PyVib2 Version 1.0 Manual*

A Program for Analyzing Vibrational Motion and Vibrational Spectra

Maxim Fedorovsky

Department of Chemistry
University of Fribourg, ch. du Musée 9
Fribourg 1700, Switzerland

---

*. This document has been written using the GNU TEXMACS text editor (see `www.texmacs.org`).

Table of contents

1 Introduction

This is a documentation for the PyVib2 program, a program for analyzing vibrational motion and vibrational spectra, version 1.0, February 2007. The program is released under the terms of the GNU General Public License (GNU GPL). For downloading, please visit http://sourceforge.net/projects/pyvib2. Supplementary material will be soon available on http://voa.net.

The main idea of the program was to create a simple and efficient tool for the automatic correlation of vibrational motions of molecules, exploring their Raman, Raman optical activity (ROA), infrared (IR), and vibrational circular dichroism (VCD) spectra. PyVib2 is supposed to be an open source "all-in-one" solution available to the international community of scientists, working in the field of vibrational and vibrational Raman optical activity (VROA) spectroscopy.

2 Features of PyVib2 1.0

- Extraction of the VROA data from results of calculations with the DALTON [1] and Gaussian [2] quantum chemistry packages.

- Intuitive graphical user interface (GUI) which allows to handle several molecules simultaneously.
- Comprehensive range of supported output formats.
- The program is designed as a class library, which can be used independently of the GUI.
- Versatile representation of vibrational motion :
  a) cartesian excursions and vibrational energy distribution represented as shaded spheres;
  b) usual arrow representation;
  c) animation with the possibility to save in the animated GIF or Autodesk Animator FLI formats;
- Automatic correlation of the normal modes of molecules with the possibility of removing translational and rotational contaminations.
- Visualization techniques for vibrational intensities :
  a) Nuclear and Group Couling matrices (NCMs and GCMs) for the individual Raman/ROA invariants or the differential cross-sections;
  b) Atomic and Group Contribution Patterns (ACPs and GCPs);
  c) Publication quality Raman/ROA/Degree of circularity as well as infrared vibrational absorption/VCD spectra in the stick and curve representations.

3 Installation Guide

The program is implemented in pure Python. Make sure that you have Python 2.3 or later (http://python.org). Once the Python environment is operational, one has to install packages on which PyVib2 depends :

- **Python megawidgets** (Pmw), refer to http://pmw.sourceforge.net/.
  A library for a flexible GUI building, based on Tkinter (Python's de-facto standard GUI package).
- **NumPy**, refer to http://numpy.scipy.org/.
  The fundamental package for scientific computing.
- **VTK** (Visualization ToolKit), refer to http://vtk.org/.
  A high-level 3D rendering library.
- **Matplotlib**, refer to http://matplotlib.sourceforge.net/.
  A 2D plotting library for producing publication quality figures.

Do not forget that the administrator privileges are required in order to succeed the installation. The user of a Debian-based Linux distribution can profit from the **apt-get** utility, since all the required packages are already in the Debian repository. To install e.g. **Matplotlib**, execute

```
$ apt-get update && apt-get install python-matplotlib
```

The PyVib2 program itself can be installed on your system using the standard Distribution Utilities for Python (distutils) :

- Download the program archive **pyvib2-1.0.tar.gz** from http://sourceforge.net/projects/pyvib2.

- Unpack it e.g. by executing in the command prompt :

  ```
  $ tar xvfz pyvib2-1.0.tar.gz
  ```

- Change to the installation directory, created in the previous step :

  ```
  $ cd pyvib2-1.0
  ```

- Execute the setup.py script as follows :

  ```
  $ python setup.py install
  ```

After that, the **pyvib2** script, which starts the program, should be accessible from the command prompt. It is usually placed by distutils in */usr/bin* under Linux and in *%pythonroot%\Scripts* under Windows (*%pythonroot%* is a directory where Python is installed).

To produce PDF files **ps2pdf** must be installed. If the user desires to create animations of vibrations in the animated GIF or Autodesk Animator FLI formats, the installation of additional utilities is needed. For the former choice, install the **Netpbm** http://netpbm.sourceforget.net and the **gifsicle** http://www.lcdf.org/gifsicle/ packages. For the latter choice, install **ppm2fli** http://vento.pi.tu-berlin.de/ppm2fli/main.html. As these utilities are primarily designed for Linux/Unix, Windows users might want to install **Cygwin** http://www.cygwin.com/ in order to be able to use them.

4 User's Guide

4.1 Input files

PyVib2 can directly extract all the required data from outputs of VROA calculations conducted with DALTON 1.x or 2.0 [1]. The program can also get the data from Gaussian98 and Gaussian03 [2] via formatted checkpoint (FCHK) files, which can be created with the formchk utility program available in the Gaussian package. VOAView [3] files can likewise be handled. A partial support for MOLDEN [4] files is provided, from which only the normal modes can be extracted. XMol XYZ [5] files can be opened for viewing the structure.

4.2 Preparing input files

It is briefly described in this subsection how to request a ROA and a VCD calculation with DALTON 1.x or 2.0 and Gaussian 03. The results of such calculations can be directly opened with PyVib2. It is assumed here, that the user has already an optimized geometry of a molecule of interest. As an example, let us consider methyloxirane.

4.2.1 DALTON

Earlier versions of DALTON required several files as input. The input specification has been changed in DALTON 2.0, but the old format is still supported for the backward compatibility. The user is instructed bellow on how to perform a calculation with DALTON 2.0 using input files produced for the older version. Discussing all the details is far out of the scope of this manual, for explanation refer to the documentation http://www.kjemi.uio.no/software/dalton/dalton.html.

The so called molecule specification file has to contain the geometry of a molecule and a basis set for a calculation. Save the following input as meox_TDHF_aug-cc-pVDZ.mol (coordinates are given in atomic units i.e. bohrs):

```
BASIS
aug-cc-pVDZ
IR/VCD or Raman/ROA for methyloxirane @ TDHF/aug-cc-pVDZ.

   3 0 0
      8.    1
O001     1.5654116200    -1.4893215100    -0.4579504440
      6.    3
C002     1.9701227300     1.1644266000    -0.1106471260
C003    -0.2917697530    -0.0707325890     0.9160939940
C004    -2.8519480600     0.1876438060    -0.2808812160
      1.    6
H005     3.5401090600     1.6542116000     1.1409732900
H006     1.8079463500     2.3036101900    -1.8285083400
H007    -0.2907700570    -0.4889270930     2.9449531000
H008    -2.6780158100     0.6093702210    -2.3041524100
H009    -3.9227199200     1.7180365500     0.6308719600
H010    -3.9382721200    -1.5697562300    -0.0679279775
```

In the so called DALTON input file, the user has to specify the type of the calculation. To request a VCD calculation at the TDHF/aug–cc-pVDZ level of theory, save the following input as `prop_vcd.dal` :

```
**DALTON INPUT
.RUN PROPERTIES
.PRINT 1
**WAVE FUNCTIONS
.HF
*ORBITAL INPUT
.AO DELETE
1.0D-07
**PROPERTIES
.VCD
.VIBANA
*VIBANA
.HESFIL
**END OF INPUT
```

Do *not* request a verbose output with `.PRINT >= 2`. The `.HESFIL` keyword specifies, that the hessian in the hes format is passed to DALTON. Rename the hessian file to `DALTON.HES` (case-sensitive) and make a gzipped tarball from it (the name is arbitrary) :

```
$ tar cvfz hes.tar.gz DALTON.HES
```

One can generate automatically both molecule input and hessian file from a Gaussian formatted checkpoint file (`*.fchk`) with the `FCHKtoHES` utility distributed with DALTON. The following command creates `test.mol` and `test.hes` files from `test.fchk` (passed *without* extension):

```
$ FCHKtoHES test
```

The VCD calculation can be started as follows :

```
$ dalton -o meox_TDHF_aug-cc-pVDZ_vcd.out -f hes prop_vcd meox_TDHF_aug-cc-pVDZ
```

Note, that *all* the input files are passed *without* extensions ! After the calculation has been successfully finished, the meox_TDHF_aug-cc-pVDZ.out output file can be opened with PyVib2.

To request a ROA calculation, the user can use the following DALTON input file :

```
**DALTON INPUT
.RUN PROPERTIES
.WALK
.MAX IT
   200
.PRINT
   1
*WALK
.NUMERI
.DISPLACEMENT
   0.001
**WAVE FUNCTIONS
.HF
*ORBITAL INPUT
.AO DELETE
   1.0D-07
**START
.VROA
*ABALNR
.THRESH
   1.0D-08
.FREQUE
   1
   0.08564539532
**EACH STEP
.VROA
*ABALNR
.THRESH 1.0D-08
.FREQUE
   1
   0.08564539532
**PROPERTIES
.VROA
.RAMAN
.VIBANA
*RESPON
.THRESH
   1.0D-06
*ABALNR
.THRESH
   1.0D-08
.FREQUE
   1
```

```
    0.08564539532
*VIBANA
.HESFIL
**END OF DALTON INPUT
```

Wavelength of the incident light is set to be 532 nm.

