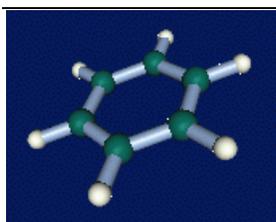# VIBRATE!

Introduction (Version 2.5)

VIBRATE! Is a program to compute from a crystal structure the irreducible representations for normal modes of vibration using *Factor Group Analysis*. The default is to carry out the analysis for modes at the centre of the Brillouin zone. Another program (SAM) that can produce similar information can be found on the Bilbao Crystallographic Server.

Below is shown a typical screen view.

Acknowledgments

With thanks to M.I. Aroyo and H. Wondratschek for permission to include Brillouin-zone diagrams from the Bilbao Crystallographic Server (Depto de Física de la Materia Condensada, Universidad del País Vasco).

Panel

The top left-hand panel shows a record of the calculation and results. The top right-hand panel shows the process of obtaining the reducible and irreducible representations.

Top Left-hand panel

This list all the input details as well as the all the results computed.

(1) The first part gives the crystallographic information (unit cell parameters, symmetry information) followed by a list of atomic positions in the unit cell.

(2) This is followed by a list of symmetry operators in the form:

Serial Number	General equivalent position	Point symmetry symbol **in** International notation
1	x,y,z	1
2	-x,-y,-z	-1
3	-y+1/2, x+1/2, z+1/2	4
Etc	Etc	Etc

(3) Then there is a list of symmetry operators given in matrix form separated into the rotation/inversion and translational components:

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

$$\begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1/2 \\ 1/2 \\ 1/2 \end{bmatrix}$$

Etc.

(4) After this any lattice centring operators are given.

(5) The program then outputs the list of characters for the reducible representation, assuming normal mode analysis. i.e. three directional degrees of freedom per atom.

(6) The reducible representation is then decomposed into a sum of irreducible representations. Mulliken and Bethe notation is used.

(7) Information on 1st and 2nd order invariances, divided up into those that are Infra-Red active and those that are Raman active.

(8) Other results depending on selection: effect of <u>individual atoms</u>, <u>symmetry-adapted vectors</u>.

Top Right-hand panel

This shows the results of the computation. At the top is shown a table with columns marked A, B, C and D.

A	Serial number for operator
B	Point symmetry symbol in International notation
C	General equivalent position
D	Reducible character under each symmetry operator

Below this is given the decomposition into a sum of irreducible representations .

Bottom Left-hand panel

Information on 1st and 2nd order invariants relevant to Infra-Red and Raman activity. Mulliken notation is used for the irreducible representation labels.

How to use VIBRATE!

Operation of the program is very simple. It is first necessary to input the crystal structure and once this is done the program automatically computes the rest.

Input of crystal structure

Input of crystal structure parameters is via the Crystallographic Information File or CIF. These days most crystal structure determination results in a CIF that can be downloaded from publishing sites. It is possible with VIBRATE! to create a CIF by supplying the relevant crystal structure parameters manually and saving as a CIF.

An example of a typical CIF is given below:

```
#### CIF created by Mike Glazer ####
data_BaTiO3 tetragonal


_audit_creation_method              'Crystallographica 2'
_cell_angle_alpha               90
_cell_angle_beta                90
_cell_angle_gamma                90
_cell_length_a              3.9972
_cell_length_b              3.9972
_cell_length_c              4.041
_cell_volume                64.5655
_cgraph_title               'BaTiO3 tetragonal'
_chemical_formula_sum            'Ba1 O3 Ti1'
_symmetry_space_group_name_H-M      'P 4 m m'
_symmetry_space_group_name_Hall      ' P 4 -2'

loop_
    _symmetry_equiv_pos_as_xyz
    'x, y, z'
    '-y, x, z'
    '-x, -y, z'
    'y, -x, z'
    '-x, y, z'
    'x, -y, z'
    '-y, -x, z'
    'y, x, z'

loop_
    _atom_site_label
    _atom_site_type_symbol
    _atom_site_fract_x
    _atom_site_fract_y
    _atom_site_fract_z
```

```
    _atom_site_U_iso_or_equiv
    _atom_site_thermal_displace_type
    _atom_site_occupancy
    Ba1 Ba2+ 0 0 0 0.0126651 Uiso 1
    O1 O2- 0.5 0.5 0 0.0126651 Uiso 1
    O2 O2- 0.5 0 0.5 0.0126651 Uiso 1
    Ti1 Ti4+ 0.5 0.5 0.518 0.0126651 Uiso 1

loop_
    _cgraph_atom_site_label
    _cgraph_atom_bond_type
    _cgraph_atom_bond_radius
    _cgraph_atom_display_radius
    _cgraph_atom_display_colour_red
    _cgraph_atom_display_colour_green
    _cgraph_atom_display_colour_blue
    'Ba1' custom 1.34 0.804 0 0 255
    'O1' custom 1.4 0.84 255 0 0
    'O2' custom 1.4 0.84 255 0 0
    'Ti1' custom 0.68 0.408 255 0 255

_eof

#### End of Crystallographic Information File ####
```

