \text{cube root}(d_1 * d_2 * d_3 * d_1 * d_2 * d_3) = \text{cube root}(d_1^2 * d_2^2 * d_3^2)$$

This gives the possibilities excluding interactions involving tau or psi, which are more complex. In the case of angle/angle interactions, one pair of distances may be the same if one leg is shared, or all four may be different. In bond/angle interactions the two bond lengths are those of the legs of the angle, and the length of the bond does not enter unless it is also a leg of the angle. Because force-constant specifications in VIBRATZ may involve more than one specific symmetry-unique bond or angle (internal coordinate), or combinations thereof in the case of interactions, it will not always be possible to use the above formulas to convert from one system of units to the other. However, by narrowing the specifications so that each applies to only one specific bond or angle (and its symmetry equivalents) an exact conversion should be possible. Bond lengths and angles may be examined with the [Coordination](#) option in the [Input Atoms](#) dialog ([Input](#) menu).

The units for kappa force constants in [Urey-Bradley](#) models are always md-A - this is unaffected by the units setting.

The following three settings in this dialog involve scaling of atomic motions, which influence the calculation of intensities and least-square adjustment - they have no effect on the calculation of frequencies.

**Atomic displacements represent** radio buttons. First, the eigenvectors of the normal equations are divided by the atomic masses, to give actual atomic motions; the square-root of the masses, to give mass-weighted normal coordinates; or not at all (raw eigenvectors). The first option is the normal one, the others being used only for special purposes.

**Normalize photon energy to** radio buttons. For comparison between compounds and among vibrations of a single compound, the motions are then scaled by apportioning the energy of a photon in either of two ways; to a constant number of atoms, nominally 100, or to the actual number of atoms in the molecule or unit cell.

**Scale atomic displacements by factor.** After normalization, the motions are multiplied by an arbitrary factor, entered in this edit box. The calculation of intensities, especially Raman, assume that atomic motions are small in relation to interatomic distances.

If the photon energy is normalized to 100 atoms, then this scale factor should be in the neighborhood of 0.1. Factors much larger than this may result in motions which violate the assumptions of the calculations (next paragraph), and factors much smaller may cause inaccuracy because the motions may become smaller than the general level of precision of atom locations and other factors. One way of checking the accuracy of the calculated atomic motions is by selecting least squares ([Control](#) window) and comparing the "Frequency recalculated from atomic motions" with that calculated directly from the secular equation (see [Output](#)).

When forces are very weak, atomic displacements may be large enough to cause inaccuracies. This is especially likely for modes that are due to or dominated by torsion forces. If the "frequency recalculated" for such modes is very different from the observed frequency it may be necessary to reduce the scaling factor.

Atomic motions shown in the [Atoms](#) window are scaled by a further factor, in the [Atom Plot Parameters](#) dialog ([Setting](#) menu) or in the Dialog Bar attached to the [Atoms](#) window itself. This factor has no effect on intensities. The "average" or non-polarized Raman intensity as shown in the output window as well as the [Spectra](#) window is also influenced by two additional parameters in the [Spectra Plot Parameters](#) dialog ([Setting](#) menu).

**Initial rotation angle.** The rotation angle in the [Atoms](#) window can be reset at will, but the initial or default value is set in this dialog.

**Sort modes in final list.** The final list of frequencies can be sorted in descending order of frequency either by species or including all modes together. When sorted by species the result is often, but not always, the same as standard numbering schemes as v1, v2, etc.

**Sound at end of calculation.** If this box is checked, a sound will be emitted at the end of the calculation.

#### -----Windows only-----

The WAV file named in the **Sound file** edit box will be played. If the file cannot be found or the system does not support multimedia sounds, the system sound will be emitted. Some sample.wav files are in the \SOUNDS folder

#### -----Macintosh/Linux only-----

The system sound is emitted.

**File name filtering in Open File dialogs (Macintosh).** When you want to open a file, it is usually best if the **Open File** dialog shows only the type of file you want, rather than every single file in the current folder. Every Macintosh file other than an application or program file has two four-character keywords or signatures - the Creator and the Type, and it is standard practice for Macintosh programs to use these to filter the file names shown in the Open File dialogs. The main data files for Vibratz have Creator 'VIBR' and Type 'TEXT'.

If the "**Main data files (.VBR) - show only Creator = 'VIBR'...**" box is checked, Vibratz use the Creator to filter file names for the File/Open dialog. If you only use the Macintosh, this box

can usually be kept checked. Files from the IBM-PC (DOS or Windows) versions of Vibratz normally have Creator 'dosa', so this will not work - the Vibratz data files will be invisible. If you use files created on the IBM-PC, you will need to uncheck this box.

Many other types of auxiliary data files are used by Vibratz (see [Types of Files](#)), and it is not practicable to assign a different Type and or Creator to each of these. Atom-coordinate data files may be imported from other systems, not just IBM-PC, and such files will not have distinguishable signatures. However, it is fairly standard in non-Macintosh systems to use a three character file-name extension to distinguish different types of files. Thus if the "**Use extensions (.XXX) for import and other secondary data files**" box is checked, only those files with the appropriate extension will be shown. If not, all Type = 'TEXT' files are shown. You can change the extension for each type of import file when you select import of that type of file in the File Menu.

-----End Windows/Macintosh only -----

#### 4.4.2 Listings

**Dialog Box: Listings** [[Control Window](#); [Setting menu](#)]

This dialog controls what appears in the [Output](#) file, and the output window (if display of the window is selected in the [Control](#) windows).

#### 4.4.3 Select Mode

**Dialog Box: Select Mode** [[Dialog Bar](#), [Atoms window](#); [Setting menu](#)]

The dialog allows selection of the vibrational mode which appears in the [Atoms](#) window.

The mode is selected by double-clicking on the desired line in the list box, or by clicking the **Select Mode** button - simply selecting a line with a single-click does not set the mode. The selected mode is written out below the list box.

**Secondary atoms** are atoms outside the primitive unit cell which are needed to show all bonds and angles (i.e., those bonds and angles which cross unit-cell boundaries) in crystals and polymers. Secondary atoms are not used in molecules. If present, they may be marked with a triangle, or omitted entirely.

#### 4.4.4 Atoms Plot Parameters

**Dialog Box: Atoms Plot Parameters** [[Control Window](#); [Setting menu](#); [Atoms Window Dialog Bar](#)]

This specifies aspects of the Atoms graphics window (see [Operation - Windows, Menus](#)), showing the atoms and their displacements in the chosen mode.

This plot is rather rudimentary, with little attempt to give a "three-dimensional" appearance. A

more sophisticated plot may be made with the program ATOMS - for this it is necessary to save a.MOT file ([Control Window](#)). See below for more on the nature of the motion vectors.

Atoms are drawn as filled circles with the specified **Radius**. Note that all atoms have the same radius and that the radii specified in the [Atom Types](#) dialog are use only for discriminating among bond lengths in the [Coordination](#) option, not in the [Atoms Window](#). Only the bonds specified in the [Bonds](#) dialog (**Forces** menu) are drawn - angles are not drawn. The atomic displacements in the current mode are shown as lines or vectors. The relative magnitude of the displacement is shown by the distance along the vector from the atom surface to the end of the vector.

Secondary atoms are atoms outside the primitive unit cell which are needed to show all bonds and angles (i.e., those bonds and angles which cross unit-cell boundaries) in crystals and polymers. Secondary atoms are not used in molecules. If present, they may be marked with a triangle, or omitted entirely.

The **Title** is written along the bottom of the windows and gives information about the current mode selected.

**Atom labels.** Either the name, or input atom label, or the atom number, as in the final generated atoms list, may be shown. Adjust the size with the **Font** button.

**Show unit cell.** For crystals and polymers the primitive unit cell is shown as a box, drawn in front of all the atoms. This is the primitive unit cell, not the Bravais cell, so the edges are not necessarily parallel to the crystal axes. The unit cell is not shown if there are no lattice translations ([Title/Axes](#) dialog).

**Scale to fraction of window.** The image is scaled by making the largest dimension of the structure (furthest distance of any atom from the center, doubled) equal to the specified fraction of the shortest dimension of the graphics area (window, frame or page). This scaling applies to atomic centers and does not include the atomic radius or the displacement vectors

*Arrowhead on Vectors.* Why don't the motion vectors in VIBRATZ have arrowheads on the ends? Drawings of atomic motions in vibrational modes usually have arrowheads on the ends - but only if the vectors are close to being in the plane of the drawing. If the motion is nearly perpendicular to the plane of the drawing, "+" and "-" symbols are typically used instead. Using an arrowhead in this case might wrongly indicate motion in the plane. These symbols may be placed on the atoms or next to them, depending on where open space is available. Making a finished drawing, choosing when to use arrowheads and when to use symbols and where to place the symbols, is something that a human can do much more easily than a computer program - the computer results would in fact be unsatisfactory in many cases. Thus the VIBRATZ drawings can be used unchanged, if a simple line is adequate to represent motion, or as the basis for slightly more elaborate drawings with arrowheads and/or symbols.

The program ATOMS can read the .mot file written by VIBRATZ and draw motion vectors with arrowheads in a much more "3-dimensional" way - that is as cylinders and cones, even when in the 2-dimensional or "Standard" (non-OpenGL) drawing mode. These vectors are much more likely to be satisfactory without modification than simple lines and arrowheads.

### 4.4.5 Spectra Plotting Parameters

#### Dialog Box: Spectra Plotting Parameters [[Settings menu](#)]

This dialog sets parameters for the [Spectra](#) window.

**Gaussian line widths.** Gaussian half-widths of infrared and Raman modes in plotted spectrum (default 25 cm<sup>-1</sup> for infrared and 10 cm<sup>-1</sup> for Raman).

**Minimum transmission, infrared.** (Default 1.0). This only applies when the **Infrared mode** (below) is Resonance down. A value of 1.0 will give an absorbance spectrum. A small value (0.1 or less) will mimic an optically dense sample and will accentuate weak peaks and truncate strong ones. This value affects only the shape of the IR spectrum; the maximum absorption is still normalized to the same value (that is, decreasing this value won't cause the spectrum to disappear).

**Atomic motion scaling factor.** This factor affects the calculated atomic motions before intensities are calculated. This factor also appears in the [Basic Parameters](#) dialog; see that dialog for other factors which affect the magnitude of atomic motions.

**Raman intensity factors.** These are the coefficients for the isotropic or spherical (alpha) and anisotropic (beta) components of the polarizability tensor, as described in WDC Ch. 3, p. 47; they are only used in spatially averaged Raman spectra. Default values are 45.0 and 0.1, which have been found to give a reasonable approximation to silicate glass and powdered crystal spectra.

**Maximum intensities.** These are the full-scale intensities for the plots of infrared and Raman spectra, respectively. If they are set to zero (or left blank), the plots will be scaled so that the maximum intensity is full scale. Full scale will be half the window or page height if both infrared and Raman spectra are shown, and full height if only one is selected. Note that absolute intensities depends on the atomic-motion scaling parameter above as well as the method of normalization selected in the Basic Parameters dialog in the Settings menu.

**Infrared mode.** If resonance is down, the spectrum mimics the usual absorption spectrum and the **Minimum transmission** parameter applies. If resonance is up, as for FTIR, simple gaussian lineshapes are used.

**Horizontal scale factor.** This is used only if the plot must have a fixed scale in wavenumbers per inch. If this value is zero, the plot will be scaled horizontally to fill the window.

The **Minimum and Maximum wavenumber** are the starting and ending values shown in the plot. The necessary maximum value may be very different depending on the compound; especially whether or not hydrogen is present.

If the **Print title** and/or **Print species** boxes are checked the relevant information will be printed at the top of the plot.

The components shown in the calculated spectra, whether polarized components or average, and

whether an individual species or all species, are selected in the Dialog Bar which resides on the upper edge of the [Spectra](#) window itself.

**[NRVS Parameters](#)**. See [Spectra Window](#) for details of NRVS spectra.

**[Read Observed](#)**. With this you can read digital or digitized spectral data for display in the Spectra Window.

The **PED curves** section sets the FCONs which contribute to each curve in the PED (potential energy distribution) section of the Window (if selected with the **PED** checkbox in the [Spectra Window](#)). The numbers which are entered in each edit box are the FCON numbers from the listings of the force in the various dialogs of the Forces menu, or from the [Force List](#) called from the [Control Window](#). There may be up to 20 FCONs in each curve - the numbers may be separated by spaces, commas or semicolons.

The contributions from each FCON in each mode are those which appear in the printed Output, in the part label "Bnd En/Gp" and the like. These contributions are summed up during calculation, so if there are any changes in this dialog, the Calculation must be repeated. The contributions from each mode are given a Gaussian shape with the specified linewidth and summed up at each frequency.

The colors of the curves can also be set, by entering the red, green and blue components as numbers from 0 to 255. The curves are plotted in reverse order (4-3-2-1).

As selected in the **Mode** combo box, the energy distribution curves can be shown either as raw fractions (just as in the printed output), or multiplied by the calculated intensities for any of the spectra, infrared, Raman or NRVS. The raw fractions curves are applicable to all modes (in species selected in the Species dialog in the Input menu), whether they have significant intensity or not. This type of curve may be ambiguous when modes are very close together. The specified **Line width** is used for the raw fractions mode, but for the infrared, Raman or NRVS the respective linewidths for these individual spectra are used.

Contributions to the energy (frequency) from interactions may be negative which in turn means that the coefficient for even a single mode may be more than one (the contributions are fractions which sum to one for each mode in the raw fraction option). Generally the baseline (zero) will be obvious from the part of the spectrum where there are no modes.