4.2.2 Gaussian

To request a VCD calculation at the B3PW91/aug-cc-pVDZ level of theory, save the following input as meox_B3PW91_aug-cc-pVDZ_vcd.in :

```
%chk=meox_B3PW91_aug–cc-pVDZ_vcd.chk
# B3PW91/aug–cc-pVDZ FREQ=VCD

IR/VCD for methyloxirane @ B3PW91/aug-cc-pVDZ.

0 1
8   0.828380  -0.788115  -0.242337
6   1.042544   0.616188  -0.058552
6  -0.154398  -0.037430   0.484776
6  -1.509186   0.099297  -0.148636
1   1.873345   0.875371   0.603777
1   0.956724   1.219018  -0.967605
1  -0.153869  -0.258729   1.558402
1  -1.417145   0.322465  -1.219305
1  -2.075814   0.909146   0.333843
1  -2.084044  -0.830679  -0.035946
```

Start the calculation (the environment variables for Gaussian should be set up properly) :

```
$ g03 < meox_B3PW91_aug-cc-pVDZ_vcd.in > meox_B3PW91_aug-cc-pVDZ_vcd.out
```

After the calculation has **successfully** finished, produce a formatted checkpoint file :

```
$ formchk meox_B3PW91_aug-cc-pVDZ_vcd.chk meox_B3PW91_aug-cc-pVDZ_vcd.fchk
```

The meox_B3PW91_aug–cc-pVDZ_vcd.fchk file is now ready to be opened with PyVib2. To request a ROA calculation, use the following input file :

```
%chk=meox_B3PW91_aug–cc-pVDZ_roa.chk
# B3PW91/aug–cc-pVDZ FREQ=ROA CPHF=RDFREQ

Raman/ROA for methyloxirane @ B3PW91/aug-cc-pVDZ.
Wavelength of the incident light is 532 nm.

0 1
8   0.828380  -0.788115  -0.242337
6   1.042544   0.616188  -0.058552
6  -0.154398  -0.037430   0.484776
6  -1.509186   0.099297  -0.148636
1   1.873345   0.875371   0.603777
1   0.956724   1.219018  -0.967605
```

```
1   -0.153869   -0.258729    1.558402
1   -1.417145    0.322465   -1.219305
1   -2.075814    0.909146    0.333843
1   -2.084044   -0.830679   -0.035946

532nm
```

Note, that Gaussian calculates also VCD if the user requests a ROA task ! For details refer to http://gaussian.com.

4.3 Overview : what can be done with PyVib2

The following diagram summarizes what can be done with PyVib2 :

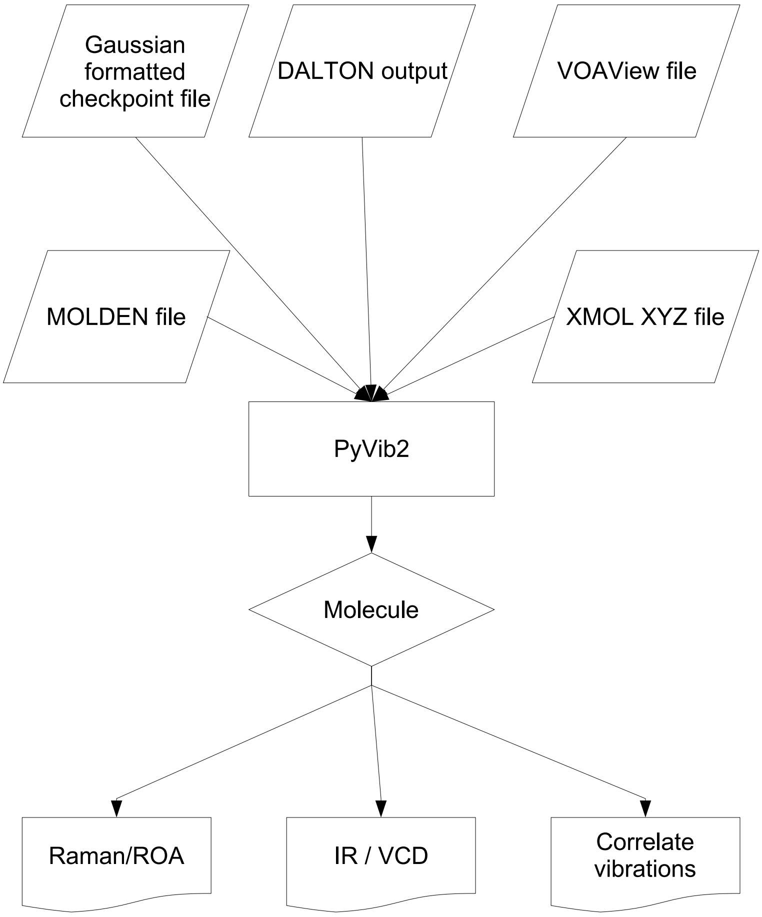


Figure 1. What can be done with PyVib2.

4.4 Quick Start Guide

To show the base possibilities of PyVib2, let us analyze the results of the ROA calculation on methyloxirane with Gaussian as described in section 4.2.2. The final meox_B3PW91_aug–cc-pVDZ_roa.fchk file can be downloaded from http://pyvib2.sourceforge.net/material.shtml or produced from the input. This file contains all the required data such as the geometry, hessian, Raman/ROA as well as IR/VCD tensors. In order to follow the instructions given bellow, start the program by executing pyvib2 script in the command prompt.

4.4.1 Opening a file

Once the main window of PyVib2 appears, use the **File|Open...** menu to open a file. Locate meox_B3PW91_aug–cc-pVDZ_roa.fchk and press the Ok button. Since the hessian is present in this file, it is possible to perform the vibrational analysis for an arbitrary isotopic composition of the molecule. The program enables the user to do it in a dialog (for details see section 4.6.4), which is popped up after the file has been opened. Press the Ok button to use the default isotopic composition. After that, a thumbnail of the opened molecule should appear in the main window as shown on the following figure :

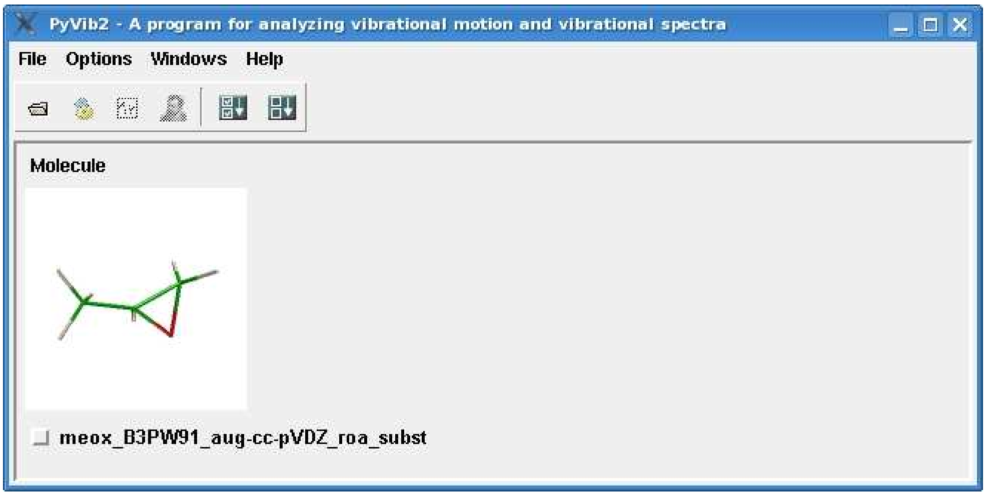


Figure 2. Main window of PyVib2 with opened methyloxirane.

Note, that other formats currently supported by PyVib2 (see section 4.1) do *not* contain the hessian and so the user will see opened files immediately after specifying their location (provided that the data were considered to be valid).

4.4.2 Summary of the available data

After a file has been successfully opened, the program examines which data are actually available in that file. The **Molecule** menu, located at the top of each thumbnail, shows the visualization options. The content of the menu for our test example is given on the following figure :

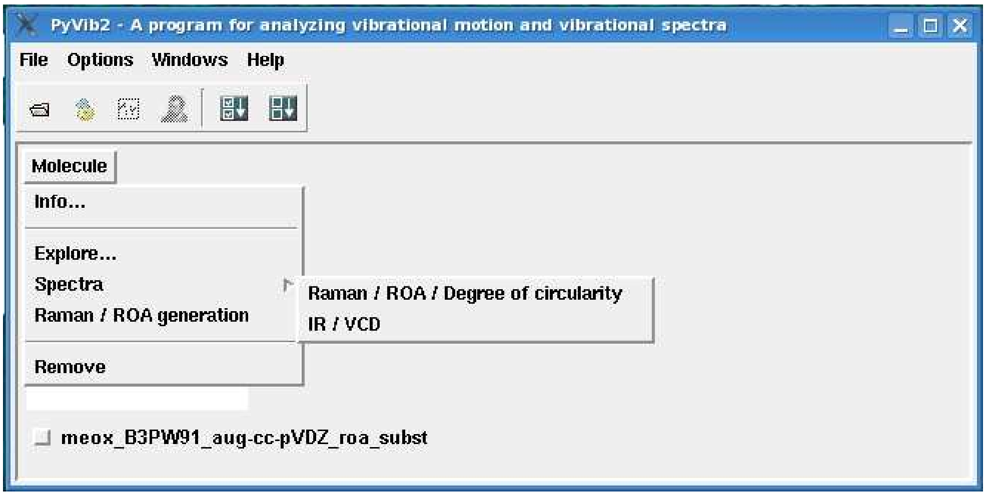
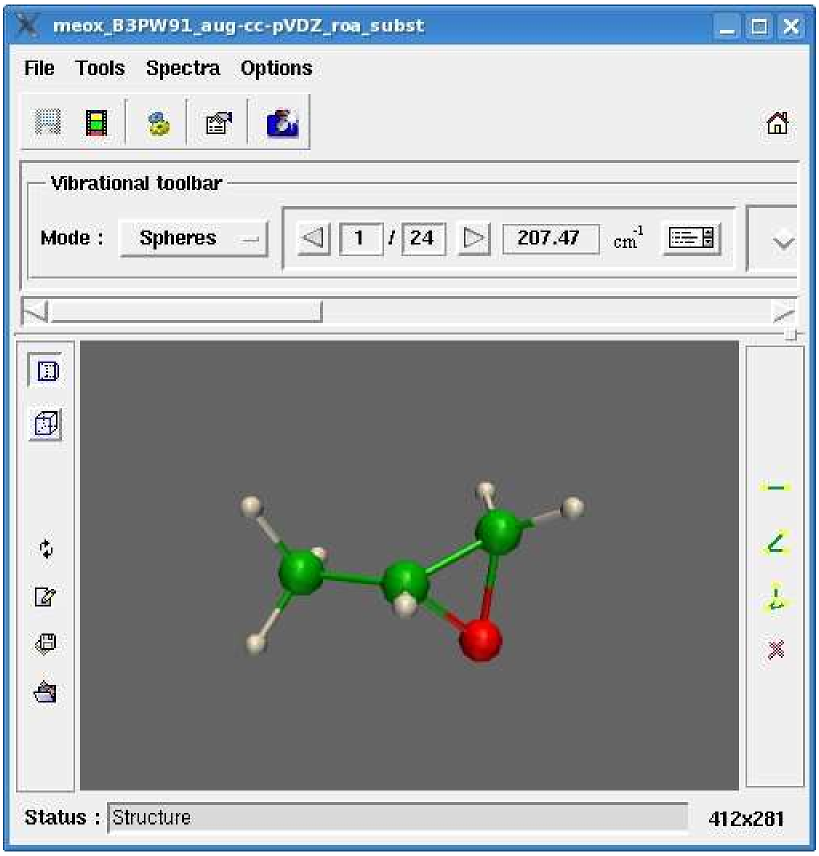


Figure 3. Molecule menu for methyloxirane.