File

Open

Opens the current Crystallographic Information File (CIF) for editing using NotePad.

Read CIF

To read in a prepared CIF. As soon as it is read in VIBRATE! Automatically carries out the Factor Group Analysis of the normal modes. The CIF can also be read in by dragging and dropping the file directly onto the VIBRATE! Window.

Create CIF

Export a Crystallographic Information File (CIF).

⊟ Save RTF

To save the output in the left-hand panel to a rich-text file (rtf) which can be read in by standard word-processing programs such as WORD.

🖨 Print

To output the information in the left-hand panel to a printer.

Execute

TITLE

Add a title of your choice

❄ Space Group

A dialog box opens that allows you to select any space group (in International Notation) from a comprehensive list. Pressing the More… button gives further information about any particular space group, including the symmetry generators for the space group. Once selected, VIBRATE! Automatically applies this symmetry and carries out the Factor Group Analysis.

This dialog allows the symmetry of the crystal structure to be viewed or altered. The following methods are available:

Choose Space Group	Use the tree control to browse for a space group. All the cell choices, origin choices and axis choices contained in International Tables are listed.
Find Space Group	Type a symbol or number here and hit return or press the Go button. Symbols from International Tables Vol. 1 and Vol. A will be recognized, as well as numbers in the range 1 to 230 and Hall symbols.
More…	Press this button to display the Symmetry Properties dialog, described under its own heading. This may be used to customize the symmetry still further by adding or removing generators.

Pressing OK will close the dialog, saving the information indicated in the Selected Symmetry box to the active crystal. (This can also be achieved by double-clicking the required space group in the tree control.) Pressing Cancel closes the dialog, discarding any changes. The Apply button will update the active structure with the selected symmetry, but without closing the dialog.

Note that changing the symmetry of a crystal structure may have implications for the cell parameters.

Symmetry Properties

This dialog serves two purposes.

First, it displays detailed information on the current symmetry settings. This includes the properties listed in the Information section as well as a list of the general equivalent positions which define the symmetry. (In the General Equivalent Positions list, the selected generators are marked with a *G* symbol.)

The dialog may also be used to customize the current symmetry, either by adding to the existing generators, or else by clearing the list of generators using the Clear button and then adding new ones. To add a new generator, enter the appropriate string (for example "-x, -y, -z") add press the Add button.

Pressing OK will close the dialog, passing the changed symmetry on to the parent Symmetry dialog. Pressing Cancel closes the dialog, discarding any changes.
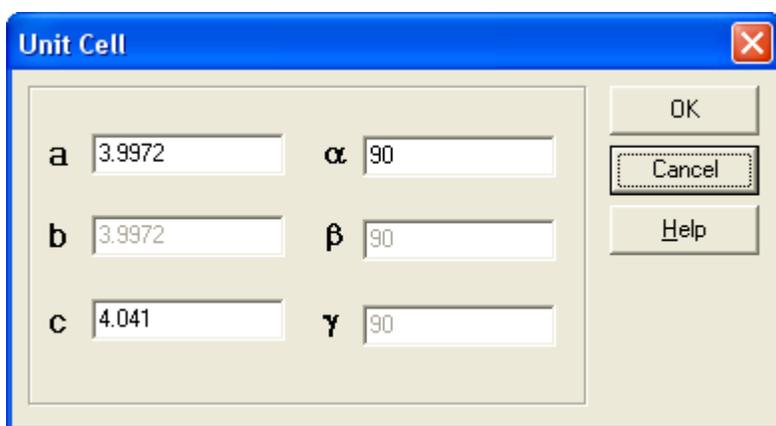
Cell

Here unit cell parameters can be entered. This has no effect on the Factor Group Analysis since this deals only with the symmetry in connection with the atomic positions. However, it is useful to give the correct unit cell parameters in order to form a CIF. Only free parameters according to the crystal system can be changed.