#### 4.4.6 NRVS Parameters

**Dialog Box: NRVS Parameters** [[Settings menu](#), [Spectra Plotting Parameters](#)]

See [Spectra Window](#) for details of NRVS spectra.

The file name from which the current NRVS observed (if any) has been read is shown.

**Read button.** This will read a file with the data for an observed NRVS spectrum. Each line in the file must be a data point. The energy in meV should be in the first column (first number on



each line), and you can specify which column contains the actual scattering intensities.

**Divide by frequency.** The peak heights in experimental NRVS spectra are inversely proportional to energy or frequency, but this dependence on frequency is sometimes removed in data processing. If this box is checked, the spectrum will show the fraction of kinetic energy in the iron atoms, divided by frequency, as in the "raw" data. Note that the NRVS values in the [Output](#) are not divided by frequency.

**Normalization.** This specifies how the values in the observed data (entered by reading a file, above) are scaled or normalized to give an overall match to the observed. The factors or coefficients from the last redraw of the Spectra Window are shown below the options. There are currently three options:

--- **Maximum to full.** This applies a single scale factor to make the maximum value in the observed equal to the maximum value of the calculated. Note that the maxima for the calculated and observed do not necessarily occur at the same mode or frequency.

--- **Integrated Intensity.** This applies a single scale factor to the observed to make the total intensities, calculated at each of the wavelengths specified by the minimum and maximum frequencies and the frequency interval, equal. Observed values are interpolated if necessary, and maximum and minimum may be taken from the observed if these do not extend as far as the specified frequencies.

--- **Fixed factor.** The specified factor is applied to the observed.

**Lineshape.** The theoretical lineshape is Lorentzian, but broadening of various kinds typically produces a lineshape that is effectively Gaussian. The Voigt lineshape is a Gaussian convolution of Lorentzian lines - an approximation to it is used in many real-life situations in which the lineshape must be fitted rather closely. If Voigt is chosen the intensity contribution from a given mode is simply a linear combination of Gaussian and Lorentzian terms, with the line width in common between the two terms. **Gaussian in Voigt** is the fraction applied to the Gaussian term - this fraction is applied to all modes. See P. Thompson, D.E. Cox, J.B. Hastings, J. Appl. Cryst. 1987, **20**, 79, for details of this approximation to the Voigt profile.

**Use dashes in black/white.** The observed curve may be drawn dashed in black-and-white output, with the specified repeat length and dash/blank ratio.

**Show bars only.** If this box is checked, the calculated curve will not be shown, only the bars. The specified Normalization option will still be used, comparing the observed to the calculated curve.

**Orientation to show in Spectra Window.** This could be the spatial average, or any of three other orientations if present (usually x, y and z). This can be changed in the Spectra Window itself

**Observed spatial average spectra group**



This controls the input of observed spatial average NRVs spectra for multiple isotope configurations. The isotope configurations themselves are set up in the [Isotopes - Multiple Spectra](#) dialog, accessed with the Isotopes button in the Control dialog or from the Input menu.. That dialog also controls whether each of the configurations is calculated and refined by least-squares. You can read a file or delete the data for each configuration. In the data files, frequency is expected to be in column one, and the data in the column specified in the **Read from column** field to the right.

### Observed spectra for orientations group

This controls the observed data and parameters for different orientations of a single isotope configuration (just now, only the first or main configuration). The **Read** and **Delete** buttons operate as for the spatial average data, and the **Read from** column field applies here as well.

When the **Normalization mode** is set to **Fixed factor**, the **Scale factor** entered here for each orientation is used instead of the **Fixed factor** entered in the **Normalization** setting. If the orientations differ from the Cartesian axis orientation used by VIBRATZ (which can be changed with the [Pre-Calculation Rotations](#) option in the Input menu), the **Theta** (angle of the x axis from the z axis) and **Phi** (angle of the plane of the y and z axes from the x axis) values can be changed. The default values of theta and phi are: x - 90,0; y - 90, 90; z - 0, 90. The angles values should be checked to be sure that bad values have not got in somehow.

The first or Average line in this group is essentially the same as the Iso configuration 1-main in the **Observed spatial average spectra** group - the **Read** and **Delete** buttons operate on the same data, and changing the **Scale** value also changes the **Fixed factor** value in the **Normalization** group and vice-versa.

At the moment it is assumed that either spatially-averaged data for different isotope configurations, or orientation data for the first or main isotope configuration, will be refined by least-squares, but not both. This is controlled by the **Refine** drop-down box in the [Control Window](#).

The NRVs fractions for all orientations including the average can be obtained in a single calculation (solution of the normal equations), so the frequency intervals are required to be the same (that is there is only one set of frequencies for all orientations). When a new file is read in, if the frequencies do not agree within 0.1 cm<sup>-1</sup> at the maximum frequency of the new data, the observed intensities will be linearly interpolated. You can choose whether to use the frequency intervals of the new data or of the old. It is assumed that frequency intervals are uniform in each spectrum.

### 4.4.7 IXS Parameters

**Dialog Box: IXS Parameters** [[Settings menu](#), [Control Window](#)]

This sets parameters for the calculation of Inelastic X-Ray Scattering intensities. The calculated spectrum appears in the Spectra Window, and the output may be sent to a file with the **Spectral Data Text File** option in the **File Menu** of that window.

You must specify the location of the calculation in reciprocal space, that is the Q-point or k-point. This can be done by giving the indices of a central zone (uvw) and a 2-theta value, or actual indices, which may be fractional. The choice is made in the radio box to the left, and this determines which of the sets of indices is used.

If you select the **Zone** and **2-theta**, then the actual indices will be given in the Spectra Window; or if you select the actual **Indices**, then the 2-theta will be calculated and shown in the Spectra Window.

The Base frequency (in cm-1) determines where the calculations starts. The two width values are for the half-width at half height for either Gaussian or Lorentzian lines. You set widths for zero frequency and 1000 cm-1 and the width of each mode is interpolated based on the location of the peak. If the width at 1000 cm-1 is zero it will be set equal to the width at zero cm-1.

The calculation uses a single isotropic Debye-Waller (temperature) factor for all atoms - this is not affected by the Temperature value.

**Lineshape.** The theoretical lineshape is Lorentzian, but broadening of various kinds typically produces a lineshape that is effectively Gaussian. The Voigt lineshape is a Gaussian convolution of Lorentzian lines - an approximation to it is used in many real-life situations in which the lineshape must be fitted rather closely. If Voigt is chosen the intensity contribution from a given mode is simply a linear combination of Gaussian and Lorentzian terms, with the line width in common between the two terms. **Gaussian in Voigt** is the fraction applied to the Gaussian term - this fraction is applied to all modes. See P. Thompson, D.E. Cox, J.B. Hastings, J. Appl. Cryst. 1987, **20**, 79, for details of this approximation to the Voigt profile.

The **Read Observed** button calls up the [Read Observed Spectra Data](#) dialog.

#### 4.4.8 Read Observed Spectra Data

**Dialog Box: Read Observed Spectra Data** [[Settings menu](#), [Spectra Plotting Parameters](#)]

This is for reading digital or digitized data for actual spectral curves, for display in the Spectra window. To input the numerical observed frequencies of individual modes, see [Observed Wavenumbers](#) in the Input Menu.

**Isotope Configurations** spin control. You can read spectra for up to three [Isotope Configurations](#). The base configuration is number 1.

The spectrum in which the data will be shown is selected in the **Read data for** combo box. The data are expected to be in a text file, with the frequency in the first column - select the frequency scale with the **Units** radio box. The actual absorption (resonance) values may be in any of columns 2-6, as selected with the **Data in column** spin control. If a file contains data for more than one type of spectrum, you will have to read the file more than once, selecting different columns.

The **Infrared resonance** may be up, as usually shown in FTIR, or down, as usually shown in

absorption spectra. You must select this correctly on reading the file - although you can select display as up or down in the [Spectra Parameters](#) dialog, that affects both observed and calculated data together.

You can **Subtract a baseline** or background value from the input spectrum. If **minimum** is selected the lowest value in the entire spectrum (or highest if **Infrared Resonance** is down) is subtracted.

The files from which the current values were read are shown at the bottom of the dialog.

## 4.5 Rotation Menu

This menu is present only when the [Atoms Window](#) is active, and pertains only to the orientation of the structure as displayed in that window. The [Pre-Calculation Rotation](#) option in the Input menu is used to rotate the structure before calculation, to insure consistency with the basis functions - this should not be used to orient the view of the structure in the [Atoms Window](#).

[Cartesian Axes](#) Rotate the structure around the Cartesian reference axes.

[Structure Axes](#) Rotates around directions specified in the coordinate system attached to the structure.

[Remove Rotations](#) Will remove all rotations made in this menu and with the buttons in the [Atoms Window](#).

[Align on Face or Vector](#) Will align a crystal face to be parallel to the screen or paper, or a vector to be perpendicular.

[Current Orientation](#) Gives the direction of the structure axes in the Cartesian reference system.

[Continuous Rotation](#) Will automatically rotate the structure around one of the reference axes by a specified angle.

### 4.5.1 Rotate on Cartesian Axes

**Dialog Box: Rotate on Cartesian Axes** [[Rotation](#) Menu - [Atoms](#) window only]

This rotates the structure any of the Cartesian reference axes: x coming straight out towards the observer, y in the plane of the screen or paper pointing to the right and z upwards.

Each time you click the **Rotate** button, a rotation is added to a master rotation matrix; the number of such rotations is listed at the bottom of the dialog box. When you have finished rotating, click the **Done** button and the master rotation matrix is applied to the structure. If you click **Cancel**, no rotations are applied.

## 4.5.2 Rotate on Structure Vector

**Dialog Box: Rotate on Structure Vector** [[Rotation](#) Menu - [Atoms](#) window only]

This will rotate about a rational structure direction  $[uvw]$ , regardless of the current display mode or orientation of the structure. If you are drawing a molecule and have used Cartesian reference axes, the rotation direction is simply a vector with the coefficients  $u$ ,  $v$  and  $w$  in the original molecule axis directions  $a$ ,  $b$  and  $c$ . The indices or coefficients refer to a coordinate system fixed with respect to the structure (always rotating with it). The indices must be integers, but this is not a bar in practice to rotation about irrational vectors, since the indices may take very large values.

Each time you click the **Rotate** button, a rotation is added to a master rotation matrix; the number of such rotations is listed at the bottom of the dialog box. When you have finished rotating, click the **Done** button and the master rotation matrix is applied to the structure. If you click **Cancel**, no rotations are applied.

## 4.5.3 Remove Rotations

**Dialog Box: Remove Rotations** [[Rotation](#) Menu - [Atoms Window](#) only]

This will counteract all rotations made by the dialogs in the **Rotation** menu as well as any made on-screen with buttons in the dialog bar of the Atoms Window, and take you back to the standard orientation which is used in the symmetry analysis. This standard orientation includes any [Pre-Calculation Rotations](#) ([Input](#) menu) - that is Pre-Calculation Rotations are not removed.

See [Orientation](#) for a review of standard orientation.

## 4.5.4 Align Face or Vector

**Dialog Box: Align Face or Vector** [[Rotation](#) Menu - [Atoms](#) window only]

This will rotate a specified crystal face ( $hkl$ ) to lie flat in the screen or paper (face-normal parallel to  $x$  observer), or a vector ( $uvw$ ) to be perpendicular to the screen or paper. To align a face, it is also necessary to specify a vector lying in the face which will be vertical in the screen or paper ( $z$  direction). Conversely, to align a vector, it is necessary to specify a face, containing the vector, whose normal will be vertical. If a vector  $[uvw]$  lies in a face ( $hkl$ ), the indices satisfy the condition  $hu + kv + lw = 0$ .

You can elect to use the default alignment vector or face, instead of specifying it. The default vector will be the intersection of the face ( $hkl$ ) with the face (100), whose indices are given by the cross product  $(hkl) \times (100)$ . If the face ( $hkl$ ) is (100), the default alignment vector will be the vector [001]. For aligning a vector the algebra is just the same, with interchange of face and vector.

When dealing with a molecule or polymer, using a Cartesian axial system, this rotation option can be used to obtain a view down a given vector direction. Use the vector alignment option,

although when the structure axes are Cartesian the two cases of aligning a face or a vector are identical. After specifying the initial vector or view direction, if you do not accept the default you must then give another vector, in place of the "face indices", which is perpendicular to the first vector, and which is to be vertical ( $z$  direction). If the two vectors are at right angles, their coefficients or "indices" multiplied together (the vector dot product) should equal zero as in the above condition for a vector lying in a face.

#### 4.5.5 Current Orientation

**Dialog Box: Current Orientation** [[Rotation](#) Menu - [Atoms](#) window only]

This gives the current orientation of the structure in terms of the structure vectors lying in the  $x$  (reverse view direction) and  $z$  (vertical) Cartesian reference axes.

#### 4.5.6 Continuous Rotation

**Dialog Box: Continuous Rotation** [[Rotation](#) Menu - [Atoms](#) window only]

This option will rotate the image about any of the three Cartesian reference axes, by the given increment in degrees.

The **Time delay** is the delay after the image is finished before redrawing is started again. The time required to draw the image is not included in this value. For maximum rotation rate set this to zero.

Pressing any key or mouse button will halt the rotation.

### 4.6 Window Menu

This menu allows you to switch between the different active windows, in case any are not visible.

**Font.** This applies only to Text Windows (see [Operation - Windows, Menus](#)). It brings up a standard font dialog. All text in the window is affected.

### 4.7 Help Menu

**VIBRATZ Help Topics.** Brings you to the Contents section of this Help system. Individual dialogs have **Help** buttons which bring up the pertinent topics.