For further details, refer to section 4.6.3.1.

4.4.3 Exploring structure and vibrational motion

The user can explore the structure of the molecule and its vibrational motion (if the normal modes are available) by choosing **Explore...** menu item. The following window should appear for our test example :



Status : Structure

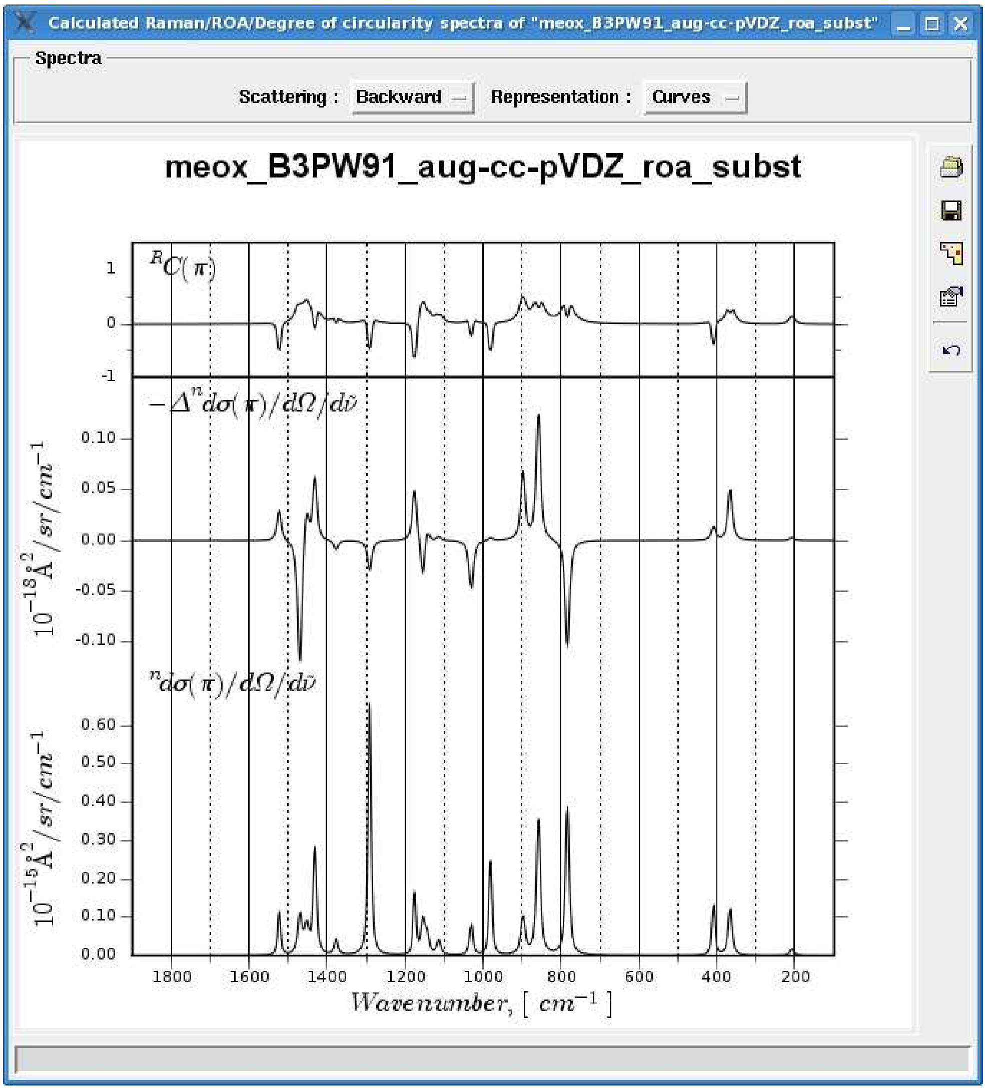
412x281

Figure 4. Window for exploring structure and vibrational motion of methyloxirane.

The visualization options are discussed in detail in section 4.7. For theoretical explanation of the representation of vibrational motion refer to sections 5.1 and 5.2.

4.4.4 Plotting spectra

If the **Spectra** submenu of the **Molecule** menu is present, the user can plot the Raman/ROA and/or IR/VCD spectra by choosing correspondent menu item. The Raman/ROA spectra for our test example are shown on the following figure :



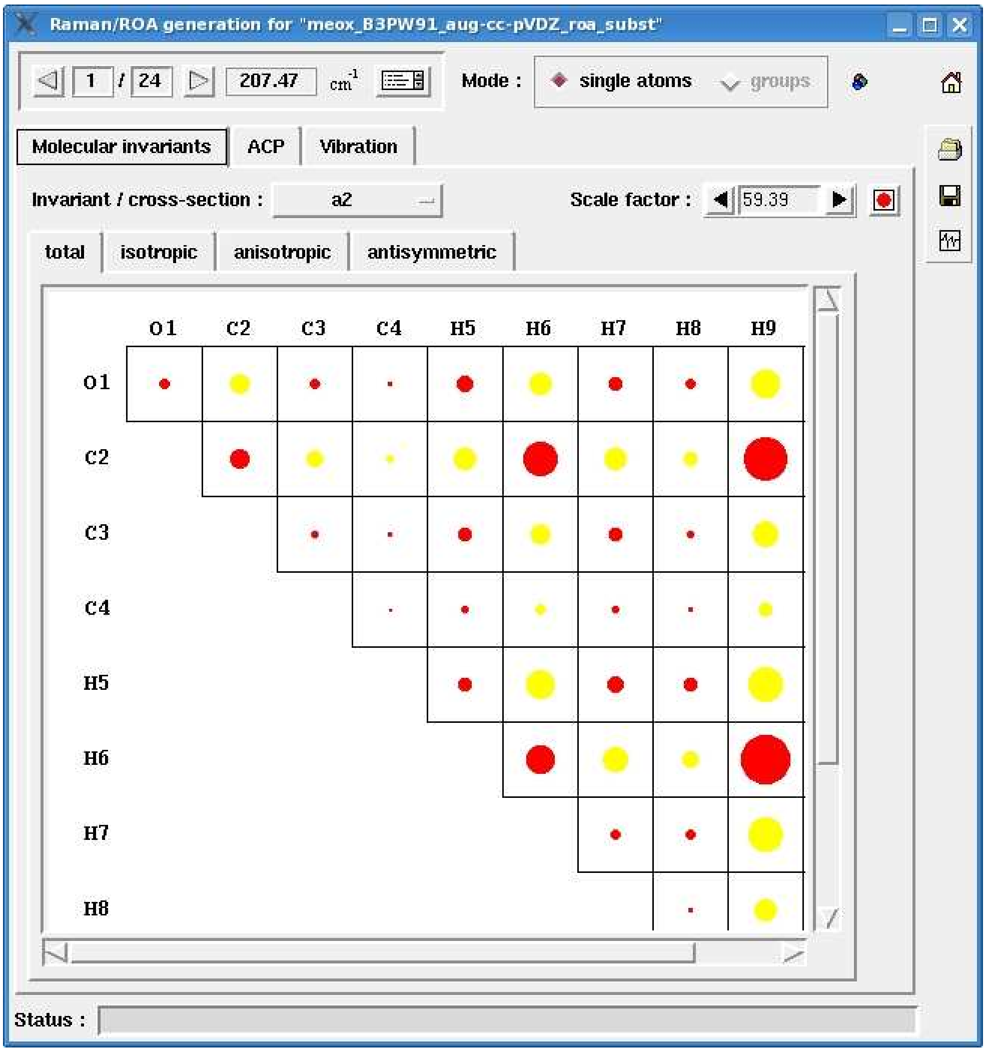
Scattering : Backward
Representation : Curves

Figure 5. Raman/ROA spectra of methyloxirane.

The visualization options for the spectra are discussed in detail in sections 4.11.1 and 4.11.7. For theoretical explanation refer to section 5.5.

4.4.5 Raman / ROA generation

This menu item is present if the Raman/ROA data are available for the molecule. The user is offered to use the visualization techniques for Raman/ROA intensities such as e.g. group coupling matrices (GCMs) and atomic contribution patterns (ACPs). For our test example the following window should appear :



Raman/ROA generation for "meox_B3PW91_aug-cc-pVDZ_roa_subst"

1 / 24 207.47 cm^{-1}

Mode : ◆ single atoms ◇ groups

Invariant / cross-section : a2

Scale factor : 59.39

Status :

Figure 6. Raman/ROA generation interface for methyloxirane.

The visualization options are discussed in detail in section 4.9. For theoretical explanation refer to sections 5.3 and 5.4. Examples of successful application of the above mentioned visulization techniques can be found in [6] [7] [8].

4.5 Starting PyVib2

The program can be started from the command prompt with an optional list of files to be opened at startup :

```
$ pyvib2 [file1 file2 ...]
```

Another alternative to launch the program would be to create a link on the user desktop.