Atoms

This opens up a dialog box:
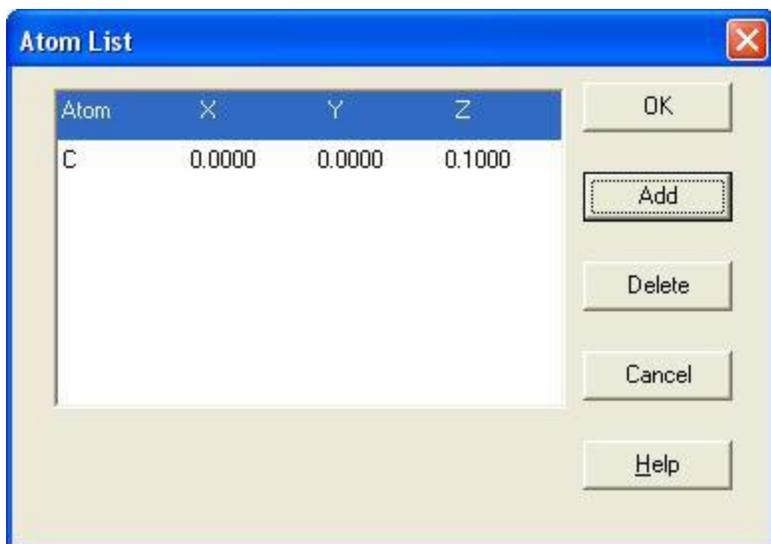
This lists the fractional coordinates of the atoms already entered. Pressing the Add button opens up another dialog box in which you can add new atoms.

Pressing OK takes you back to the previous dialog box and the list is updated. The delete button deletes a highlighted entry. Pressing OK then closes the dialog box.
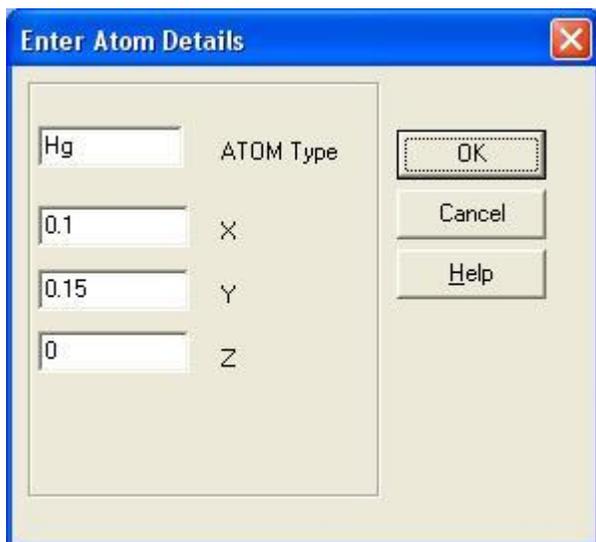
✕ Clear

Removes all atoms and sets space group to triclinic P1.

⬤ Individual Atoms

Run through the reduction process again but this time atom by atom so that one can check individual contributions to the set of irreducible representations.

## ⬇ Character Projection Operators

Calculate the character projection operators for each irreducible representation and each atomic coordinate. This enables the *symmetry-adapted vectors* for the modes of vibration to be found. Note that these vectors refer to crystallographic axes rather than Cartesian. As an example of the use of this, read in from the Examples menu (under Help) the perovskite

CIF. After activating the Character Projection Operator button, you will obtain for the T_{2u} (Γ_5^-) irreducible representation the following symmetry-adapted vectors:

$$O1\_1 \quad (y_1) \quad \text{---->} \quad +8y_1-8y_3$$

$$O1\_1 \quad (z_1) \quad \text{---->} \quad +8z_1-8z_2$$

$$O1\_2 \quad (x_2) \quad \text{---->} \quad +8x_2-8x_3$$

$$O1\_2 \quad (z_2) \quad \text{---->} \quad -8z_1+8z_2$$

$$O1\_3 \quad (x_3) \quad \text{---->} \quad -8x_2+8x_3$$

$$O1\_3 \quad (y_3) \quad \text{---->} \quad -8y_1+8y_3$$

We see from this that only the oxygen atoms are involved in motion corresponding to this irreducible representation. For example, the y movement of O1 is opposite to the y movement of O3 (first line), the z movement of O1 is opposite to the z movement of O2 (second line), and the x movement of O2 is opposite to the x movement of O3 (third line). One such solution is shown below plotted down the [111] direcrtion:
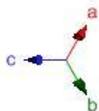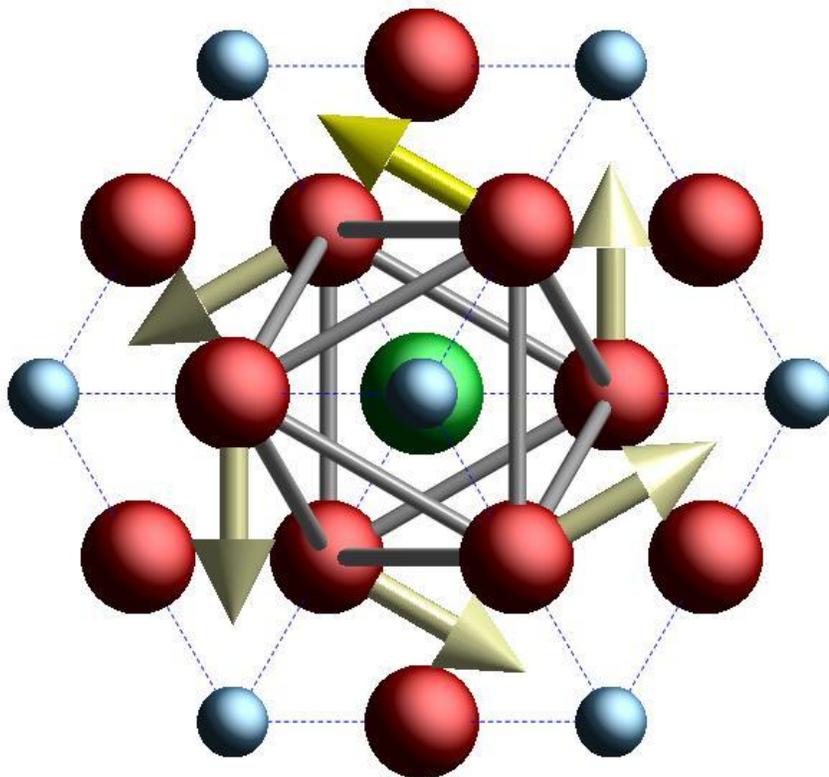
The red atoms are oxygen and this solution shows that a component of the triply-degenerate T_{2u} (Γ_5^-) mode is a rotation of the oxygen framework about the [111] direction. As this is a triply-degenerate mode, the same is occurring about the other <111> axes.

 VRML

This button automatically opens a dialog box from which a VRML plot of the structure can be obtained.
In order to use the VRML facility, it is first necessary to install a suitable VRML Viewer. I recommend the Cortona Viewer which can be downloaded from http://www.cortona3d.com/Products/Cortona-3D-Viewer.aspx. However there are many others available on the Internet that will do equally well. The VRML image will appear within your default browser. The button changes to a black butterfly when the viewer appears and this then close the viewer.
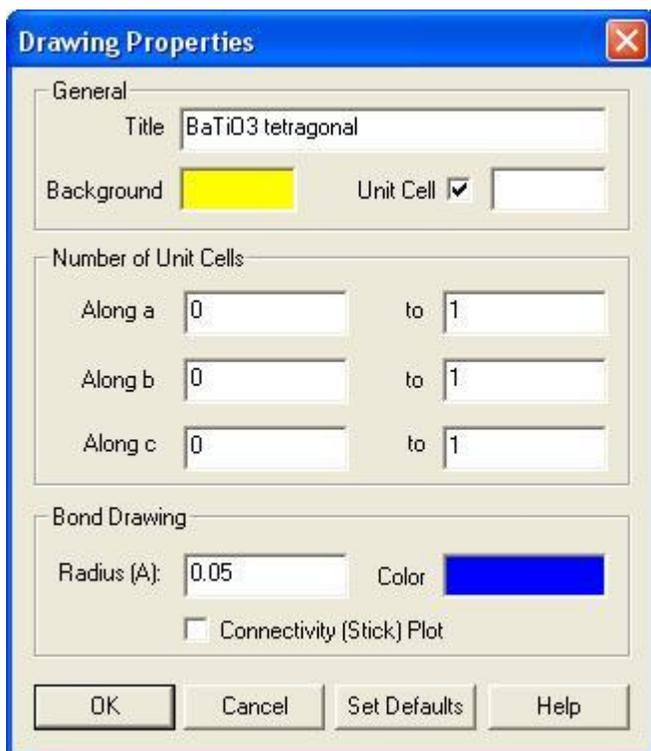
This dialog box controls the appearance of an individual VRML view. Each such view may have the following properties set independently.