**About VIBRATZ.** Version number and copyright notice.

## 5 Operation - Special Topics

[Common Problems - Troubleshooting](#)

[Frames](#)[Making Symmetry \(.sym\) Files](#)[Orientation](#)[Output, Printed](#)[Reading Old VIBRAT Files](#)[Types of Files Used by VIBRATZ](#)

## 5.1 Common Problems - Troubleshooting

Whenever problems are encountered, the first thing to check is usually the generation of atoms by symmetry. The generated atoms are in the list **All Atoms in Molecule/Unit Cell** section in the printed [Output](#). If the number of generated atoms is wrong, or if their coordinates are wrong, check the [Input Atoms](#), the [Atom Types](#) and the [Symmetry](#).

It may be that the input atom coordinates are not consistent with the symmetry matrices. If the misorientation is caused by a rotation about the z-axis, this can be corrected in the [Input Atoms](#) dialog.

Atom coordinates are often simple fractions by symmetry - that is 1/2, 1/3, 1/6, etc. Atoms with such coordinates are in special positions, and may be generated by more than one symmetry matrix. VIBRATZ must apply numerical tests to determine whether atoms are duplicated, and the decimal coordinates entered must be precise enough for these tests. They should be given to the 5th decimal place - e.g. enter 0.66667 for 2/3, not 0.667.

*Wrong number of modes in individual species or overall.* Be sure that all boxes are checked in the [Species](#) dialog before the initial calculation. For crystals, it may be that space group is not oriented correctly with respect to the basis function used for symmetry analysis. This is most likely if the [Custom Symmetry](#) option is used, and this is also possible if this symmetry option is used for molecules. See [Orientation](#) and/or [Space-Group Symmetry](#) for details. This situation is corrected by supplying rotations in [the Pre-Calculation Rotation](#) dialog (Input menu). Actually, there is only a small number of possible rotations of this type. Monoclinic crystals (or molecules) must have the unique axis parallel to z (or the mirror plane perpendicular to z), and for crystals in the second setting (unique axis = b) the required rotation is -90 degrees on x. Some tetragonal crystals may need to be rotated 45 degrees on z, and some trigonal and hexagonal crystals may need to be rotated 30 degrees on z.

*All frequencies are zero.* See *Wrong number...* above. Be sure [Atom Types](#) are correct, i.e. that the numbers given for [Input Atoms](#) match those in the [Atom Types](#) list.

*Some frequencies are zero.* Normally this is a result of an insufficient number of force constants. First, check the output to see if the forces specified in the dialogs in the [Forces](#) menu have actually been located correctly. If zero internal coordinates are located for a given specification, an error message is printed, but if the number located is incorrect there is no special indication. If you are sure that there is a sufficient number of bonds and 3-atom angles,

then it is probably necessary to add out-of-plane 3-atom angle coordinates, [Tau](#) forces or [Psi](#) forces. Generally, if a given atom is central atom to only one 3-atom angle, it is necessary to have some other type of force involved. It is easy to add 3-atom bending forces perpendicular to the plane of the angle in the Angle Force Data dialog; simply select the **Both...** radio button. If this solves the problem, a separate force constant can be defined if desired. 180 degree angles should probably always use the **Both...** option, that is have bending coordinates in two perpendicular directions. In some cases the second coordinate is superfluous, but its presence does no harm.

*Calculated frequencies differ from published (calculated) values by a large amount.* The choice of units for angle force constants must be consistent. It is easy to change this in the [Control Window](#).

*Calculated frequencies differ from published (calculated) values by a small amount.* If the choice of units for angle force constants is md/A (not md-A), there may still be small differences because of different choices of bond lengths used to convert unit. If the bond lengths used are specified in a published calculation, it is safer to convert the published force-constant values to md-A. Small differences may also arise from different choices for atomic weights, which are seldom given in published work. If natural isotopes are used and two or more are present in significant abundance, some observed absorption or reflectance bands may show a complete splitting while others may represent an average (see [Atom Types](#)).

## 5.2 Frames

With printed output from the [Atoms](#) or [Spectra](#) windows, you have a choice of using the full page, or confining the graphics output to a *frame*. For [Raster Files](#) and [Metafiles \[Windows\]](#) or [PICT files \[Macintosh\]](#) ([File](#) menu) output always goes to a frame. This applies either to the spectrum plot or to the atoms plot

In printed and pen-plot output, the frame can be positioned on the page; the offset gives the displacement of the upper left corner of the frame from the upper left corner of the page.

For [Raster Files](#) and [Metafiles](#) or [PICT files](#) you can choose the units for the size and offset of the window; either inches, centimeters or dots (pixels), and for Raster Files you can also specify the nominal dots per inch or centimeter.

The image is scaled to the frame in the way specified in the [Spectra Plot Parameters](#) or the [Atoms Plot Parameters](#) ([Settings menu](#)).

## 5.3 Making Symmetry (.sym) Files

All the .SYM files for the non-crystallographic point groups in the [Point-Group Symmetry](#) dialog are in the /SYM directory or folder, which should be directly beneath (or inside) the directory or folder containing the VIBRATZ.EXE file. These files may be consulted as examples.

### File Format



All data is read in a free-form manner (no restriction of the fields to particular columns), the various fields being separated by spaces. The following descriptions gives the input in terms of lines, but in fact line breaks are disregarded.

The first line contains four fields; the point-group label; the centric/non-centric flag; the number of Cartesian symmetry matrices; and the number of symmetry species. The label should contain no blanks. The centric flag is 0 if the group is centric and non-zero if non-centric. If the group is centric, the center should not be present in the matrices - that is, only half of the total number of matrices should be given.

Following this are the Cartesian symmetry matrices, nine floating-point numbers per matrix. For clarity it is best to enter these three per line, with blank lines between matrices. These can be taken directly from the output of the SYMGRP program (see below).

Next come two lines which indicate which species contain the infrared and Raman polarization components.

The line for infrared has 3 pairs of numbers, the first number of each pair indicating the number of the species, and the second number indicating the x, y or z polarization components, with numbers 1, 2 or 3 respectively.

Likewise the line for Raman has 6 pairs of numbers, the first number of each pair indicating the number of the species, and the second number, from 1 to 9, indicating the Raman polarization component; the choices are xx, yy, zz, xy, xz, yz, xx+yy, xx-yy, xx+xx+zz and 2zz-xx-yy respectively. Of course components such as "xx" are often given as "x2".

Now come the data for each species in succession, with four or more lines for each species.

The first line for each species contains four fields, the species label, the degeneracy, the number of basis functions and the total number of terms in the basis functions. Degeneracy is 3 for T species, 2 for E species with non-complex characters, and 1 for "doubly-degenerate" E species with complex characters and all A and B species. The number of functions should be equal to the true degeneracy of the species, which is 2 for all E species.

The second line for each species contains flags for pure translation and rotation, in the order x, y, z translation, x, y, z rotation (6 numbers total).

The third line for each species consists of triplets of integer numbers giving the exponents for x, y and z in each term of the basis functions - these exponents apply to all the basis functions. There should be as many triplets as there are numbers of terms specified in species line 1 above. The individual exponents can be as large as 8, but the sum of exponents in each term is also limited to 8 (i.e. maximum is 8th order).

Finally, the fourth set of lines for each species contains the coefficients for each term, in each basis function. There should be as many lines as there are basis functions specified in species line 1 above, and each line should have as many coefficients as there are total terms.

The arrangement of terms in the basis functions is important, because the matrix of coefficients



must be inverted, as a square matrix. If there are  $n$  functions and  $m$  terms, and  $m$  is larger than  $n$ , only the leftmost  $n$  terms in each function are used in this inversion (although all terms must always be entered in this input). The terms should be arranged so as to give a non-singular  $n$  by  $n$  matrix on the left. To do this it is usually sufficient to make sure that diagonal terms are non-zero. For example, consider the pair of basis functions  $xx-yy$  and  $2xy$ , which are common for E species. Lines 3 and 4 could be entered as

```
2 0 0 0 2 0 1 1 0
1    -1    0
0    0    2
```

but disregarding the last term and taking the square matrix of coefficients on the left gives a singular matrix, since there is no longer any information from the second function. The terms in this case can be arranged as follows (although other arrangements are possible):

```
2 0 0 1 1 0 0 2 0
1    0   -1
0    2    0
```

The completed.sym file should be placed in the /SYM directory or folder, which should be directly beneath (or inside) the directory or folder containing the VIBRATZ.EXE file. This folder contains all the files for the non-crystallographic point groups in the [Point-Group Symmetry](#) dialog, and these files may be consulted as examples.

### Derivation of Symmetry Matrices.

The easiest way to provide Cartesian symmetry matrices is to use the program SYMGRP, provided with VIBRATZ (also with ATOMS and SHAPE Professional). In principle, the symmetry matrices can have any orientation, provided the basis functions for the species (next section) are consistent with this orientation. In practice there may be difficulties with non-standard orientations, such as the fact that VIBRATZ is not set up for any arbitrary mixtures of Cartesian coordinates - for example only certain Raman polarization components may be listed. It is best to conform to the standards given in the [Orientation](#) section.

### Polynomial Basis Functions for Species.

Provided a character table for the desired group is available, it is usually possible to specify the first and second order basis functions which are the infrared and Raman polarization components, since these are a standard part of the tables. Since only the species which contain these polarization components are active in the infrared and Raman, this information suffices to calculate the modes which can be observed in the spectra. The character tables in the book *Symmetry and Spectroscopy* (D. C. Harris and M. D. Bertolucci, 1978, Dover) also gives the third-order functions representing the  $f$  atomic orbitals (except for icosahedral groups). This book also gives character tables for groups with axes up to order 10. Note that these functions often assume a certain orientation of the symmetry elements with respect to the reference axes - see the previous section.

The basis functions beyond third order for the non-crystallographic point groups in the [Point-](#)

[Group Symmetry](#) dialog were obtained with a program which steps systematically through possible basis-function terms up to the desired order (VIBRATZ currently accepts 8th order), and derives the complete functions with the projection-operator technique. This program requires as input the complete characters for the group, as well as the symmetry matrices in the same order as in the character table.

## 5.4 Orientation

**Crystal-Cartesian** conversion. For crystals the mutual orientation of the crystal axes with the Cartesian axes used in the calculation must be specified. The c crystallographic axis is parallel to z, and the b crystallographic axis is in the y-z plane ( $a^* = x$ ). If non-Cartesian axes are used for molecules (which may be convenient for trigonal and hexagonal symmetry), the conversion is the same.

**Symmetry elements.** The basis functions used for symmetry analysis in VIBRATZ require that symmetry elements have a standard orientation as follows. Any unique axis is parallel to z. Note that this includes the two-fold axis in monoclinic. If a group contains mirror planes parallel to the unique axis and does not contain perpendicular 2-fold axes, one mirror plane is perpendicular to x. If perpendicular 2-fold axes are present, one of them is parallel to x and other mirror planes and 2-fold axes are disposed accordingly. Cubic groups have 3-fold axes on the cube body diagonal. Icosahedral groups have one 5-fold axis parallel to z and an adjacent 3-fold axis in the x-z plane.

The standard symmetry orientation may affect input in three ways.

First, for point groups, input atom coordinates may not be consistent with the orientation of the symmetry matrices. Usually this is a matter of rotation about the z axis, and there is an option to rotate the input atoms about z in the [Input Atoms](#) dialog ([Input](#) menu).

Second, some space groups in standard settings do not have the orientation specified above. The atom coordinates may be entered for the standard space-group settings, but for proper symmetry analysis it is then necessary to rotate both the symmetry matrices and the atoms to attain the VIBRATZ orientation. The particular space-groups affected are given in the [Space-Group Symmetry](#) dialog. When [Space-Group Symmetry](#) is selected, usually VIBRATZ automatically supplies the appropriate rotations to the [Pre-Calculation Rotations](#) dialog, but it may sometimes be necessary to specify these rotations, for example if the [Custom Symmetry](#) option is used. All calculated [Output](#), such as atomic displacements and spectral intensities, assumes the orientation after the [Pre-Calculation Rotations](#).

Third, if a special symmetry file is provided for a point group which is not one of those provided in the [Point-Group Symmetry](#) dialog, the basis functions given in that file must be consistent with the symmetry matrices and the polarization components also in that file, but the orientation does not have to be the VIBRATZ standard (see [Making Symmetry Files](#)).

**Orientation in Atoms graphics window.** The orientation of reference Cartesian axes in this window is x pointing directly out of the screen or paper, towards the observer; y horizontal to

the observer's right; and z vertical. In the dialog bar of the Atoms Windows itself, and in the [Rotation menu](#) which is present when this window is active, there are options to rotate the image of the structure and the atomic displacement vectors. The original or base orientation for this image is that attained after the [Pre-Calculation Rotations](#). Any rotations of this image have no effect on the calculations; they are all erased every time a calculation is made.

## 5.5 Output, Printed

Output - Printed to the file *infile.VBD* and shown in the Output window

This section describes the main computational output of VIBRATZ, which is written to a file called *infile.VBD*, if *infile.VBR* is the name of the input data file. If the **Window** radio button in the **Output File** group of the [Control Window](#) is checked, this output is shown on screen in a Text window (see [Operation - Windows, Menus, Dialogs](#)).

The first line contains the version and release date of VIBRATZ and the date and time of the calculation.

The file name and the title ([Title/Axes](#) dialog, Input menu) are on the next two lines.

**Use lattice vectors.** This shows which of the axes a, b and c (or x, y and z) have lattice translations - non-zero indicates presence of translation. Molecules should have all zeros and crystals all ones ([Title/Axes](#) dialog, Input menu).

**Cell Parameters.** For a molecule the axes are normally 1.0 and the angles are 90.0 ([Title/Axes](#) dialog, Input menu).