4.5.1 Troubleshooting

If the program does not start, check first whether all of the dependencies were properly installed. This can be done by executing following import statements in a Python shell :

```
>>> import Pmw
>>> import numpy
>>> import vtk
>>> import matplotlib
```

Sometimes distutils does not set the rights to read for some files needed by the program e.g. pse.dat during the installation under Linux. If it is the case, the following import statement should raise an exception :

```
>>> import pyviblib.util.pse
```

To correct this problem :

1. Find the site-specific directory prefix of Python :

   ```
   $ python -c ’import sys; print sys.prefix’
   ```

2. Find the number of the major version of Python :

   ```
   $ python -c ’import sys; print sys.version[:3]’
   ```

3. The installation directory of pyviblib is **prefix**/lib/python**version**/site-packages/pyviblib, where the strings written in bold are results of the previous two commands. Go to that directory (suppose that you have Python 2.4 with the /usr prefix) and change the read rights as follows (under root) :

   ```
   # cd /usr/lib/python2.4/site-packages/pyviblib
   # chmod a+r util/*.dat
   # chmod a+r doc/*
   ```

If none of these remedies works, please report the problem on the web site of PyVib2.

4.6 Main window

Upon a successful start, the main window will appear (here the program was invoked without any arguments) :

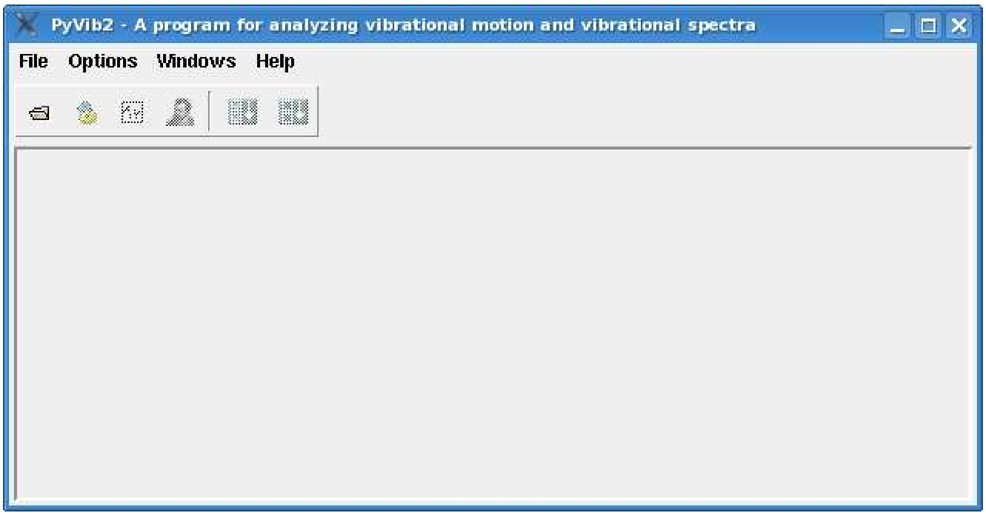


Figure 7. The main window of PyVib2.

The main window consists of a menu bar at the bottom, a button toolbar beneath the menu bar and a scrollable thumbnails pane. The latter lists opened molecules and should provide the user with a quick overview and offer further options.

4.6.1 Menu bar

File

- **Open...**

  Open one or multiple files. The standard File Open dialog will be popped up.

- **Recent files**

  This submenu contains at most 13 recently opened files (their base names are shown).

- **Close all**

  Close all the opened thumbnails, windows, spectra etc.

- **Exit**

  Exit from PyVib2. The configuration file .pyvib2rc will be saved in the user home directory. See section 4.13.3.

Options

- **Configure PyVib2...**

  Configure the program settings, see section 4.6.5.

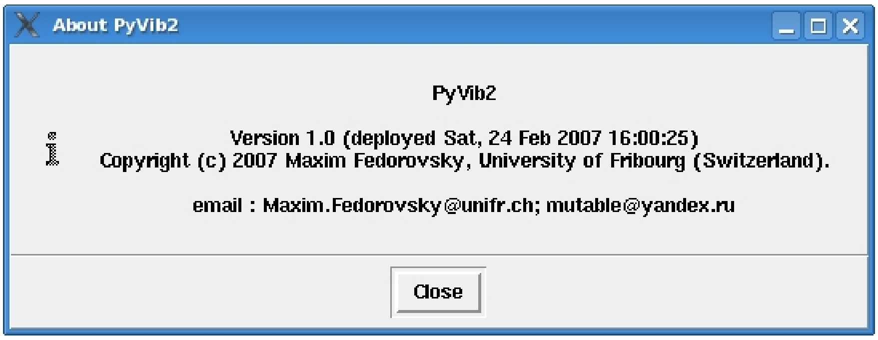
Windows

In this menu all opened windows, spectra etc are listed. Selecting an item will activate the correspondent window. Note : this feature does not work properly under present versions of KDE.

Help

- **About...**

  Show the informations about PyVib2 :



About PyVib2

PyVib2

Version 1.0 (deployed Sat, 24 Feb 2007 16:00:25)
Copyright (c) 2007 Maxim Fedorovsky, University of Fribourg (Switzerland).

email : Maxim.Fedorovsky@unifr.ch; mutable@yandex.ru

Figure 8. About PyVib2 dialog.

- **pyviblib Class Library Reference**

Browse the documentation for pyviblib, generated automatically with pydoc from the source code.

If one opens a FCHK file, which contains the hessian, then the program will offer to specify isotopes for the atoms. See section 4.6.4.

4.6.2 Button toolbar

Button	Explanation
📂	Open one or multiple files. The same as the menu **File|Open...**
⚙	Correlate vibrations.
📈	Plot spectra.
👤	Plot spectra of a mixture.
☑	Check all thumbnails.
☐	Uncheck all thumbnails.

The behaviour of some of these buttons depends on the state of the thumbnails' check boxes. The **Plot spectra** and **Correlate vibrations** buttons appear disables unless at least one thumbnail with the appropriate data is checked.

Should the user check several thumbnails with the Raman/ROA data, then their spectra will be plotted in the same frame. If only one thumbnail is checked, the spectra for that single molecule appear. See section 4.11.

The behaviour of the **Correlate vibrations** button is slightly different. Checking several thumbnails will constrain the set of molecules, the vibrational motion of which is to be correlated, to the chosen ones, provided that the normal modes are available for them. In contrast, checking only one thumbnail implies the correlation for all molecules. See section 4.8.

4.6.3 Thumbnails pane

For each opened file, a thumbnail appears in the thumbnails pane. The main window with the pseudo-axial and -equatorial conformers of (R)-1-methylindane [9] opened is shown on figure 9.

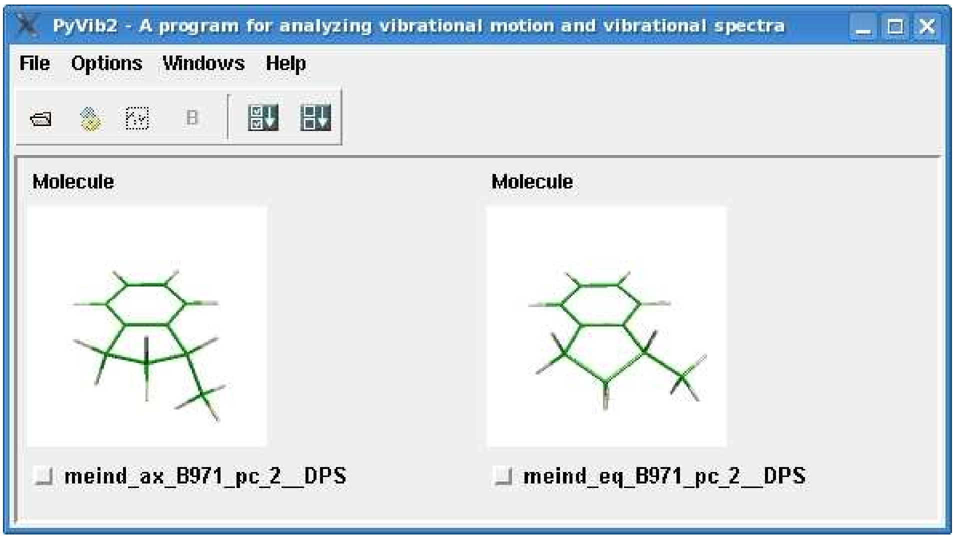


Figure 9. Main window with two thumbnails.

Each thumbnail consists of the menu “Molecule” at the top, a small 3D window (render widget) with the molecule at the middle and a check box with the name of the molecule at the bottom.

Menu Molecule

The contents of this menu depends on the type of the opened file and data stored in it. Figure 10 shows an example for a DALTON job output, from which the Raman/ROA data were successfully extracted.

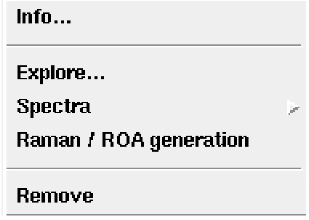
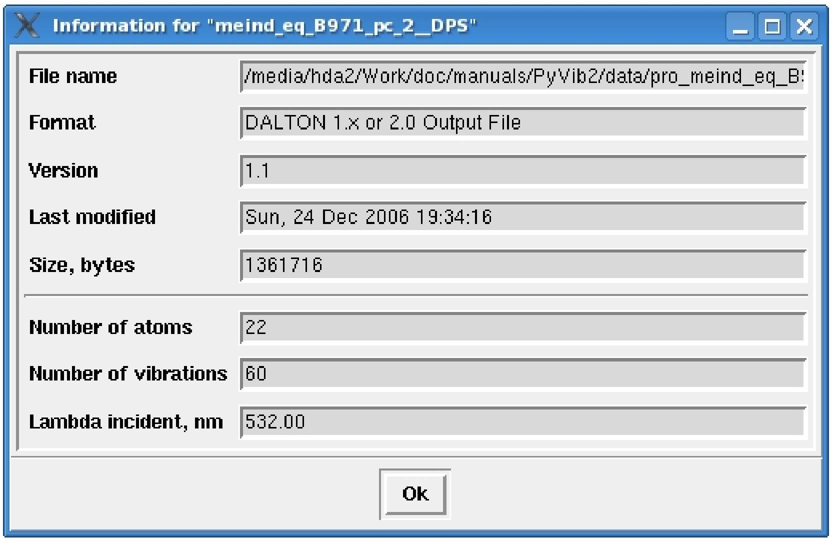


Figure 10. Example of the Molecule menu.