Title	The title of the view
Background	Displays the background colour. Click the box to change the colour.
Draw Unit Cell	If this item is checked then the outline of the unit cell is drawn.
Unit Cell Colour	Click the box adjacent to the Draw Unit Cell checkbox to set the colour of the unit cell cylinders.
Number of Unit Cells	Specifies the extent of the drawing, measured along the a, b and c axes.

	Fractional and negative values are permitted.
Bond Radius	The drawing radius of the bond cylinders.
Connectivity (Stick) Plot	If this item is checked then the bonds are drawn as thin cylinders and the atoms omitted.
Colour	The colour of the bonds.

Pressing OK will close the dialog, passing the changed settings to the parent view. Pressing Cancel closes the dialog, discarding any changes. The Set Defaults button takes the dialog settings and writes them to the registry, where they are used as the initial setting for new views.

Plot Crystal Structure

This enables you to send the crystal data to a custom crystal plotting program. Locate the program (as an executable .exe file) using the dialog box: this only works if the crystal plotting program can accept a command line entry. A highly recommended program is CrystalMaker (http://www.crystalmaker.com/) or Vesta (http://www.geocities.jp/kmo_mma/crystal/en/vesta.html).

Magnetic/Polar Calculation

Toggle between calculating irreducible representations for normal vibrational modes and for magnetic modes for $\mathbf{k} = 0$.

Non-Zero k

This feature enables mode analysis to be carried out for special critical points in the Brillouin zone whose wave-vectors are not equal to zero. **This part of the program is limited to a maximum of 24 atoms**. A drawing of the Brillouin zone taken from the Bilbao Crystallographic Server may be shown as well as a selection of critical points. This window looks like this:
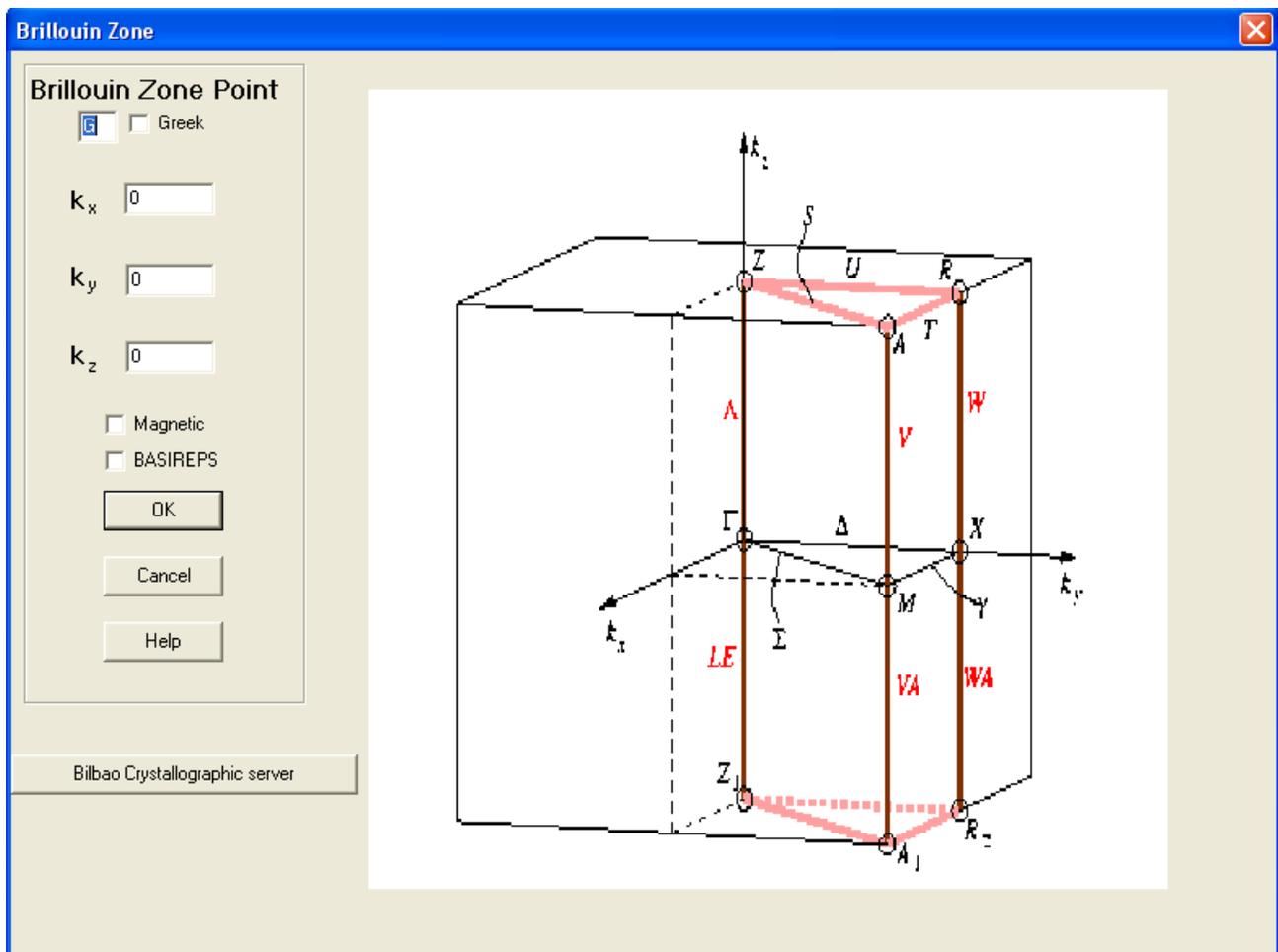
You can specify a symbol for the *critical point* of interest (must be a letter): the Greek checkbox converts it to a Greek letter in the output. In the example above we have set the X point to be $k_x = 0$ $k_y = 0$ $k_z = 0.5$.