**Pre-Calculation Rotations.** These are the rotations on the x, y and z Cartesian axes which are required to bring the structure and symmetry matrices into proper orientation for symmetry analysis. The **Final Atom List** and detailed results for each mode are all given for the orientation attained after these rotations ([Pre-Calculation Rotations](#) dialog, Input menu).

**Point or Factor Group.** The Schoenflies symbol for the point or factor group. Whether centric or acentric is printed on the next line. If a point group is centric, only half of the symmetry operators in the next group will be given ([Symmetry](#) dialog, Input menu).

**Symmetry Operators.** In the case of space groups and crystallographic point groups, this gives the symmetry operations in *International Tables* or "xyz" form ([Symmetry](#) dialog, Input menu).

**Bravais Cell Type.** For a crystal, unless this is P, the unit cell which is used by VIBRATZ is not the Bravais cell but the primitive cell ([Symmetry](#) dialog, Input menu).

**P-Cell Vectors.** For a crystal or polymer, this gives the primitive unit-cell edges or axes in terms of the conventional or Bravais cell axes ([Symmetry](#) dialog, Input menu).

**Input Atoms.** This gives the label, type and coordinates for the input atoms, untransformed by

the [Pre-Calculation Rotations](#) ([Input Atoms](#) dialog, Input menu).

**Atom Types.** This gives the atomic weights and charges for the atom types used in the input atom list ([Atom Types](#), Input menu).

**Symmetry Matrices (Cartesian).** This gives the symmetry matrices in Cartesian form, which are the input matrices for non-crystallographic point groups ([Symmetry](#) dialog, Input menu).

**All Atoms in Unit Cell or Molecule (Structure Coordinates).** This gives all the atoms generated by symmetry, untransformed by the [PreCalculation Rotations](#), and in the case of crystals, in fractional coordinate on the original axes.

**P-Cell Vectors (Cartesian, rotated).** This gives the primitive unit-cell vectors in transformed Cartesian coordinates (for crystals  $c = z$ ,  $a^* = x$ ), rotated by the [PreCalculation Rotations](#).

**Internal Coordinate Types.** This section gives the specifications for the internal coordinates and interactions thereof, or valence forces. This is basically a printout of the data entered in the dialogs of the [Forces](#) menu. Where there is more than one specification for a given internal coordinate or force constant, the specifications are simply given one after the other, with the same "Fcon" or force constant number (dialogs of [Forces](#) menu).

**Internal Coordinates Located.** This gives the complete list of individual bonds and angles, and interactions thereof, which have been located according to the given specifications. In each group are listed the number of the individual bond, angle, or interaction, the input force constant (Fcon) number and the actual atoms involved. Two types of atoms are listed, primary and secondary, and in the case of crystals or polymers these may be different (for molecules the secondary atoms are exactly the same as the primary atoms). The secondary atoms are those outside the unit cell which are necessary to specify a complete list of bonds and angles; they are related by lattice translation to the corresponding primary atoms. These numbers refer to the **Final Atom List** given below. For bonds, one or the other of the two atoms must be in the unit cell; for 3-atom angles, the central atom must be in the unit cell; for tau angles one of the two middle atoms must be in the unit cell, and for psi angles the central atom (number 2) must be in the unit cell. For interactions, the Primary Coordinate numbers refer back to the list of bonds and angles located (from which the common atoms may be determined).

**Final Atom List (Cartesian) - Rotated, Translated.** This gives all the atoms generated by symmetry, transformed by the [PreCalculation Rotations](#), and for crystals and polymers, any secondary atoms outside the unit cell needed to complete the specified bonds and angles. These atom coordinates are also translated to put the center of gravity of the molecule or unit cell (primary atoms only) at the origin of coordinates. The atomic displacements listed below in the Calculated Mode section as well as the symmetry coordinates in the Symmetry Analysis section apply to this list, and to this orientation, not to the orientation of the input atoms or that of the non-rotated molecule/unit-cell list above.

**Atomic Displacement Parameters.** This gives the way the atomic displacements are normalized and rescaled, as specified in the [Basic Parameters](#) dialog ([Setting](#) menu).

## Symmetry Analysis Section

---

For each species, this gives the starting parameters including the basis functions; the full-matrix representations; and the Cartesian symmetry coordinates.

The first line gives the species label, the degeneracy, the number of basis functions and total number of terms therein, and the translations and rotations present. The latter are given in the order translations on x, y and z and rotations on x, y and z.

**Exponents** give the exponents on the x, y and z coordinates in each term used in the basis function for this species. Each term is shown as a triplet of exponents. The Coefficient matrix then gives the coefficients on each term, in each basis function. Actually, this section gives the complete basis functions, in n lines if there are n functions, showing all m terms (the matrix uses only the leftmost n by n terms).

**Representations** gives the full-matrix representation derived from the original symmetry matrices (Cartesian symmetry matrices above), although of course there is only one number for A and B species.

Finally the **Symmetry coordinates** gives the Cartesian symmetry coordinates obtained by transforming in turn the x, y and z coordinates of each input atom. The first line of each coordinate gives the starting atom number and the x, y or z, and succeeding lines give the transformed coordinates, in terms of x, y and z coordinates on the symmetry-derived atoms (in the **All Atoms in Unit Cell or Molecule List**). Several components may be given per line, with asterisks separating them.

### Least-Squares Section.

The reduction factor and end criterion ([Control Window](#)) are first listed.

For each cycle, the average deviation and average squared deviation of the calculated from observed, the determinant of the least-squares matrix, and the new, derived values of the force constants are given. If the average squared deviation (not the average deviation) is worse than the last cycle, or if the change is less than the end criterion value ([Control Window](#)), the process is halted, and in the first case the force-constant values revert to those of the last cycle. The force constants are listed across the window or page in order of the "coord." number given in the **Internal Coordinate Types** lists above.

If **Correlation Coefficients** are selected in the [Listings](#) dialog, they are printed out in lower diagonal form, omitting diagonal elements:

```
21
31 32
41 42 43
```

that is 21, 31, 32, 41, 42, 43 and so on. Only the force constants selected for least-squares adjustment appear here. Normally, absolute values of correlation coefficients must be very close to 1.0 (say 0.95 or greater, very roughly) to indicate significant interdependency of the force constants.

**Calculated Mode Section.**

Each species is headed by the Species label followed by the number of modes. The polarization components for infrared and Raman are also given. Modes are listed within species in decreasing order of frequency.

The first line for each mode (marked by "####") gives the overall sequence number, the calculated frequency in reciprocal centimeters with observed frequency in parentheses, the infrared intensity, the Raman intensity, the Raman depolarization ratio and the NRVS fraction (not divided by frequency). The intensities are the averages, which are influenced by some parameters in the [Spectra Plotting Parameters](#) dialog, as well as the atomic-motion scaling parameters in the [Basic Parameters](#) dialog. The intensities are all weighted by the degeneracy for the species.

If least-squares is in effect, the wavenumber calculated from the energies derived from atomic displacements is given. This is a check on the process of calculating energies, on which least-squares analysis is based (see [Theory and Implementation](#)), and indeed on all aspects of the calculation of atomic displacements and changes in internal coordinates and interactions. In view of the assumptions involved, exact correspondence between this value and the wavenumber directly determined from the secular equation is not expected, but deviation by more than a few wavenumbers may indicate a bug or other problems. It may be possible to improve agreement by using the atomic displacement scale factor ([Basic Parameters](#) dialog, [Setting](#) menu) to reduce the magnitude of calculated atomic motions. This may be necessary especially if there are weak forces such as torsion which may lead to particularly large atomic motions.

Following this are some totals for internal coordinates and interactions thereof, arranged across the page in order of the input number in the dialogs of the Forces menu. That is for the "Net Bnds/Grp" item (for example), if there are three input bond force constants (Fcons), there are three corresponding numbers, which are the sum of the changes of all bonds derived from each input specification. These values may be carried over onto successive lines.

For bonds there is a "Net Bds/Gp" item, which is simply the sum of all the bond changes in each group, and also an "Av Bds/Gp", which is the sum of the absolute changes in bonds in the group. Comparison of these two can show whether the mode is mostly of the symmetric or antisymmetric stretching character, where this is not strictly determined by symmetry. For angles the net category is omitted and there is only an average or absolute sum of changes (in degrees).

For every type of force constant there is an energy ("En") category. These numbers are given in fractions of the total potential energy. This is a direct measure of the importance of the group or input coordinate force constant on the frequency of the mode in question. Again, the sum of these energies is used for the "Energy recalculated..." number above. Note that the value of individual entries in this section may be greater than one, since some may also be less than zero (realistically only interactions should be less than zero, although if other force constants are allowed to go negative their contribution will be negative).

Following these group results are the individual polarization components for Raman and



infrared. For Raman, the components are xx, yy, zz, xy, xz and yz, and for infrared they are x, y, z. (see [Theory and Implementation](#) for the derivation of these numbers). The allowed infrared and Raman components are given in the header line for the species, or can be obtained from the [Species](#) dialog in the Input menu. For multidimensional species not all components are present, and it may be necessary to take sums and/or differences of the given simple Raman components to see the activity. Generally, x is preferred over y and z, xx-yy over xy, and xz over xy and yz. To make sure which component is present, in the [Listings](#) dialog ([Setting](#) menu, [Control Window](#)) select **Representations of species** to print out the basis functions used. The first one given should be the component which appears. However, this may depend on proper orientation of the symmetry elements with respect to the Cartesian axes (see [Orientation](#))

If selected in the [Listings](#) dialog ([Setting](#) menu), the changes in individual bonds and angles are given. These are given in the order of the **Coordinates Located** lists above.

The **Atomic Displacements** are the displacements in the x, y and z directions of each primary atom in the **Final Atom List**, with two atoms per line, separated by a slash.

Finally, for each species the **Average Energy Contributions...** shows which force constants or groups of internal coordinates are absent from that species (since this information is not a direct outcome of the symmetry analysis).

**List of Frequencies.** This gives an overall list sorted in decreasing order of frequency, either by species or for all species together ([Basic Parameters](#) dialog, [Setting](#) menu). The intensities are the averages, which are influenced by some parameters in the [Spectra Plotting Parameters](#) dialog, as well as the atomic-motion scaling parameters in the [Basic Parameters](#) dialog.

**Contributions of F's to modes.** This lists the force constants (F's), giving the number and force-constant value for each, and then gives up to 12 modes to which this force constant is a significant contributor, ranked in decreasing order of contribution. For each mode, the frequency, the species and the energy contribution in percent is given. The contribution is exactly the same number (as percent) as the energy ("En") category discussed above for each mode.

## 5.6 Reading Old VIBRAT Files

VIBRATZ should be able to read input files written for the old DOS version, called VIBRAT. The **Open** command recognizes only files with extension .VIB and .VBR, so it will be necessary to add the .VIB extension (not .VBR).

The only change which is likely to affect the calculation of frequencies is the treatment of "2-coordinate" 3-atom angles ([Angle](#) forces). In the old VIBRAT, if the "2-coordinate" option was selected, a second bending coordinate was constructed with s-vectors perpendicular to those of the standard or in-plane coordinate, and this coordinate was assigned a force constant  $f'$  related to the standard force constant by  $f' = f(1 + \cos(\theta)/2)$ . Currently, for such "2-coordinate" angles, the second force constant  $f'$  is exactly equal to the first one. For 180 degree angles there should be no difference. If you want to keep the internal coordinates as defined by the old version, you can define two separate angles, one in-plane and one out-of-plane, with the force



constant for the second as above.

The atomic displacements for the second coordinate in 2-coordinate angles were not computed correctly in the old version, and least-squares refinement of these forces was not effective. This has been corrected.

Computation of the polarizability tensor has changed (see [Theory and Implementation](#)), but this has little effect on spatially averaged Raman intensities, keeping in mind that the intensity estimates are qualitative or semi-quantitative at best.

## 5.7 Types of Files used by VIBRATZ

VIBRATZ uses many types of files for data storage, input and output. With the exception of the.mds atomic-motion file, these are all text or ASCII files. Where file extensions are given, this is only a preference - it is always possible to specify "all files (\*.\*)" when opening a file, or to override the extension when writing.

**Main data storage files (.VBR, .VIB).** The data for each VIBRATZ problem or structure are contained in a text file with extension .VBR. After changing any parameters (mostly in the Input and Forces dialogs), it is necessary to save these files with the Save or Save As commands in the File menu or the buttons in the Control Window, although if a file has not been saved before you read in a new one or quit the program you will be asked if you want to save it.

Input files for the old Fortran version (called VIBRAT) should have extension .VIB. These are read with the same **Open** command (File menu) as the current .VBR files. However, you cannot save a file of type .VIB - once such a file has been read in the extension is changed to .VBR.

**Setup files.** VIBRATZ uses a setup or preferences file called SCRPTR, which is in the same folder as the VIBRATZ application. This contains operating parameters which are not specific to individual structures. Parameters which are specific to individual structures and which are saved in the main data (.vbr) file, but which are not absolutely intrinsic to the structures, i.e. pertain to the way the structure is displayed or calculated, are also saved in the file DEFAULTS. This file is read whenever VIBRATZ is started up, and it is saved with the Save Defaults command in the Settings menu. It may be re-read at any time, with the Read Defaults command in the Settings menu, to replace the current values. The SCRPTR and DEFAULTS files are actually replaced after the first startup by a single [user- and platform-specific file](#).