The menu items are as follows :

- **Info...**

  Information about the opened file, see figure 11. Available for all types of files.



Information for "meind_eq_B971_pc_2_DPS"

File name	/media/hda2/Work/doc/manuals/PyVib2/data/pro_meind_eq_B
Format	DALTON 1.x or 2.0 Output File
Version	1.1
Last modified	Sun, 24 Dec 2006 19:34:16
Size, bytes	1361716
Number of atoms	22
Number of vibrations	60
Lambda incident, nm	532.00

Figure 11. Information about the opened pseudo-equatorial conformer of (R)-methylindane.

- **Explore...**

  Explore the molecule in a separate window. See section 4.7. Available for all types of files.

- **Spectra**

This submenu appears only if the Raman/ROA or IR/VCD data are available and so its items are :

→ **Raman / ROA / Degree of circularity**

See section 4.11.1.

→ **IR / VCD**

See section 4.11.7.

- **Raman / ROA generation**

  Start the **Raman/ROA generation** interface. Appears if the Raman/ROA data are available. See section 4.9.

- **Remove**

  Remove the thumbnail from the pane. Available for all types of files.

3D render widget

The molecule in the stick representation will be rendered in this widget. The size of the window is constrained to be 150x150 pixel. Regardless of this fact, this is a full-featured 3D window where the user can navigate. See section 4.7.3.

Check box

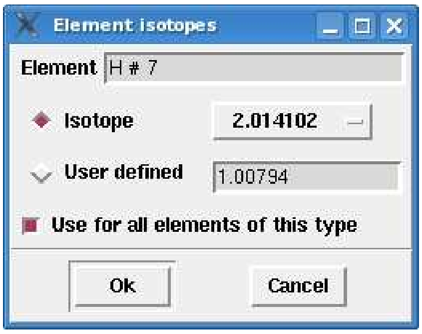
The check box bellow the 3D render widget is labeled with the name of the molecule, which is derived from its file name. The user can change the status of the check box and so affect the further visualization options. See section 4.6.2.

4.6.4 Isotopic composition dialog

The dialog is invoked automatically by the program if one opens a Gaussin formatted checkpoint file, which contains the hessian (it cannot be extracted from DALTON outputs). It allows to specify isotopes for the atoms. The GUI of the dialog consists of an information panel at the top, a molecule panel and a panel listing affected atoms. Should the default isotopic composition be used, press the **Ok** button.

Molecule panel

The user can specify a new name for the molecule at the top of the molecule panel to reflect the fact of an isotopic substitution. A 3D render widget shows the actual changes being made by the user. Picking an atom in the render widget causes the following dialog to pop up :



Element isotopes

Element: H # 7

● Isotope: 2.014102

○ User defined: 1.00794

☑ Use for all elements of this type

Figure 12. Element isotopes dialog.

This dialog has the following GUI components :

- **Element** read-only entry field

  Shows the information about the element being clicked.

- **Isotope** option menu

  Allows to choose a certain isotope from a list of the known isotopes for the element.

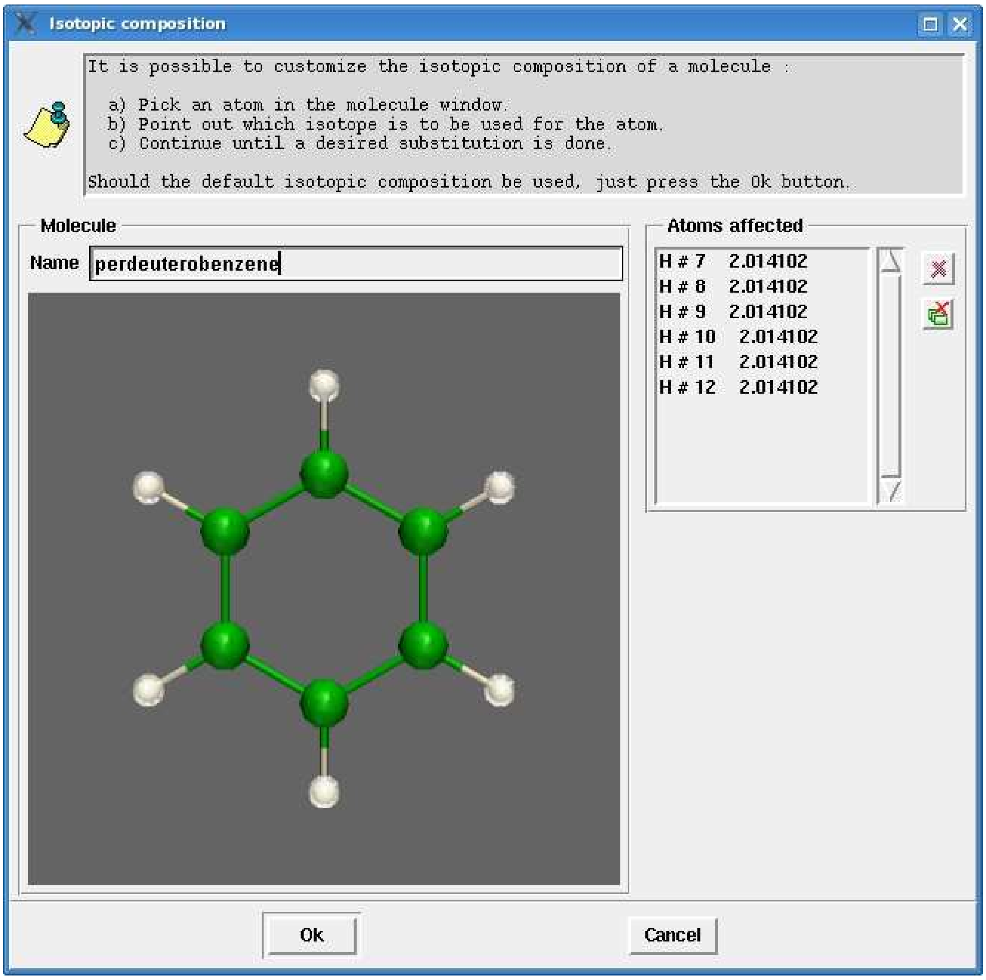
- **User defined** entry field

  Another option would be to specify directly the mass.

- **Use for all elements of this type** check box

  If checked, use the specified mass for all elements of this type. Can be useful e.g. to substitute all hydrogen atoms by deuterium atoms.

The following figure shows the result of a substitution in the benzene molecule :



It is possible to customize the isotopic composition of a molecule :

a) Pick an atom in the molecule window.
b) Point out which isotope is to be used for the atom.
c) Continue until a desired substitution is done.

Should the default isotopic composition be used, just press the Ok button.

Name: perdeuterobenzene

H # 7 2.014102
H # 8 2.014102
H # 9 2.014102
H # 10 2.014102
H # 11 2.014102
H # 12 2.014102

Figure 13. Benzene molecule with all hydrogen atoms substituted by deuterium atoms.

Atoms affected panel

It is made up of a list box with affected atoms and a vertical button toolbar. By clicking atoms in the list box the user can see that atoms in the 3D render widget and delete them. The toolbar has two buttons :

Button	Explanation
✘	Remove atoms selected in the list box.
⊠	Remove all atoms from the list box.

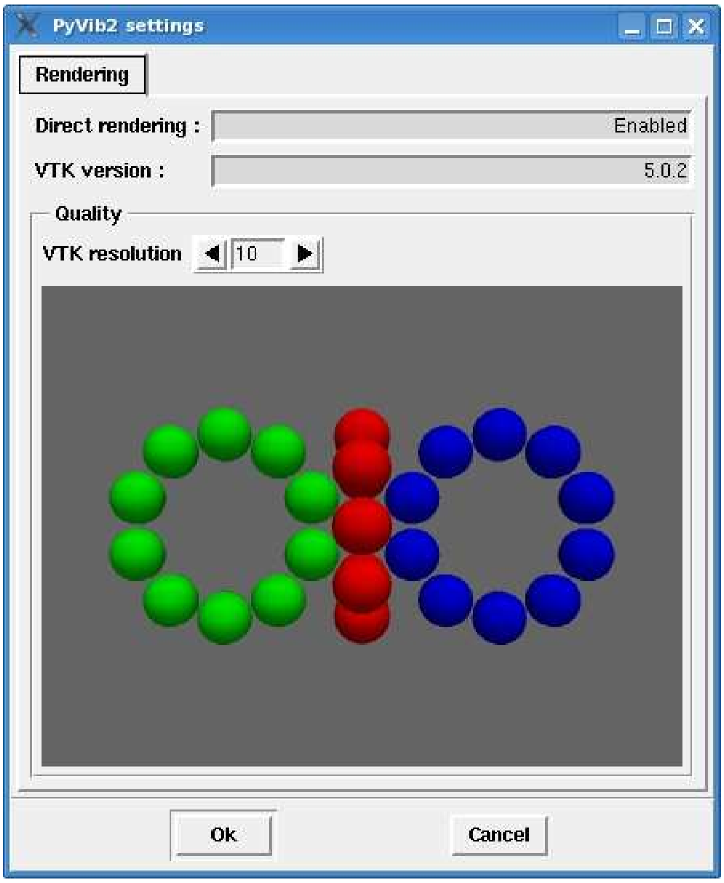
Finally, press the **Ok** button to finish the dialog. Atoms, for which the substitution has been performed, will appear with darker diffuse colors compared to ones with the default isotopic composition.