The calculation of representations etc uses the computer program BASIREPS written by Juan Rodríguez-Carvajal and implemented in the FULLPROF suite of programs (so you can blame him if it is wrong!). The output first of all lists the relevant character table for the little group for this critical point: both real and imaginary characters are listed.

If the BASIREPS box is checked the full output of the BASIREPS program will be added.

If the Magnetic box is checked the calculation will be made for magnetic representations.

Clicking on the button marked Bilbao Crystallographic Server will open the browser at the KVEC page of the Bilbao Crystallographic Server.

Symmetry Operators and Character Table for Little Group G(k): Real Characters

		X1	X2	X3	X4	X5	X6	X7	X8	X9	X10
1	x,y,z	1	1	1	1	1	1	1	1	2	2
2 (0, 0, z)	-x,-y,z	1	1	1	1	1	1	1	1	-2	-2
2 (x, 0, 0)	x,-y,-z	1	1	1	1	-1	-1	-1	-1	0	0
2 (0, y, 0)	-x,y,-z	1	1	1	1	-1	-1	-1	-1	0	0
2 (x, -x, 0)	-y,-x,-z	1	1	-1	-1	1	1	-1	-1	0	0
2 (x, x, 0)	y,x,-z	1	1	-1	-1	1	1	-1	-1	0	0
4 - (0, 0, z)	y,-x,z	1	1	-1	-1	-1	-1	1	1	0	0
4+ (0, 0, z)	-y,x,z	1	1	-1	-1	-1	-1	1	1	0	0
-1	-x,-y,-z	1	-1	1	-1	1	-1	1	-1	-2	2
m (x, y, 0)	x,y,-z	1	-1	1	-1	1	-1	1	-1	2	-2
m (0, y, z)	-x,y,z	1	-1	1	-1	-1	1	-1	1	0	0
m (x, 0, z)	x,-y,z	1	-1	1	-1	-1	1	-1	1	0	0
m (x, x, z)	y,x,z	1	-1	-1	1	1	-1	-1	1	0	0
m (x, -x, z)	-y,-x,z	1	-1	-1	1	1	-1	-1	1	0	0
-4 - (0, 0, z)	-y,x,-z	1	-1	-1	1	-1	1	1	-1	0	0
-4+ (0, 0, z)	y,-x,-z	1	-1	-1	1	-1	1	1	-1	0	0

In order to get these onto the page I have adopted a different convention from the usual way to present this information by listing the irreducible representations along the top and the symmetry operators (blue) down the page. In the latter case, in addition to the symmetry operators, their positions in the unit cell are given in parentheses. The red boxes list the general positions for each symmetry operation.