**ELEMENTS.DAT file.** This file is used by VIBRATZ for two functions: it is read on startup to supply the default Atom Type List, which gives standard atomic numbers, weights and charges. It is also read when a data file from other software is imported, to assign atomic numbers (type numbers) to input atoms based on standard elemental symbols. Each line of this file refers to one element or atom type and contains the following fields: the atomic number or type number; the one- or two-letter symbol; the red, green and blue components, as numbers from 0 to 255, of the atom color (for the Atoms graphics window or output when in color), the gray shade as a number from 0 (white) to 15 (black) (for the Atoms graphics window or output when in black-and-white); the atomic weight; and the formal charge. There must be 102 lines or

atom types, but otherwise the values may be edited as desired. Following are the first four lines from the standard file:

```
1 H 0.32 148 148 148 8 1.00797 1.000
2 HE 1.50 0 0 255 6 4.0026 0.000
3 LI 1.52 255 0 255 6 6.939 1.000
4 BE 1.11 255 0 255 6 9.0122 2.000
```

**Output files.** Files with extension .VBD, when opened by VIBRATZ, are displayed in a Text window, which has its own menu bar with standard commands for text editing, printing, etc. VIBRATZ itself generates some files of this type, including the main output file in which are printed the results of the calculation. This file is given the name *infile.VBD*, if *infile.vbr* is the name of the main data file for this problem. The Coordination option in the Input Atoms dialog (Input menu) also writes a text file called BONDS.VBD. Both of these files are displayed in a text window as soon as they are written.

**Special input files.** VIBRATZ may need to read several types of files to get certain special types of data. Cartesian symmetry files, with extension.SYM provide symmetry for non-crystallographic point groups. Instead of using valence forces, a matrix of Cartesian atomic forces may be read in, and conversely, transformed valence forces may be written as a matrix of Cartesian atomic forces - files of this type are given the extension.CAR. Lists of atomic coordinates, with labels, may be read in with.INP files. A complete set of valence force specifications may be written and reread; this type of file has extension.FRC. The observed wavenumbers may be read in in a text file with extension.FRQ.

**Structure import files.** VIBRATZ can import structure data from many different program systems. The file extensions are too numerous to mention and are sometimes not exclusive.

**Special output files.** Two special types of output file are written by VIBRATZ. The spectrum data file, with extension.SPC, contains data on the calculated intensity and polarization components of the frequencies, primarily for use in plotting spectra. VIBRATZ itself will produce plots of spectra, so these files are not needed unless a specialized plotting program is written. The atomic-motion data file, with extension.MOT, contains the basic data on location of atoms in the molecule or unit cell, plus the displacements of atoms in each mode. This is intended specifically for the program ATOMS, which can give a more sophisticated representation of the structure.

**Binary atomic-motion files.** When atomic-motion plotting is selected in VIBRATZ, the atomic motions are saved in a binary file named *infile.MDS*, if *infile.VBR* is the name of the main data file. This allows quick recovery of the data for each mode. Also, when atomic-motion data are transmitted to ATOMS using a.MOT file, ATOMS constructs an identical.MDS file. ATOMS can read.MDS files written by VIBRATZ, which allows updating of the atomic motions without disturbing the display characteristics for the structure which are set up in ATOMS.

**Standard graphics output files.** VIBRATZ can write graphics output files for the spectrum and atomic-motion plots in several standard formats, including both.WMF and.EMF metafiles,

and .BMP, .PCX and .TIF raster files (Windows) or Pict files and .PNG raster files (Macintosh)

### **Alphabetical list of file extensions used by VIBRATZ**

**.CAR** Input or output file containing a force field in terms of the Cartesian coordinates of the atoms. Specified in the Cartesian forces option in the Control Window, when Cartesian input forces are to be used instead of valence forces; or in the Write Cartesian File option in the Forces menu, when writing a file.

**.DAT** The ELEMENTS.DAT file, containing standard data on the elements. This file is read automatically by VIBRATZ when needed.

**.FRC** File containing valence force specifications, which can be written and read with commands in the Settings menu.

**.FRQ** File containing observed wavenumbers. Read through the Observed Wavenumbers dialog in the Input menu.

**.MDS** Binary file containing the atomic motions for each mode. This may be used by the program ATOMS as well as the Atoms window in VIBRATZ.

**.MOT** Text output file containing atom locations and motions in each mode, for export to the structure-display program ATOMS.

**.VBD** Text output files. These are displayed in text windows on screen. Infile.out is written during every calculation and contains the printed results. BONDS.OUT contains the result of the Coordination option (Input Atoms dialog, Input menu). These files had the extension .OUT in earlier versions of VIBRATZ.

**.SPC** Output file containing intensities and polarization data for each mode

**.SYM** Input file containing symmetry information for non-crystallographic point groups

**.VBR** Main data file, containing complete information on the current problem.

**.VIB** Old data file from VIBRAT (Fortran precursor to VIBRATZ)

### **-----Macintosh only -----**

All Macintosh files have two identifying 4-character strings, the file type and the creator signature. The file type for all files listed above, with the exception of binary .MDS files is "TEXT". The creator for main data files (.VBR) and for text output files (.VBD) is "VIBR". The assignment of creator "VIBR" to the .VBR and .VBD files allows startup of VIBRATZ by double-clicking on these files. The creator for other types of text files is "ttxx"; double-clicking on these files will start up the standard Macintosh word-processing program TeachText or SimpleText.

## 5.8 Isotope Configurations

You may have up to three isotope configurations - (the abbreviation "isoconfig" may be used where required by space restrictions). To set up for isotope calculations, you must enter data in two or three places, the [Isotopes](#) dialog, the [Observed Wavenumbers](#) dialog and the [Read Observed Spectra Data](#).

**Isotopes dialog.** This is accessed either from the Control window (Isotopes... button), or from the Input/Atom Types dialog. Spectrum 1 uses the atomic weights listed in the Atom Types dialog. For spectra 2 and 3, you specify the type numbers of all atoms whose atomic weights are to be changed. For example if S atoms with type 16 are to have atomic weight 36 instead of 32, you would enter 16 and 36.0. If more than one atomic type is substituted, for example types 16 and 116 for sulfur, both must be given. If the Calculate box is not checked, the 2nd and 3rd spectra will be skipped.

**Observed Wavenumbers dialog.** Here you select the configuration with the Isotope Configuration spin control.

**Reading NRVS intensity data.** This is done in the same way as for the base configuration, through the [Read Observed Spectra Data](#), which is accessed through the Settings menu or the [Parameters](#) dialog from the Spectra window. The Read Observed ... dialog now has a Spectrum number option in the upper left.

**The Spectra Window** now also has the configuration ("isoconfig") option in the upper left. If you have read in observed data but have not entered a new isotope substitution configuration in the [Isotopes](#) dialog, you will have to recalculate. The PED will be for the selected spectrum.

**Text Output.** The listed data for individual modes, including atomic motions, energies, etc. is for the main or original isotope configuration. There are lists of modes for the main configuration and each of the isotope configurations. The modes in each species in the lists for isotope configuration are given in order of decreasing frequency, but this order may be different from that of the main configuration if the isotope shifts are larger than the intervals between modes - in other words modes strongly affected by the changed atomic weight may jump over others. There is a column labeled "Main" which gives the mode number in the main list to which the given mode corresponds, and for which the isotope shift is computed.

**Atoms Window.** This will show the motions for the main (number 1) configuration.

**Least Squares.** The configurations (1 to 3) which are included are controlled by the check boxes in the [Isotopes](#) dialog. Of course you must enter either some [Observed Wavenumbers](#) for (step-by-step) refinement on frequencies, or NRVS intensity data for NRVS refinement.

## 6 Identifying Atoms

In the Atoms Window, clicking with the mouse on the location of an atom brings up a dialog with information about that atom.

If atoms are superimposed, the [Atoms at Cursor](#) dialog appears. If the atom is isolated, the

[Generated Atom Data](#) dialog appears.

## 6.1 Atoms at Cursor

**Dialog Box: Atoms at Cursor** [Mouse click in Atoms Window]

When you click with the mouse cursor on the outline of an atom in the [Atoms graphics window](#) (in the Atom Identification mode), you may get either this dialog, or the [Generated Atom Data](#) dialog. If the click point lies within the outline of more than one atom (including those which may be partially or completely hidden), this dialog appears listing the atoms from front to back. Selecting an atom from the list by double-clicking or using the **View/Revise** button then brings up the Atom Data dialog.

## 6.2 Generated Atom Data

**Dialog Box: Generated Atom Data** [click on atom in Atoms Window]

This gives information on the currently selected atom, in the currently selected mode.

The first line gives the generated atom number, as in the **Final Atom List** in the [output](#), the label and the input atom number, as in the [Input Atoms](#) dialog ([Input](#) menu). In the case of a crystal or polymer, the atom is identified as either a primary or secondary atom.

Three sets of atomic coordinates are given; the current Cartesian coordinates, which include any rotations applied in the [Atoms Window](#); the Original coordinates, which are the Cartesian coordinate in standard orientation (including rotations specified in the [Pre-Calculation Rotations](#) dialog, [Input](#) menu, and displacements to put the center of gravity on the zero point), and for a crystal or polymer, the fractional coordinates on the structure axes, in original orientation.

The motion vector is always Cartesian and is given in both the current orientation and the standard orientation as above. See the [Basic Parameters](#) dialog ([Setting](#) menu) for factors affecting the magnitude of the vectors.

The four lines at the bottom of the dialog give the distance from the current atom to the last atom selected, the angle defined by the current atom and the last two, the tau dihedral angle involving the last four atoms, and the bond-plane psi angle involving the last four atoms. See [Construct Molecule from Z-Matrix](#) for the definition of the dihedral angle and the sign convention. For psi angles, the sequence is 1) outer atom defining the "bond" of the bond-plane; 2) central atom; and 3) and 4) outer atoms defining the plane (see the diagram in [Psi Angles](#) or [Manual Psi](#)).

The buttons to the right of each of the lines for bond, angle, tau and psi allow specification of individual bonds and angles "manually", instead of "automatically" as in the dialogs in the [Forces menu](#). Clicking on these buttons you will be shown respectively the Add Atoms to Manual [Bond](#) / [Angle](#) / [Tau](#) / [Psi](#) dialogs, which in turn lead to the [Manual Bonds](#), [Manual Angles](#), [Manual Tau](#) or [Manual Psi](#) dialogs. If the atoms specified are either in a pre-existing Manual Bond or angle, or have been generated with "automatic" bond or angle specifications, you will be given a warning, but will not be prevented from adding the atoms.

### 6.2.1 Add Atoms to Manual Bond Specification

**Dialog Box:** Add Atoms to Manual Bond Specification [[Generated Atom Data](#)]

This dialog appears when you click the Manual Bond button in the [Generated Atom Data](#) dialog.

You are shown the atoms selected, and the number of Manual Bond groups already defined. The radio box at the bottom allows you to choose whether to make a new group or add the current atoms to an existing group (if any already exist).

If you click OK, you will be taken to the [Manual Bonds](#) dialog, giving the complete data for the bond groups. In that dialog you can specify the bond force constant and the polarizability for calculated Raman spectra.

### 6.2.2 Add Atoms to Manual Angle Specification

**Dialog Box:** Add Atoms to Manual Angle Specification [[Generated Atom Data](#)]

This dialog appears when you click the Manual Angle button in the [Generated Atom Data](#) dialog.

You are shown the atoms selected, and the number of Manual Angle groups already defined. The radio box at the bottom allows you to choose whether to make a new group or add the current atoms to an existing group (if any already exist).

If you click OK, you will be taken to the [Manual Angles](#) dialog, giving the complete data for the angle groups. In that dialog you can specify the angle force constant.

### 6.2.3 Add Atoms to Manual Tau Specification

**Dialog Box:** Add Atoms to Manual Tau Specification [[Generated Atom Data](#)]

This dialog appears when you click the Manual Tau button in the [Generated Atom Data](#) dialog.

You are shown the atoms selected, and the number of Manual Tau groups already defined. The radio box at the bottom allows you to choose whether to make a new group or add the current atoms to an existing group (if any already exist).

If you click OK, you will be taken to the [Manual Tau](#) dialog, giving the complete data for the tau groups. In that dialog you can specify the tau force constant.

### 6.2.4 Add Atoms to Manual Psi Specification

**Dialog Box:** Add Atoms to Manual Psi Specification [[Generated Atom Data](#)]

This dialog appears when you click the Manual Psi button in the [Generated Atom Data](#) dialog.

You are shown the atoms selected, and the number of Manual Psi groups already defined. The radio box at the bottom allows you to choose whether to make a new group or add the current atoms to an existing group (if any already exist).

If you click OK, you will be taken to the [Manual Psi](#) dialog, giving the complete data for the psi groups. In that dialog you can specify the psi force constant.

## 7 Background

[What VIBRATZ Does](#)

[What You Need to Know to Make a Calculation](#)

[Theory and Implementation](#)

[Forces - General Considerations](#)

[Urey-Bradley Forces - Theory](#)

[Terminology](#)

### 7.1 What VIBRATZ Does

VIBRATZ is a program for modeling the fundamental optical vibrations of any compound, using valence forces (interatomic bonds and angles). VIBRATZ calculates only fundamental frequencies, not overtones and combinations (which are usually much weaker in spectra). In a molecule, there are  $3n-6$  fundamental vibrations, where  $n$  is the number of atoms.

In crystals, optical vibrations (or more strictly limit optical vibrations) are defined as those in which the wavevector  $\kappa$  is zero. In such vibrations, all unit cells behave identically, whereas in non-optical vibrations, atoms in different unit cells have different motions. There is only a limited number of optical vibrational modes, namely  $3n-3$  for crystals, where  $n$  is the number of atoms in the unit cell, whereas the number of non-optical modes depends on the total number of atoms in the actual crystal. The capability to calculate all crystal vibrations and phonon dispersion curves may be added to VIBRATZ in the future.