4.6.5 PyVib2 settings dialog

The dialog is invoked from the **Options|Configure PyVib2...** menu.

Rendering tab

At the time being, one can set up the default VTK resolution, which reflects the quality of rendering spheres, cylinders, cones used to represent molecules, their vibrational motion etc. Higher values of this parameter provide a better appearance but also imply a slower speed of rendering. The default value is chosen to be 10, a compromise between speed and quality. See figure 14.



Direct rendering : Enabled

VTK version : 5.0.2

Quality

VTK resolution 10

Figure 14. PyVib2 settings dialog.

4.7 Molecule window

The window is invoked from the **Molecule|Explore...** menu of a molecule's thumbnail.

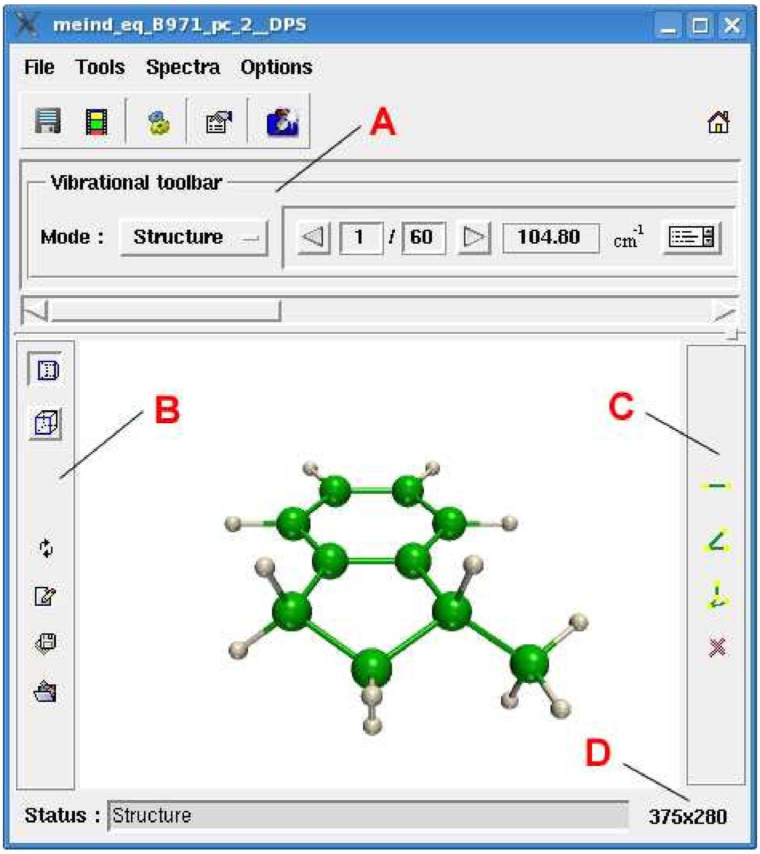


Figure 15. Molecule window for the pseudo-equatorial conformer of (R)-methylindane.

As one can see, the window is constructed from many GUI components, providing useful functionalities. In addition to a menu bar and a button toolbar like in the main window of PyVib2, there are a 3D rendering widget in the middle, three different toolbars and a status line.

4.7.1 Menu bar

File

- **Info...**
  The same as the menu **Molecule|Info...** of the molecule's thumbnail. See section 4.6.3.
- **Save as...**
  Save the data to a different format. Currently, only the VOAView format is offered.
- **Export...**
  Export the data to a different format. Currently, the MOLDEN and XMol XYZ formats are offered.
- **Clone**
  Create a clone of the molecule window.
- **Close**
  Close the molecule window.

Tools

- **Correlate vibrations...**

Correlate vibrations taking a set of all the opened molecules with the current one as the reference at startup of the **Correlate Vibrations** interface. Enabled if the normal modes are available. See section 4.8.

- **Raman / ROA generation**
  Start the **Raman/ROA generation** interface. Enabled if the Raman/ROA data are available. See section 4.9.

Spectra

- **Raman / ROA / Degree of circularity**
  Enabled if Raman/ROA data are available. See section 4.11.1.
- **IR / VCD**
  Enabled if IR/VCD data are available. See section 4.11.7.

Options

- **Settings**
  Pop up the dialog with the settings of the molecule window. See section 4.6.5.

4.7.2 Button toolbar

Button	Explanation
💾	Save vibrations. See section 4.7.9.
🎞	Save an animation of the current vibration. See section 4.7.10.
⚙	Correlate vibrations. The same as the **Tools|Correlate vibrations...** menu.
🗒	Settings of the molecule window. The same as the **Options|Settings** menu.
📷	Make a snapshot of the 3D render widget.

4.7.3 3D render widget

This is the widget where the rendering of the molecule's structure, vibrational motion etc. is done. A camera (viewport in the 3D world) is installed within the widget in order to explore its objects. The state of the camera is affected with the mouse buttons :

- **Left mouse button with dragging**
  Rotate the camera. If the Control button is pressed on the keyboard, the camera is rotated around the direction of projection.
- **Right mouse button with dragging**
  Zoom in/out.
- **Middle mouse button with dragging**
  Translation of the focal point of the camera. The same effect is achieved by pressing the mouse wheel or the left and right mouse buttons simultaneously with dragging.

The properties of the camera can be also changed in the navigation toolbar. See section 4.7.5.

4.7.4 Vibrational toolbar

This toolbar is located under the button toolbar (marked with A on figure 15). Its purpose is to provide a convenient navigation through the molecule's normal modes. The components of the vibrational toolbar are summarized here :

- **Mode** option menu

Figure 16. Option menu **Mode**.

Specifies which type of renpresentation of vibrational motion is to be used. There are several options :

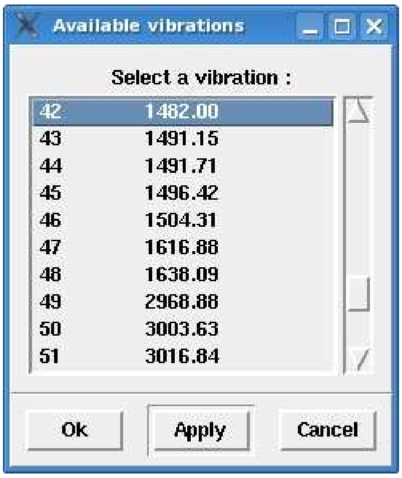
- → **Spheres**
  Render shaded spheres.
- → **Arrows**
  Render arrows;
- → **Animation**
  Animate the current vibration;
- → **Structure**
  Show the structure of the molecule;

- Navigation panel

42 / 60 1482.00 cm^{-1}

Figure 17. Navigation panel.

Allows to select the current vibration and shows its number as well as the wavenumber in cm^{-1}. One can use the back and forward buttons or select directly a certain vibration from the list by pressing the rightmost button :



42	1482.00
43	1491.15
44	1491.71
45	1496.42
46	1504.31
47	1616.88
48	1638.09
49	2968.88
50	3003.63
51	3016.84

Figure 18. List of the available vibrations.

- Representation panel

● Energy (volume) ○ Excursions (diameter) Total volume fix

Figure 19. Representation panel.

Allows to specify the representation of vibrational motion. For theoretical explanation see section 5.1. The contents of the rightmost option menu depends on what is chosen in the radiobutton box. Two possible choices are :

- → **Energy (volume)**
  - – **Total volume fix**

    - **Zero-point**
  - → **Excursions (diameter)**
    - **Total surface fix**
    - **Zero-point**
    - **Standard normalization**
- Panel for adjusting size and phase

Scale factor: 1.0

☐ Invert phase

Figure 20. Panel for adjusting size and phase.

The **scale factor** is a number with which the radii of the spheres and the lengths of the arrows (used for the rendering of vibrational motion) are multiplied. The check box **invert phase** allows to change the phase of vibrational motion, which is arbitrary.

The following keyboard shortcuts are associated with the vibrational toolbar :

- **Left arrow**
  Go one vibration back (the same as ◁ button).
- **Right arrow**
  Go one vibration forward (the same as ▷ button).
- **PgUp**
  Increase the scale factor by 0.1.
- **PgDn**
  Decrease the scale factor by 0.1.

Examples of different representations of vibrational motion are shown on figures 21 and 22.

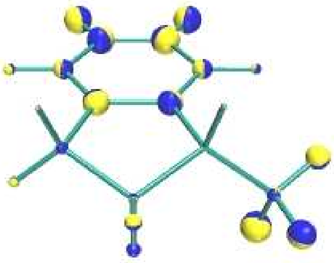


Figure 21. Vibration 42 of the pseudo-equatorial conformer of (R)-methylindane in the shaded spheres representation of the vibrational energy distribution.

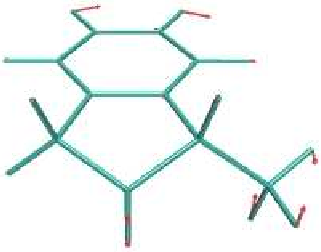


Figure 22. Vibration 42 of the pseudo-equatorial conformer of (R)-methylindane in the arrow representation of the cartesian excursions.

4.7.5 Navigation toolbar

With the navigation toolbar (marked with B on figure 15) the user can control the state of the camera installed in the 3D render widget. The most important properties of the camera are its position, orientation, focal point (where it looks to) and the type of projection.