Finally the sum of irreducible representations for each atom type are given.

Note: There are many different notations used for points in the Brillouin zone (**it is an utter disgraceful mess and is high time some international body standardized the notation).**

Help

Help Vibrate

This help file

Help Symmetry

Help file explaining use of space group routine.

Examples

A list of example CIF's that can be read in.

Molecular Analysis

While VIBRATE! is designed to work with crystal structures, it can with judicious choice of structure also work with individual molecules. The trick is to embed a molecule into a relevant space group so that it is the only set of atoms in the unit cell. For instance, consider the case of the water molecule. Its point symmetry is mm2 in the International Notation. So we choose the space group Pmm2 and add into it the three atoms, O and two H atoms like this:

H1	0.0000	0.7000	0.2000
H2	0.0000	0.3000	0.2000
O	0.0000	0.5000	0.7000

This gives the following structure.
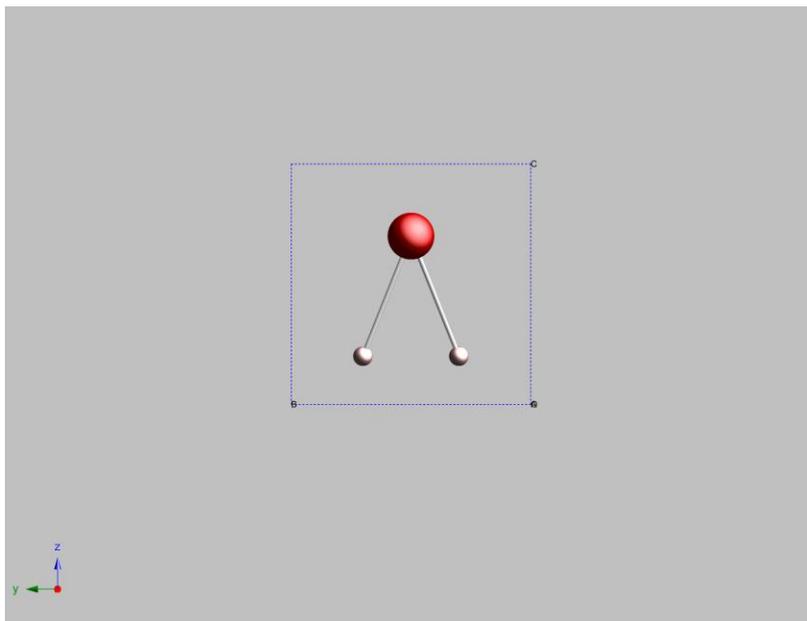
Save this into a CIF and VIBRATE will find the sum of irreducible representations thus

VIBRATE!

Water molecule
Hall Symbol: P 2 -2
Space Group: P m m 2 (C_{2v}^1)
Space Group Number: 25
a = 5
b = 5
c = 5
α = 90
β = 90
γ = 90
Crystal System: Orthorhombic
Setting: Standard
Point Group: mm2 (C_{2v})

Atomic Coordinates
H	1	0.000000	0.700000	0.200000
H	2	0.000000	0.300000	0.200000
O	3	0.000000	0.500000	0.700000

Lattice Centring Operators
1: 0.0000000   0.0000000   0.0000000

A	B	C	D
1	1	x,y,z + (0 , 0 , 0)	9
2	2	-x,-y,z + (0 , 0 , 0)	-1
3	m	x,-y,z + (0 , 0 , 0)	1
4	m	-x,y,z + (0 , 0 , 0)	3

IR Active - Acoustic Modes (translations)
A_1 z
B_1 x
B_2 y
Rotations
A_2 R_z
B_1 R_y
B_2 R_x
Raman Active
A_1 x^2, y^2, z^2

Γ_{red} = 3A_1 +A_2 +2B_1 +3B_2

A : Serial Number
B: Point symmetry symbol
C: Point symmetry operator
D: Reducible character