VIBRATZ requires input of 1) unit cell axis lengths and interaxial angles for crystals; 2) selection or input of the point-or space-group symmetry; 3) the atomic coordinates; and 4) specifications for locating the bonds and angles involved in the valence forces, and a force constant for each specification.

The bonds and angles in category 4) are the internal coordinates (or groups thereof) of a traditional normal-coordinate analysis. Because VIBRATZ converts all forces to Cartesian, and carries out the symmetry analysis and solution of the secular equation using Cartesian matrices, there is no limit to the number of internal coordinates which may be used, nor is it necessary to consider explicitly any redundancy relations among them.

Bond and angle specifications can be given in either of two ways: automatically, by specifying the atom types involved and limits on bond lengths and angle values, or manually, by specifying



the individual atoms. Atom types are normally chemical species (atomic number), although they can also be symmetrically distinct input atoms for more precise definition of bonds and angles. Angles include 4-atom torsion and bond-plane bending as well as 3-atom valence angles. Interactions between any pairs of internal coordinates may be specified.

Given this information, VIBRATZ then analyzes the symmetry and calculates the frequencies, classified into symmetry species. It provides the atomic displacements involved in each vibration and the fraction of the total energy of the vibrations contributed by each bond or angle (and interactions thereof). An interatomic force matrix in terms of Cartesian displacements of the individual atoms is a by-product of the calculation, and may be exported for other purposes, such as calculating elastic properties.

Least-squares adjustment of the force constants may be done, with selection of both force constants and symmetry species.

Synthetic infrared and Raman spectra may be drawn, using simple models of intensities. Individual polarization components or average spectra may be shown. The atomic motions may be shown graphically.

## 7.2 What You Need to Know to Make a Calculation

There are two kinds of information you need; 1) the data on the atomic structure itself; and 2) at least preliminary information on interatomic forces.

Regarding data on the atomic structure itself, especially its symmetry, exactly what you need to provide depends on the nature of the structure and the source of information. The main categories, and the dialogs in [the Input Menu](#) in which they are entered are

1) *Structure axes and lattice translations*. For a crystal, the unit-cell axis lengths and angles are required. For a molecule, Cartesian axes are normally used. You can do a calculation for a crystal by using lattice translations in all three axis directions; for a molecule by using no lattice translations; or for a polymer by using translations in one or two directions. ([Title/Axes](#) dialog)

2) *Symmetry*. You need to know the space group for a crystal or polymer or the point group for a molecule. Of course, if you are not interested in symmetry, and you know the location of all atoms, the calculation can be made disregarding symmetry, but this is generally slower and takes more computer memory. ([Symmetry](#) dialog)

3) *Rotations* required to attain standard orientation (see [Orientation and Rotations](#)). Some space groups are oriented in a way which is not consistent with the basis functions used for symmetry analysis. A rotation of both the symmetry matrices and the atoms of 30 or 45 degrees about the z axis may be required. However, this is normally done automatically when you specify the space group. ([Pre-Calculation Rotations](#) dialog)

4) *Coordinates* for a symmetry-unique set of atoms, or for all atoms. These are fractional in terms of the unit-cell axes for a crystal, and normally Cartesian for a molecule ([Input Atoms](#) dialog). Each atom is given a type, which is typically the atomic number.

5) *Types* of atoms present. For each atom type used in the preceeding category, it is necessary to specify the mass, and also the charge for calculating infrared intensities. ([Atom Types](#) dialog). For natural isotopic mixtures the standard atom list may usually be used, but if particular isotopes are used it may be necessary to use their atomic weights.

If you import data for a crystal from one of the supported data-base formats, all this information, except possibly 3), is likely to be supplied automatically in the file. For a molecule with no symmetry, default values can be used for the symmetry and structure axes. In most cases, the atoms are referred to by their atomic numbers, and the masses and charges are obtained from a standard table. However, in some cases, for example calculating structures with isotope substitutions, it will be necessary to modify the types of atoms.

Forces are entered through the dialogs of the [Forces](#) menu, or in the case of manual forces, by clicking with the mouse on the atoms involved. Determining the interatomic forces is the object of the calculation, so exact values are not normally available for input - what you must supply are educated guesses. Atoms supports valence forces of the standard types, namely bonds, three-atom angles, four-atom torsion (tau) or bond-plane (psi) angles, and interactions of bonds and three-atom angles. Apart from cases in which certain vibrations are determined uniquely, which are occur only for the simplest structures, you should look at previous calculations on similar structures to find reasonable starting values. Force constants are usually strongly dependent on bond lengths, and to a lesser extent, angle values.

If you are not very familiar with the structure, it may be very helpful to use the [Coordination](#) option in the [Input Atoms](#) dialog. This gives a printout of the possible bonds and (3-atom) angles involving each atom, and also a sorted list of bonds and angles.

### 7.3 Theory and Implementation

The basic theory and methodology used in VIBRATZ have been described before (Dowty, Phys. Chem. Minerals, 14:67, 1987). There have been no fundamental changes in basic methods described in that paper, but many additions and extensions. The following discusses some special topics which may be important for proper use of VIBRATZ.

VIBRATZ uses the general method of calculation described by E. B. Wilson, J. C. Decius and P. C. Cross for molecules (Molecular Vibrations, Dover 1955 - hereafter abbreviated WDC). Using this method for crystals requires only extending the continuity of the structure across unit-cell boundaries, which is done in VIBRATZ by using secondary or dummy atoms when necessary. These dummy atoms are used in calculating changes in bond lengths and angles, for example, but not in the calculation of frequencies, which is done on the basis of atoms in the unit cell only.

Although forces are entered in the form of internal coordinates or bonds and angles, these are transformed to Cartesian coordinates at an early stage. The solution of the secular equation is done with Wilson's fg method (it could be done in other ways), but this is applied to the Cartesian coordinates rather than internal coordinates. Symmetry coordinates are also worked out on a Cartesian basis.

In addition to facilitating computer programming, conversion to Cartesian coordinates has the advantage that there is no necessity for conforming the forces to the mathematical requirements of the secular equation. Thus it is not necessary to limit the number of internal coordinates or force constants to the number of normal modes ( $3n-3$  or  $3n-6$ ), or to provide redundancy conditions if the number is excessive. This facilitates changes in the forces used, and transferral and comparison of force constants between compounds which are chemically similar but geometrically and/or symmetrically different. If an insufficient number of force constants is specified, there will be some zero frequencies, which is harmless.

Derivation of symmetry coordinates, which has often been done on a somewhat ad hoc basis, is systematized by using the projection/transfer operator technique.

### Symmetry - Basis Functions

When symmetry is present, VIBRATZ requires a set of symmetry matrices, and a polynomial basis function for each species.

Symmetry matrices are obtained in two ways. For space groups and crystallographic point groups, they are generated using licensed excerpts from the program SgInfo by Ralf Grosse-Kunstleve. The matrices for the entire group are obtained by intermultiplying a small number of basis matrices. The information for all this is stored internally in VIBRATZ.

For non-crystallographic point groups, the symmetry matrices are read in from a file, since there is theoretically an infinite number of such point groups. The files for the most common point groups are supplied. The matrices for any point group, in any orientation, may be generated with the auxiliary program SYMGRP. This program also uses a small number of basis operators or matrices to generate the entire group.

Symmetry matrices are used in two ways in VIBRATZ; to generate all the atoms in a molecule or unit cell, starting from a symmetry-unique set; and to derive the irreducible representations and symmetry coordinates which are used to factor the large matrix of the secular equation into smaller matrices for each species. For the first use, lattice translations are included in the case of crystals and polymers, but lattice translations are ignored for the second use.

The polynomial basis functions for the space groups and crystallographic point groups are stored internally in VIBRATZ, since there is a finite number of them. In fact, only 32 sets of functions are required since translations are irrelevant in this context.

The basis functions for non-crystallographic point groups may be obtained in several ways. Firstly, infrared-active species always have first-order basis functions of the type  $x$ ,  $y$ ,  $z$ , and Raman-active species have second-order basis functions which are the components of the polarizability tensor. These functions are almost always listed in character tables. Thus the actual observed infrared and Raman species of a point group can always be calculated if a character table is available. The third-order functions which are the representations of the  $f$  atomic orbitals are also sometimes listed in character tables (e.g. D.C. Harris and M. D. Bertolucci, *Symmetry and Spectroscopy*, Dover 1978). The book by M. Lax () lists many basis functions for space groups. Finally, a program to find basis functions was written. This program steps through all products of  $x$ ,  $y$  and  $z$  up to a given order, and derives the correct

basis function(s) for a given species using the projection operator technique. It requires a valid character table for the group. Polynomial basis functions have thus been determined up to 8th order, and with a few exceptions (species xx of group xx, and optically inactive species of the icosahedral groups) this is sufficient for all the groups listed in the Point Group Symmetry dialog.

Note that published character tables may contain errors. All published character tables for group S8 so far examined show rotations on x and y in species E1, whereas test calculations indicate that they really belong in species E3 (also note that x and y rotations follow the xz and yz components in all other groups).

### Orientation and Rotations.

Orientation of symmetry elements with respect to coordinate axes is critical for several reasons. Unfortunately there are no universally accepted conventions for such orientation, and structure descriptions do not always specify orientation completely.

VIBRATZ uses the following conventions for orientation of symmetry elements. Any unique symmetry axis is parallel to z. In Cnv groups, a vertical mirror plane is perpendicular to the x axis (not the y axis if there is a difference). In groups which have both horizontal 2-fold axes and vertical mirror planes, a 2-fold axis is oriented parallel to the x axis and mirror planes are oriented accordingly. The icosahedral groups are oriented with a 5-fold axis parallel to z, and an adjacent 3-fold axis in the x-z plane. These orientations have been used for the basis functions in all cases, and for the symmetry matrices for non-crystallographic symmetry generated by the program SYMGRP. Note that trigonal and hexagonal crystals are oriented by VIBRATZ with the a2 axis parallel to y, so that a1 does not coincide with x (the crystal/Cartesian conversion is  $z = c$ ,  $x = a^*$ ).

VIBRATZ has provisions for two different kinds of rotation to correct any non-correspondence in orientation. Note that there is also a third type of rotation, which is applied in the [Rotation](#) menu and the Dialog Bar of the [Atoms Window](#). This third type of rotation is applied only to the image of the structure and the atomic displacement vectors, and has nothing to do with symmetry analysis.

Firstly, the atomic coordinates must correspond with the orientation of symmetry operators, for proper generation of all equivalent atoms. In the case of space groups, several settings may be possible, but all the common possibilities are listed in the [Space Group Symmetry](#) dialog, and it is usually only necessary to select the setting which corresponds to your atomic coordinates. In the rare case that the list is not adequate, it may be necessary to use the [Custom Symmetry](#) option.

In the case of molecules belonging to a point group, you may have a) atomic positions which do not correspond to the above standard orientation, or b) a complete set of coordinates for all atoms in the structure, rather than just a symmetry-unique set.

There are two solutions to situation a). The easiest is probably to rotate the actual atomic coordinates, using the **Rotate** option in the [Input Atoms](#) dialog - this is the first type of rotation mentioned above. Enter the original coordinates, then apply the appropriate rotation on the z-

axis. The second option is to supply symmetry matrices in the appropriate orientation for your atomic coordinates. Such matrices can be generated with SYMGRP. It is then necessary to write a.sym file for input in the [Point-Group Symmetry](#) dialog, or to modify one of the existing files (see [Making Symmetry Files](#) for preparation of .sym symmetry input files). If the point group is one of those listed, the standard basis functions may no longer be valid for your specific orientation. In this case you can either supply new basis functions, or use the [Pre-Calculation Rotations](#) option (described below) to rotate both atoms and symmetry matrices to the standard orientation.

If you have set of atomic coordinates which includes symmetry equivalents, you can simply enter the entire set and VIBRATZ will identify the redundant atoms and delete them at your option. Of course this assumes that the atomic coordinates are consistent with the symmetry matrices - if they are not, refer to the previous paragraph.

Assuming that the input atomic coordinates are consistent with the symmetry matrices, a second type of rotation may be necessary to bring both the atoms and the symmetry matrices into the orientation assumed by the basis functions. This is done with the [Pre-Calculation Rotations](#) option in the Input menu. This type of rotation is required for certain space groups, and may be required if you use your own .sym file in the [Point-Group Symmetry](#) option.

Most space groups are oriented in the standard way described above, but in some cases, namely point or factor groups D3, D3d, D2d, D3h and C3v, the *International Tables for X-Ray Crystallography* uses two different standard orientations, only one of which is consistent with the above conventions. Also, monoclinic crystals are usually given an orientation with the unique axis as b or y, instead of z. When a primitive cell is used for rhombohedral crystals instead of the non-primitive hexagonal cell, rotations are also required. In all such cases, VIBRATZ should be capable of recognizing the misorientation, and should supply appropriate rotations which appear in the [Pre-Calculation Rotations](#) dialog.

Note that results such as atomic displacements are given in terms of the rotated structure, not the input structure, since displacements should correspond to the allowed polarization components which are determined by the basis functions.

## Least Squares

Least-squares adjustment of the force constants in the analytical method (see [Control Window](#)) is based on the changes in the internal coordinates calculated from the atomic motions. The total energy of each mode is a linear function of the squares of these changes. Several aspects of this process should be noted.

It assumes in the first place that all the assignments are correct. If an observed mode is known to be missing it can be assigned observed frequency zero and it will be skipped, but the sequence of observed frequencies in each species must be correct, and each observed frequency must be matched exactly with the corresponding calculated frequency. If only two calculated modes are switched in order with respect to the observed list, which can easily happen with slight inaccuracies in force constants, least-squares adjustment of any force constants involved in these modes will probably fail.