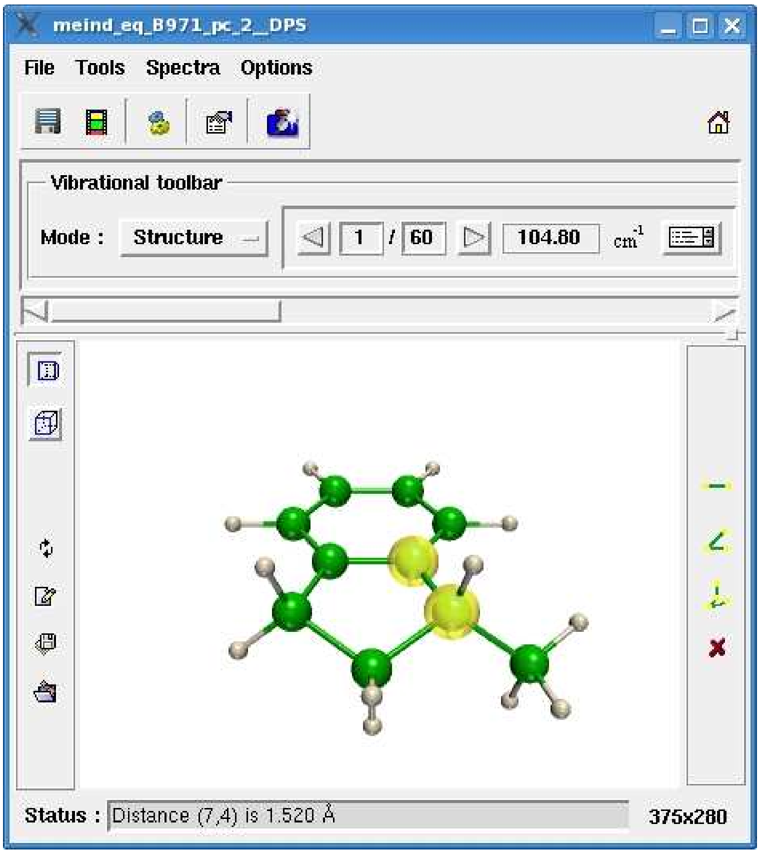
Button	Explanation
▢	Instruct the camera to do a perspective projection.
◫	Instruct the camera to do an orthogonal projection.
⟲	Restore the last remembered camera state.
✎	Remember the current camera state.
💾	Save the camera state to a file.
📂	Load the camera state from a file.

4.7.6 Geometry toolbar

The geometry toolbar (marked with C on figure 15) allows to measure distances, angles and dihedral angles in the molecule.

Button	Explanation
—	Measure a distance.
∠	Measure an angle.
⊥	Measure a dihedral angle.
✗	Cancel the marking of atoms in the 3D render widget.

To measure a distance, one has to press the topmost button of the geometry toolbar and then select two atoms. As a result, these two atoms will be marked with partially transparent yellow spheres and the distance will be displayed in a message dialog as well as in the status bar. The result of measuring the distance between the chiral carbon atom and the adjacent atom of the benzene ring in the pseudo-equatorial conformer of (R)-methylindane is shown on figure 23.



Mode : Structure

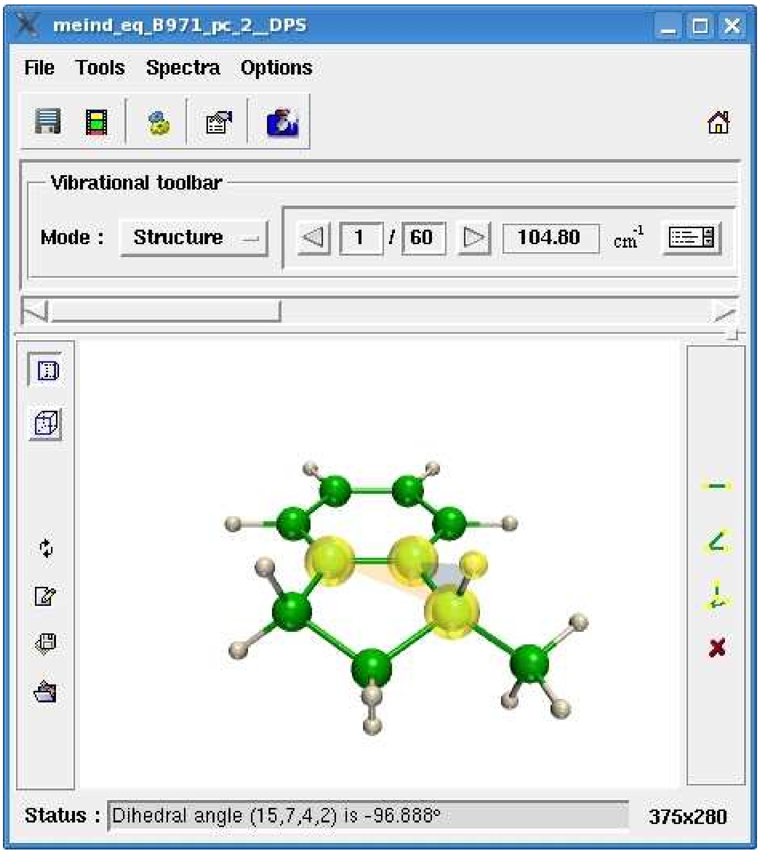
1 / 60 104.80 cm^{-1}

Status : Distance (7,4) is 1.520 Å

375x280

Figure 23. Example of measuring distance.

Similarly, to measure an angle or a dihedral angle, one has to select three or four atoms, respectively. An example of the latter case is shown on figure 24. For better visibility, the two planes defining the dihedral angles are represented in complementary colors.



Mode : Structure

1 / 60

104.80 cm^{-1}

Status : Dihedral angle (15,7,4,2) is -96.888°

375x280

Figure 24. Example of measuring dihedral angle.

4.7.7 Status line

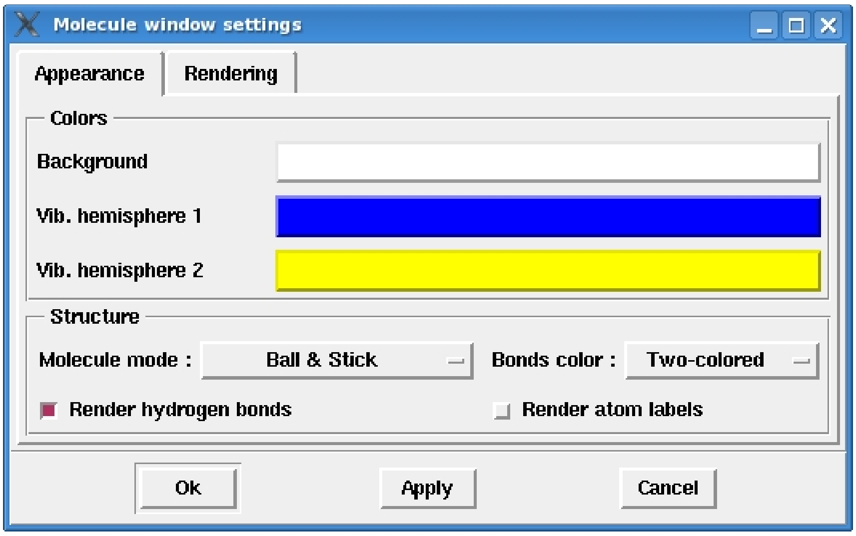
The status line consists of a status bar and a button for changing the size of the 3D render widget (marked with D on figure 15). The GUI components of the molecule window can send informative messages to the status bar. The button is labeled with the current size of the widget, which will be updated automatically upon changing the size of the window. Use the button if the exact size of the 3D render widget is desired. This could be the case e.g. for making snapshots.

4.7.8 Molecule window settings dialog

The dialog is invoked from the **Options|Settings** menu or by pressing on the button toolbar.

Appearance tab

Options related to the appearance of the molecule in the 3D render widget can be set up here.



Molecule mode : Ball & Stick

Bonds color : Two-colored

☑ Render hydrogen bonds

☐ Render atom labels

Figure 25. Appearance tab of the molecule window settings dialog.

The options are grouped as follows :

- **Colors**

  To change a particular color, press on the button to the right of the short text description and choose the appropriate one from the standard color choosing dialog (specific to the user's operating system).

  → **Background**

  Background color of the 3D render widget;

  → **Vib. hemisphere 1**

  In the shaded spheres representation, the color of a hemisphere used to indicate the positive direction of vibrational motion;

  → **Vib. hemisphere 2**

  In the shaded spheres representation, the color of a hemisphere used to indicate the negative direction of vibrational motion;

- **Structure**

  Options specific to rendering the structure are :

  → **Molecule mode** option menu

  - **Ball & Stick**

    Atoms and bonds are rendered as spheres and cylinders.

  - **Stick**

    Only bonds are rendered as cylinders;

  - **Van der Waals radii**

    Atoms and bonds are rendered as spheres and cylinders. The radii of the spheres are assumed to be proportional to the van der Waals radii of the atoms.

  → **Bonds color** option menu

  - **Two-colored**

    Bond is rendered as two cylinders, the colors of which are inherited from the atoms.

  - **Monolith**

Bond is rendered as one cylinder with a predefined color.

→ **Render hydrogen bonds** check box

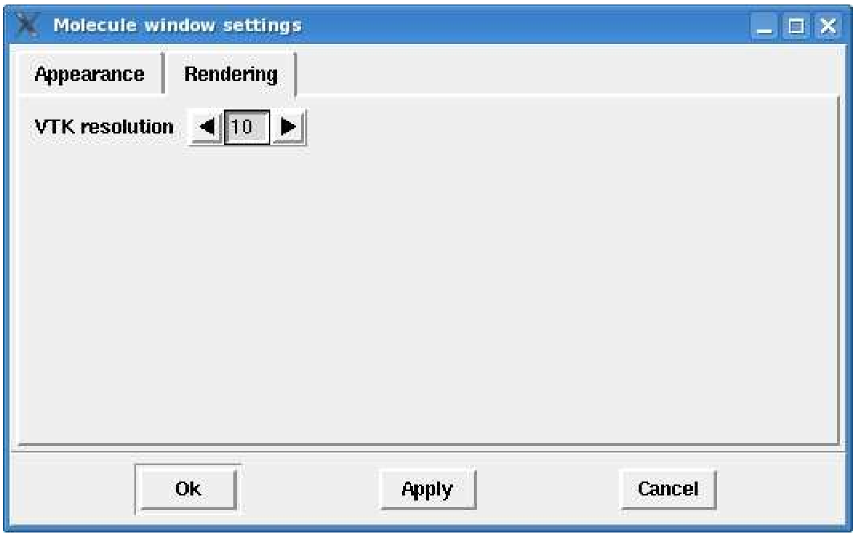
Whether render or not hydrogen bonds.