Secondly, the directions of atomic motions are assumed to be correct for each mode. Of course this is not correct unless the calculated frequencies already match the observed - obviously refinement will work only if the deviations of calculated from observed frequencies are small. This requirement becomes more stringent as the possible vibrations become more complex, i.e. as the number of modes in each species increases. If the average deviation of the calculated from observed is not much smaller than the average difference between observed modes in a given species, it is quite likely that the model is at least partially incorrect and least-squares will not be reliable.

Thirdly, there may be strong correlations between force constants because of geometric redundancies and pseudo-symmetry. Because forces are converted to Cartesian, and the calculation is not directly based on internal coordinates, there is nothing to prevent duplicate or redundant forces. There are unavoidable correlations in some cases, for example between Urey-Bradley X-X repulsive forces and X-C-X angles.

In the step-by-step method (see [Control Window](#)) the second point is not strictly applicable. Redundant forces will not halt the refinement. But success is still not to be expected unless the model is basically correct to begin with.

In summary, least-squares is appropriate only for special conditions, typically when there is a relatively small number of modes in each species, or when observed and calculated modes can be correlated precisely for other reasons. It is often necessary to refine only some force constants at a time, perhaps selecting only some of the modes which are known (positively) to be influenced by these force constants.

## Intensities

*Infrared* intensities are simply derived from the change in dipole moment, using the atomic charges in the [Atom Types](#) list.

*Raman Polarizability and Intensities.* The "differential bond-polarizability tensor"  $\rho$  is now defined as

$$\rho_{ij} = [\text{sum over all } k \text{ bonds}] P_k \delta b(i) b(j) / |b|$$

where  $P_k$  is the polarizability factor ([Bond Forces](#) dialog),  $b$  is the bond vector and  $\delta b$  is the vector giving the change in the bond. This is a change from the original paper, which has little effect on the spatially-averaged intensities, but does improve the agreement of individual polarization components with observations. The spatially averaged intensities are determined by the standard formulas (WDC, Ch. 3 - equations 23 and 24), and the factors  $\alpha$  and  $\beta$  in these formulas are adjustable ([Basic Parameters](#) dialog). A value of 0.3 for  $\beta$  instead of 4-7 has been found necessary to give qualitative agreement with spectra of silicates.

The depolarization ratio, which is given for each mode along with the spatially averaged intensity, is calculated with WDC Ch. 3, equation 26. The lower curve in the calculated Raman spectrum (average) represents the calculated intensity multiplied by the depolarization factor - thus the two curves are; upper, parallel and lower, perpendicular orientation of polars.



These very simple intensity calculations give surprisingly good qualitative agreement with powder spectra of silicate minerals or with spectra of silicate glasses, at least for modes involving significant stretching of Si-O or other strongly polarizable bonds. The agreement for individual polarized spectra is much poorer. Although much more elaborate approaches to intensity have been used, it should be kept in mind that calculating intensities of individual vibrational modes depends on near perfect description of the atomic motions, and that in complex structures, different vibrational components may intermix in complex ways in each mode. Changing force constants slightly may result in different admixtures of these components in modes which are close in frequency. For example, if bonds X-Y and Z-Y are fairly similar, but not identical, they may contribute to two or more individual modes in a fairly narrow frequency range. The exact relative intensities of these modes, and their polarizations, may not be reliable because of variable contributions of X-Y and Z-Y stretching to each mode, which is difficult to reproduce in a calculation. However, in spatially averaged (powder or glass) spectra an envelope containing all the modes with X-Y and Z-Y stretching may be reproduced fairly well even with rather approximate force constants.

### Changes from the Original Release of VIBRAT

*2-Coordinate Angle Forces.* This option, for the bending forces involved in 3-atom valence angles, has been refined and corrected. The original option (if selected) always constructed two coordinates for each angle (in-plane and out-of-plane) and assigned a force constant to the out-of-plane bending based on the value of the angle. Now, when two coordinates are assigned to each angle with the same input specification the force constants are the same - this is intended for 180 degree angles. Separate in-plane and out-of-plane coordinates, with separate force constants, may also be defined for non-180-degree angles. The calculation of changes in the out-of-plane coordinates has also been corrected.

*Calculation of Doubly-Degenerate E Species.* VIBRATZ actually calculates both the frequency-redundant vibrations of each pair in these species (to avoid using complex numbers). The original version simply listed both vibrations, but VIBRATZ now screens out half the frequencies.

*Additions and Extensions.* Symmetry is now integral with the program for all space groups and all common point groups. Force constants may be refined by least-squares. Complete Urey-Bradley forces according to the Shimanouchi transformation have been added since the initial release. Tau (torsion) and psi (bond-plane) 4-atom angle coordinates have been added. The possible types of interaction between bonds and 3-atom angles sharing one or more atoms, located with the [Automatic](#) option, have been extended, and with the [Manual](#) option it is now possible to specify interactions between any internal coordinates even if there are no shared atoms. Angle forces may now be specified in units either of md-A or md/A.

## 7.4 Forces - General Considerations

### General Approach in VIBRATZ

VIBRATZ uses traditional valence forces, but the approach is different in certain respects from that often used in the past. First, rather than frame the calculations in terms of a specific number of internal coordinates, which are the bonds and angles in which valence forces are specified,



VIBRATZ converts all the bond and angle forces to forces in the x, y and z Cartesian coordinates of each atom, and interactions thereof. The solution to the secular equation is done in terms of these Cartesian coordinates rather than internal coordinates. This eliminates any direct restrictions on the number of bonds and angles and interactions thereof, whereas when using internal coordinates the number of internal coordinates must be  $3n-3$  for crystals or  $3n-6$  for molecules where  $n$  is the number of atoms in the unit cell or molecule; or if the number of internal coordinates is greater, redundancy equations must be supplied. Results are exactly the same as if internal coordinates are used directly.

Second, the bonds and angles can be identified by providing general specifications in terms of the nature of the atoms involved and the values of bond distances and angles. VIBRATZ will then automatically locate all bonds and angles in the structure - this ensures consistency with symmetry. Alternately, for molecules (not crystals), the bonds and angles can be specified by entering the individual atoms involved.

In principle, these two considerations together allow for a general overall specification of forces which is not based on symmetric or geometric aspects of any particular structure. In fact VIBRATZ has options to read and write files containing such specifications, for purposes of transfer from one structure to another.

The addition of Badger's rule variation to valence-bond and Urey-Bradley repulsion should cut down or eliminate in many cases the necessity for differentiating these forces on the basis of bond length.

### **Hierarchy and Ambiguity of Forces.**

The strongest forces in any structure are the valence bonds. Bonds between nearest neighbors are usually easily identified, although in ionic structures there may be no sharp cutoff between bonded and non-bonded pairs.

In covalent structures, 3-atom valence angles may be next in importance. These are also easy to identify; the problem with valence angle forces is that it may be difficult or impossible to distinguish them from non-bonded repulsion forces.

Interactions involving bonds and angles may often be identified. For example lengthening one bond in a coordination polyhedron normally increases the bond order of the other bonds, increasing the force required to stretch those other bonds. For this reason, symmetric stretch vibrations typically occur at higher frequencies than antisymmetric stretches.

In many structures the attraction of valence bonding forces non-bonding atoms into contact or repulsive relation with one another. The general model use in VIBRATZ for dealing with such repulsion is the Urey-Bradley model for  $CX_n$  coordination polyhedra. In this model, the linear X-X repulsive forces are converted to quadratic C-X bond and X-C-X angle forces, and bond-bond and bond-angle interactions. Thus it is often impossible to tell whether forces of the latter type which may be used in a non-Urey-Bradley model are true valence forces, or attributable wholly or in part to X-X repulsion. Note also that in some situations it is not possible to say whether X-X repulsion is due to electrostatic repulsion of charged ions, or to "short-range" interaction involving the electronic orbitals.

## Nature of Bending forces

Consider the bending forces in a simple A-B-C chain of bonded atoms. In a simple isolated (gaseous) triatomic bent molecule such as H<sub>2</sub>O it is necessary to consider bending only in the plane of the atoms in equilibrium configuration, because bending out of the plane can always be resolved into bending in the plane and rotation of the molecule as a whole. Likewise in a straight triatomic molecule like CO<sub>2</sub> it is theoretically necessary to consider bending in only a single plane, but in setting up the equations it is necessary to choose arbitrarily the orientation of that plane, and this choice must be consistent with the symmetry analysis if only one member of a degenerate group is calculated.

Now consider a situation in which the end atoms are fixed in a large molecule or crystal. Overall rotation is no longer possible, and it becomes necessary to account explicitly for possible bending in two directions, which can conveniently be specified as in-plane and out-of-plane in the case of a non-linear configuration, and which are arbitrary (but presumably mutually perpendicular) in the case of a linear configuration. Actually, we could still resolve such motion into bending in a single plane, combined with rotation of that plane about the axis of the end atoms, but it would still be necessary to introduce additional forces or internal coordinates to account for this rotation. Accounting for bond-bending in more than one dimension can be done in a number of ways with traditional valence forces, including tau and psi four-atom angles, and also bonding forces between non-adjacent atoms - there is no one correct way to do this.

VIBRATZ provides a means of accounting for 3-atom bending forces in both directions, which can eliminate the necessity for using more complex forces such as tau and psi 4-atom angles in some situations. Each such configuration can be assigned two bending coordinates, with s-vectors (displacement directions) perpendicular to each other. See the [Angle Coordinate Data](#) dialog for details of these coordinates.

In considering the X-C-X angles of CX<sub>n</sub> coordination polyhedra, the strictly geometric insufficiency of in-plane bending forces is removed for  $n = 4$  (tetrahedra) and for larger polyhedra there is even a redundancy of bending forces. There is no need to remove this redundancy in VIBRATZ, nor should there be any need to provide extra coordinates, provided it is understood that values of angle forces are strictly applicable only for a particular coordination number, which implies a particular redundancy. Of course we are not likely to try to transfer angle force constants between say, tetrahedra and octahedra because the bond strengths and equilibrium angle values are normally different anyway.

The example of the CO<sub>3</sub> radical (files CO3A.VBR, with psi angles, and CO3B.VBR, with external 3-atom angles) shows how the out-of-plane 3-atom bending forces may be used in place of psi 4-atom angles. Although no rigorous analysis has been attempted, it would seem that psi angles can always be replaced by out-of-plane 3-atom bending. The converse will usually, but perhaps not always, be the case.

In geometrically ambiguous situations such as discussed above the valence forces or coordinates used, for example out-of-plane 3-atom angles versus 4-atom torsion, may be a matter of preference, but whatever combination is used, it should be used in a consistent way or the forces will not be transferable or comparable between structures. It may in some cases be helpful to

start from the lowest possible symmetry of the compound in question (which might be attained by chemical or isotopic substitution) to see the nature of the force constants required.

## 7.5 Urey-Bradley Forces - Theory

VIBRATZ uses the treatment of the Urey-Bradley potential function for CX<sub>n</sub> molecules or groups given by Shimanouchi ("Simanouti", J. Chem. Phys. V. 17, p. 245, 1949), in which the potential energy V is:

$$V = \left\{ \sum \text{over } i \right\} [K'_{ri} r_i (D_{ri}) + 1/2 K_i (D_{ri})^2] \\ + \left\{ \sum \text{over } i \text{ and } j, j < i \right\} [H'_{ij} r_{ij} (D_{ij}) + 1/2 H_{ij} (D_{ij})^2] \\ + \left\{ \sum \text{over } i \text{ and } j, j < i \right\} [F'_{ij} q_{ij} (D_{qij}) + 1/2 F_{ij} (D_{qij})^2]$$

where  $r_i$  is the C-X<sub>i</sub> bond length,  $r_{ij} = (r_i r_j)^{1/2}$ ,  $a_{ij}$  is the X<sub>i</sub>-C-X<sub>j</sub> angle and  $q_{ij}$  is the X<sub>i</sub>-X<sub>j</sub> distance. Using the law of cosines to derive  $D_{qij}$  to the second order as a function of  $D_{rij}$  and  $D_{aij}$ , and the redundancy conditions for the angles within the polyhedra (also taken to the second order for tetrahedra and octahedra, but not in other cases), the above expression for V is transformed to one with no linear, only quadratic terms in the bond and angle changes. In the process, Shimanouchi defined the "internal tension",  $\kappa$ , as

$$\kappa = - (r_{ij})^2 F'_{ij} \sin(a_{ij}) - (r_{ij})^2 H'_{ij}$$

Note that  $\kappa$  must be constant for a given polyhedron. After many calculations, Shimanouchi later (Pure Appl. Chem. V. 7, p. 131, 1963) set  $F'$  empirically at -0.1 F.

The above definition of  $\kappa$  is more a mathematical necessity for the derivation than a meaningful chemical relationship. The linear angle constant  $H'$  was not included in the original Urey-Bradley treatment, and is usually assumed to be zero in perfectly regular polyhedra. In fact, it is possible to assume  $H'$  is zero in distorted polyhedra as well, relating the values of  $F'$  to the constant  $\kappa$ , as in the first model described below.

To use Urey-Bradley forces in VIBRATZ it is necessary to set up all the bonds from the central atom to the ligands in the [Bonds](#) dialog, as well as X-C-X angles in the [Angles](#) dialog, independently of the U-B specifications in the [Urey-Bradley Data](#) dialog (all in the [Forces](#) menu). Angles should correspond to X-X "bonds" or contacts; e.g. no 180 degree angles in octahedra.

**Urey-Bradley models in VIBRATZ.** VIBRATZ allows three different ways of handling  $\kappa$  and  $F'$  force constants, to accord with the different ways this has been done by Shimanouchi and others. VIBRATZ can handle polyhedra with up to eight ligands: it uses the second-order angular redundancies for tetrahedra given by Shimanouchi and those for octahedra given by Kim et al. (J. Mol. Spect., V.26, p.46, 1968), but for other polyhedra the redundancies are taken only to first order, and thus  $\kappa$  is not used for other than tetrahedra and octahedra (except for the first option). Note that second-order redundancy terms vanish anyway for strictly planar configurations.

The first option, **F' derived from kappa**, is intended primarily for strictly regular polyhedra, in which all ligands are the same. In this case, assuming that H' is zero, kappa and F' are related by the equation

$$\text{kappa} = -r^2 F' \sin(\alpha)$$

where alpha is the X-C-X angle. For tetrahedra and octahedra alpha should be 109.47 and 90 degrees respectively. There should thus be only two specifically Urey-Bradley force constants in such cases, F and kappa, and to use U-B force constants from some studies (e.g. early papers by Shimanouchi, Kim et al.) it may be necessary to convert F' to kappa. If the polyhedron is not geometrically regular or the ligands are different, the relation between kappa and F' applies only to individual ligand pairs, and if kappa is constant and H' is always assumed to be zero, F' is variable. This option may thus be a reasonable approximation for distorted polyhedra as well, although this approach does not seem to have been used before.

The second option, **Use given F'**, is the model used originally by Shimanouchi. Note, however, that Shimanouchi and others (e.g. Kim et al.) set H' to zero in the case of perfectly regular polyhedra, so that kappa and F' are directly related with the above equation. If the second option is used in such cases, kappa must be set to agree with F'.

The third option, **F' = -0.1F**, was used in later work by Shimanouchi and others. This has the advantage over option 2 of greatly reducing the number of adjustable parameters and seems to give satisfactory results in almost all cases. Note that for perfectly regular polyhedra if H' is assumed to be zero it is necessary to adjust the value of kappa with the above equation to agree with F and F' - this is not done automatically in least-squares.

It is possible to use even a lower approximation to Urey-Bradley forces than the first-order approximation used by the VIBRATZ for non-tetrahedral/octahedral coordination. This is done by simply entering the X-X interactions as bonds in the **Bonds** dialog, and entering nothing in the Urey-Bradley section. This is very roughly equivalent to neglecting F' as well as kappa, although it is not really as simple as this because of redundancies between the various forces. This has been used with some success in silicate crystals (see the quartz and diopside example files), in which even the most elaborate force fields do not produce perfect agreement.

Finally, it should be realized that the Urey-Bradley model is not uniquely distinguishable from other force models, and there is no absolute criterion for correctness of any particular model. Statements to the effect that the pure valence model is inadequate or "fails" in a particular case, whereas the Urey-Bradley model "succeeds", are unjustified in view of the fact that Urey-Bradley forces are normally converted to valence forces and that in the valence model forces can be added until the desired agreement is reached. The advantage of the Urey-Bradley model is that it often uses fewer adjustable force constants. The Urey-Bradley model is sometimes contrasted with the Orbital Valency Force Field of Heath and Linnett (Trans. Faraday Soc. 44, 873, 878, 884;1948), which frames angular or ligand-ligand forces in terms of deviation of central-ligand vectors from the optimum configuration determined by hybrid orbitals on the central atom. However, the original paper by Urey and Bradley (Phys. Review, 38, 1969; 1931) states that "Andrews has made the suggestion that the most promising assumption to make in regard to the restoring forces in molecules is that these forces to a first approximation consist of harmonic forces along the directions of the chemical bonds and perpendicular to them", and in

fact their treatment at least in its initial statement is based on this assumption and not directly on the assumption of valence angle forces.

## 7.6 Terminology

**Coordinates.** The word coordinate(s) is used in many senses in vibrational analysis, which may be confusing to the uninitiated. It may refer to:

- 1) **Atomic coordinates**, the components of an atom location in terms either of crystal axes (crystal coordinates or fractional coordinates) or Cartesian axes (Cartesian coordinates).
- 2) **Internal coordinates**, the bonds and angles which are used to specify the force constants or potential-energy function (more strictly, the relative motions of atoms in changing the magnitude of bonds and angles). Each internal coordinate should ideally be part of a set which is symmetrically distinct from other sets of internal coordinates. VIBRATZ does not actually use bonds and angles as a basis for the solution of the secular equation - it converts these to a Cartesian basis and solves the secular equation using Cartesian matrices.
- 3) **Symmetry coordinates**, the coefficients used to factor the overall secular equation into smaller matrices for the individual species (VIBRATZ automatically derives symmetry coordinates). The symmetry coordinates may be based on internal coordinates or on Cartesian displacement vectors, and in the latter case they are sometimes called external coordinates.
- 4) **Normal coordinates**, essentially the relative motions of the atoms in the normal modes, which together with the frequencies are the objects of the calculation.

If a prefix is not applied to the word coordinate(s), the context will hopefully make the meaning clear.

**Dialog Bar.** This is in effect a dialog which is attached to one edge of a window, in particular the left side of the Atoms graphics window, and the upper edge of the Spectra window. Dialog Bars contain the same type of controls (buttons, checkboxes, edit boxes, etc.) as ordinary dialogs, and these controls apply to what is shown in the window.

**Force Constants.** As far as input to VIBRATZ is concerned, these are the second derivatives of the potential energy with respect to individual members of each group of internal coordinates or bonds and angles; and also the products of the derivatives of the potential energy with respect to pairs of internal coordinates. In a traditional normal-coordinate calculation carried out using internal coordinates, the force constants correspond to symmetrically-distinct sets of internal coordinates, and interactions thereof. In VIBRATZ, because of the way internal coordinates are located, force constants may apply to more than one symmetrically-distinct set of internal coordinates. In many places in the output and the input dialogs, the abbreviation **Fcon** is used to refer to the sequence number of such groups of internal coordinates. That is, **Fcon** refers to a group of similar internal coordinates, all of which may or may not be equivalent by symmetry.

**Primary Fcons** (Force Constants). This term is used in VIBRATZ when specifying interactions, to refer to the bond or angle (internal coordinate) groups whose members (primary coordinates) may individually be involved in interactions.

**S-vectors.** These vectors, defined by WDC in Ch. 4, p55, are essentially vectors on each atom of a bond or angle (internal coordinate) which define the direction and relative magnitude of motion in changes of these bonds or angles. Succeeding pages in WDC define how these vectors are calculated for all the types of internal coordinates used by VIBRATZ except the out-of-plane three-atom angle coordinates (for which see the Angle Force Data dialog).

**Secondary Atoms.** In locating bonds and angles (internal coordinates) in crystals, VIBRATZ must search through at least part of the 26 unit cells surrounding the "primary" unit cell, to find a complete and unique set. Atoms thus identified which are outside of the "primary" unit cell are called secondary atoms. For bonds, secondary atoms are found mostly in unit cells with positive lattice translations, but secondary atoms for angles may be in any of the 26 surrounding unit cells.

## 7.7 Coordinating ATOMS and VIBRATZ

The vibrational-analysis program VIBRATZ and the structure-display program ATOMS are designed to work together. The structure-display capabilities of ATOMS, which has 3-D display and animation of vibrational motions, among many other things, are much greater than those of VIBRATZ.

Communication between the two programs is through the modes (.MDS) binary files, which can be written by either program. These files contain the detailed data for each mode, including atomic motions. These files are designed for quick access to the data for each individual mode, so all the data for all modes does not have to be in memory at the same time.

ATOMS can import the .MOT ascii (text) files written by VIBRATZ. These also contain detailed data for each mode. As ATOMS imports a .MOT file, it writes a .MDS (binary) file - this should be the same as the .MDS file written by VIBRATZ. Why bother with two different types of file? Because the binary .MDS files are not portable between platforms (e.g. Intel vs. Motorola processor).

ATOMS can also import the main VIBRATZ .VBR data files. The information in these files is not the same as in the .MOT files - the .VBR data files, like ATOMS .STR files, contain complete symmetry information and only the symmetry-unique input atoms, while .MOT files contain all atoms in the molecule or unit cell, without symmetry. The atomic motions in .MDS and .MOT files must refer to all atoms in the molecule or unit cell. Thus, **\*\*do not\*\*** import .VBR files into ATOMS if you want to display atomic motions.

When importing either type of VIBRATZ file, ATOMS will read the type numbers modulo 100 - for example, atom types number 6, 106, 206 etc. will all be converted to 6 (carbon).

*Recommended procedure for using ATOMS to show vibrational motions.*

1) If you import an ATOMS (.STR) file into VIBRATZ, it is a good idea to use two different names, for example myfile\_orig.STR for the original ATOMS files, and myfile.VBR for the VIBRATZ file. This is because you will use another .STR file, without symmetry, to display the motions.



- 2) In VIBRATZ, check the .MOT file box in the Control window so that a .MOT file is written during calculation. This will be myfile.MOT.
- 3) In ATOMS, import the myfile.MOT file. This will rewrite myfile.MDS. The new ATOMS file will be by default myfile.STR. Set up the boundary (for crystals), display parameters, vectors, etc. as desired. Most parameters dealing specifically with motion display are in the Vectors and Vibrational Modes dialogs in the Input1 menu. The bonds are just those specified in VIBRATZ.
- 4) If you return to VIBRATZ to recalculate with changed forces, it will rewrite myfile.MDS, which can be read by ATOMS, so ATOMS will remain up to date with the latest VIBRATZ calculations. On the other hand, if you want to preserve the motions for a particular calculation, you can rename the .MDS file, e.g. myfile\_1.MDS (you must do this in the operating system). You can switch between different .MDS files in the Vibrational Modes dialog in the Input1 menu. You can also reread the .MOT file, for atomic motions only, in the Vibrational Modes dialog.
- 5) *Starting a new problem.* Once you have the parameters in ATOMS set up to your liking, before importing a new .MOT file, just read an old ATOMS file with the appropriate settings. When you import a .MOT file, the new ATOMS .STR file will have the same name as the .MOT file. Or, save the desired parameters by selecting Save Defaults in the Settings menu in ATOMS. These parameters can be reread during import, or later through the Settings menu.
- 6) *Transferring problems across platforms.* The binary .MDS files may be incompatible between platforms (Macintosh and Windows computers write the bytes of numbers in opposite order). Thus you should transfer the ascii (text) files myfile\_orig.STR, myfile.VBR and myfile.MOT. When you open the myfile.STR file in ATOMS for display of atomic motions, use the option in the Vibrational Modes dialog in the Input1 menu to read in the .MOT file for atomic-motion parameters only. This will cause writing of a new myfile.MDS. Rerunning VIBRATZ should also rewrite the .MDS file.

*Display parameters in ATOMS.* The atomic radii are controlled during import with the choice between covalent and ionic radii, and by the factor which may be applied - for displaying motions the factor should normally be well under 0.5. You can later change radii globally with the Atoms-Global option in the Input1 menu. You can change the default radii and atom colors for import by editing the ELEMENTS.ION and ELEMENTS.COV files. (The file RADII contains a universal table for automatic bond generation - this should not be modified unless there are problems with automatic bond generation). Bond parameters may be set during import, or reset with automatic bond generation (Bonds dialog in the Input1 menu).

When importing a .MOT file, bond specifications are taken directly from the VIBRATZ data. If there is a structure in memory, and if there are bonds (Bonds dialog in the Input1 menu), the radius and colors of all the new bonds are taken from the first old bond - if there are no bonds, radius and colors of the bonds derived from the .MOT file will be standard (radius 0.0, black rim, white fill), or the values of the first bond when defaults were last saved.



## 7.8 Settings, Preferences or Configuration Files

VIBRATZ has in the past saved various settings in two files, SCRPTR and DEFAULTS, both of which are in the same folder or directory as the wxVIBRATZ program or executable file. SCRPTR saves general settings which may be used for all data, such as frame sizes for printing and graphics file output and is always saved before exiting the program. DEFAULTS saves settings which are more particular for each data set - these may be used as the initial or default values for a new data set. The DEFAULTS file could be read or written through options in the Settings Menu, and at other times when starting a new data set or importing a file.

Starting with V6.3, this information is saved in a standard type of file which is specific to the platform (Windows, Mac or Linux), and this file is in a location specific to each user. Thus each user will have his or her settings preserved, even if only one copy of the VIBRATZ folder/directory and executable file is present. Further, these settings will be carried on as new versions of VIBRATZ are installed.

Specifically the new settings files will be in the following locations:

**Windows:** \Documents and Settings\*username*\VIBRATZ.ini

**Macintosh:** :Users:*username*:Library:Preferences:VIBRATZ Preferences

**Linux:** /home/*username*/.VIBRATZ (note the period - this is a hidden file)

where *username* is the name of the current user logged in.

The .ini, Preferences or configuration file has separate sections containing the SCRPTR information and the DEFAULTS information.

The SCRPTR and DEFAULTS files still exist. On startup, VIBRATZ looks first for the user-specific file, and if this is not present it reads the values from the SCRPTR and DEFAULTS files in the folder or directory containing the VIBRATZ executable file. Thereafter the user-specific file is written and used.

The Windows and Linux versions have separate Help server programs, and these write their own user-specific preferences files. These files will be in the above locations, and the program name is "wxHTMLHelpController" instead of "VIBRATZ". In the Macintosh version, there is no separate Help server program and the data for the Help windows (window sizes and location and fonts) is in the VIBRATZ Preferences file.

In the Settings menu, there are now options to read and write the "archive" SCRPTR and DEFAULTS files - this writes the values currently used by VIBRATZ. If there are multiple users of VIBRATZ, these files should probably be written only the the system

administrator. All users may read the files to get the "standard" or archive values.

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