→ **Render atom labels** check box

Whether render or not the labels for the atoms.

Rendering tab

The user can override the default value of the VTK resolution (see section 4.6.5.1) for the current window. See section 4.6.5.

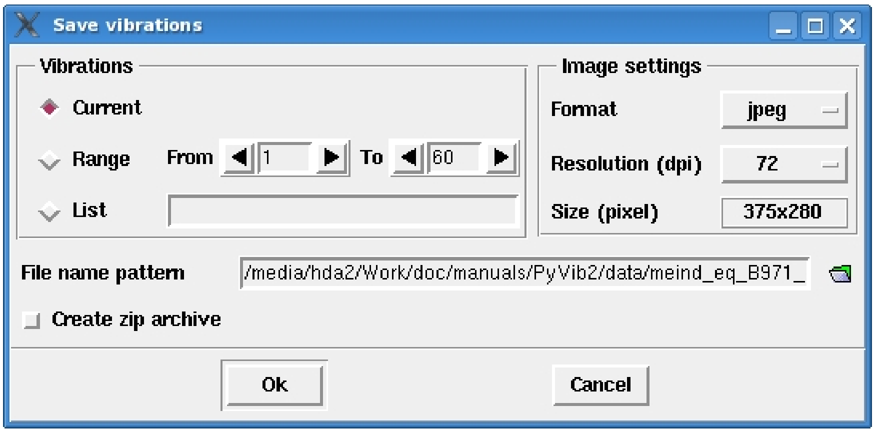


VTK resolution: 10

Figure 26. Rendering tab of the molecule window settings dialog.

4.7.9 Save vibrations dialog

The dialog is invoked by pressing the button on the button toolbar. It enables the user to save vibrations as static images in different formats and resolutions.



● Current
○ Range From 1 To 60
○ List

Format: jpeg
Resolution (dpi): 72
Size (pixel): 375x280

File name pattern: /media/hda2/Work/doc/manuals/PyVib2/data/meind_eq_B971_

☐ Create zip archive

Figure 27. Save vibrations dialog.

The options are :

- **Vibrations**
  Allows to select the vibrations to be saved :
  - → **Current**
    Take the current vibration shown in the **vibrational toolbar**.
  - → **Range**
    Take a range of vibrations definied by the **From** and **To** counters.
  - → **List**
    Take a list of vibrations, separated either by white spaces or columns or semi-columns.
- **Image settings**
  The image format and the resolution in dots per inch (dpi) can be set up.
  - → **Format** option menu
    Select an image format from :
    - **jpeg**
      Joint Photographic Experts Group format.
    - **tiff**
      Tagged Image File Format.
    - **png**
      Portable Network Graphic format.
    - **eps**
      Encapsulated PostScript format.
    - **ppm**
      Netpbm Color Image format.
  - → **Resolution (dpi)** option menu
    Possible values are : 72, 150, 300, 600.
  - → **Size (pixel)** label
    A read-only label, showing the image size in pixel taking into account the chosen image resolution.
- **File name pattern** entry field
  A pattern used to generate the file names for the resulting images. An appropriate string in the form of **_%suffix_%vibno%.%format** will be appended to the pattern in order to reflect the chosen representation of vibrational motion with **%vibno** being the number of vibration, **%format** image format. The possible values of **%suffix** are given in the following table :

%suffix	Representation of vibrational motion
energy_tvf	Energy / Total volume fix
energy_zp	Energy / Zero-point
excurs_tsf	Excursions / Total surface fix
excurs_zp	Excursions / Zero-point
excurs_sn	Excursions / Standard normalization

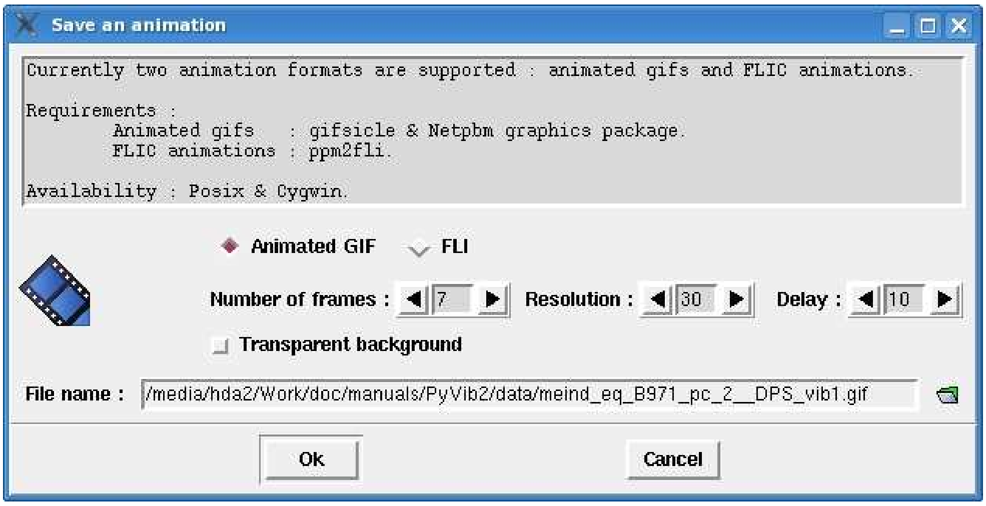
- **Select a filename pattern** button 📂
  Specify the filename pattern using the standard save dialog (specific to the user's operating system).
- **Create zip archive** check box

If checked, the resulting images will be packed with ZIP. The file name of the archive is of the form **%pattern**_vibs.zip, where **%pattern** is the file name pattern specified in the correspondent entry field.

Note : during the saving, the 3D render widget should not overlap with other windows.

4.7.10 Save animation dialog

The dialog is invoked by pressing on the button toolbar. PyVib2 offers a possibility to save animations of vibrations in the animated GIF or Autodesk Animator FLI formats. Refer to the Installation Guide (section 3) to see what utilities are needed for this to work. The program checks if the utilities are available. If they do not, the control for choosing formats appears disabled.



```
Currently two animation formats are supported : animated gifs and FLIC animations.

Requirements :
        Animated gifs    : gifsicle & Netpbm graphics package.
        FLIC animations  : ppm2fli.

Availability : Posix & Cygwin.
```

● Animated GIF ○ FLI

Number of frames : 7 Resolution : 30 Delay : 10

☐ Transparent background

File name : /media/hda2/Work/doc/manuals/PyVib2/data/meind_eq_B971_pc_2__DPS_vib1.gif

Figure 28. Save animation dialog.

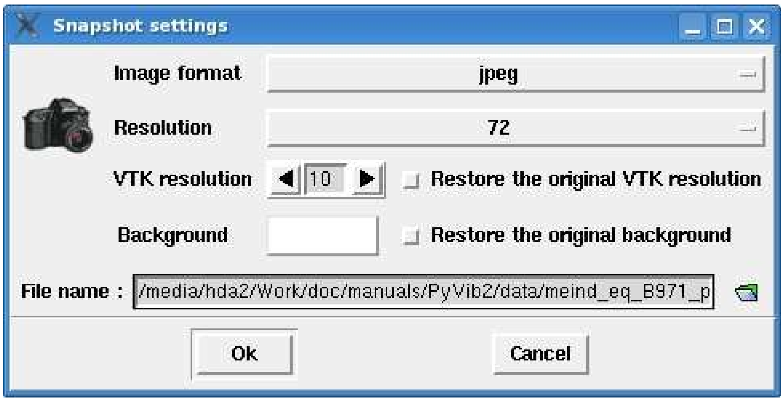
At the top of the dialog a short description is provided on which utilities are needed to succeed. First, the user has to choose a format of the animation. The remaining GUI components are :

- **Number of frames** counter
  Specifies the number of frames made in each direction.
- **Resolution** counter
  This is the VTK resolution for 3D rendering, see section 4.6.5.1.
- **Delay** counter
  Delay between single frames in hundredths of a second.
- **File name** entry field
  File name for the resulting animation.
- **Select a file name** button
  Specify the file name using the standard save dialog (specific to the user's operating system).

Note : during the saving process, the 3D render widget should not overlap with other windows.

4.7.11 Snapshot dialog

The dialog is invoked by pressing the button on the button toolbar. Allows to set up the options of a snapshot of the 3D render widget.



Snapshot settings

Image format: jpeg

Resolution: 72

VTK resolution: 10

☐ Restore the original VTK resolution

Background

☐ Restore the original background

File name : /media/hda2/Work/doc/manuals/PyVib2/data/meind_eq_B971_p

Figure 29. Snapshot dialog.

The options are :

- **Image format** option menu
  Select an image format from :
  - → **jpeg**
    Joint Photographic Experts Group format.
  - → **tiff**
    Tagged Image File Format.
  - → **png**
    Portable Network Graphic format.
  - → **eps**
    Encapsulated PostScript format.
  - → **ppm**
    Netpbm Color Image Format.
- **Resolution** option menu
  Resolution of the image in dots per inch (dpi). Possible values are : 72, 150, 300, 600.
- **VTK resolution** counter
  The VTK resolution to be used for the snapshot, see section 4.6.5.1.
- **Background** button
  Specify the background color of the snapshot by using the standard color choosing dialog (specific to the user's operating system).
- **Restore the original VTK resolution** check box
  If checked, the previous VTK resolution of the 3D render widget is restored after the snapshot is made. Otherwise, the value specified by the **VTK resolution** counter is used instead.
- **Restore the original background** check box
  If checked, the previous background of the 3D render widget is restored after the snapshot is made. Otherwise, the color specified by the **Background** button is used instead.
- **File name** entry field
  File name for the snapshot.
- **Select a file name** button

Specify the file name using the standard save dialog (specific to the user's operating system).

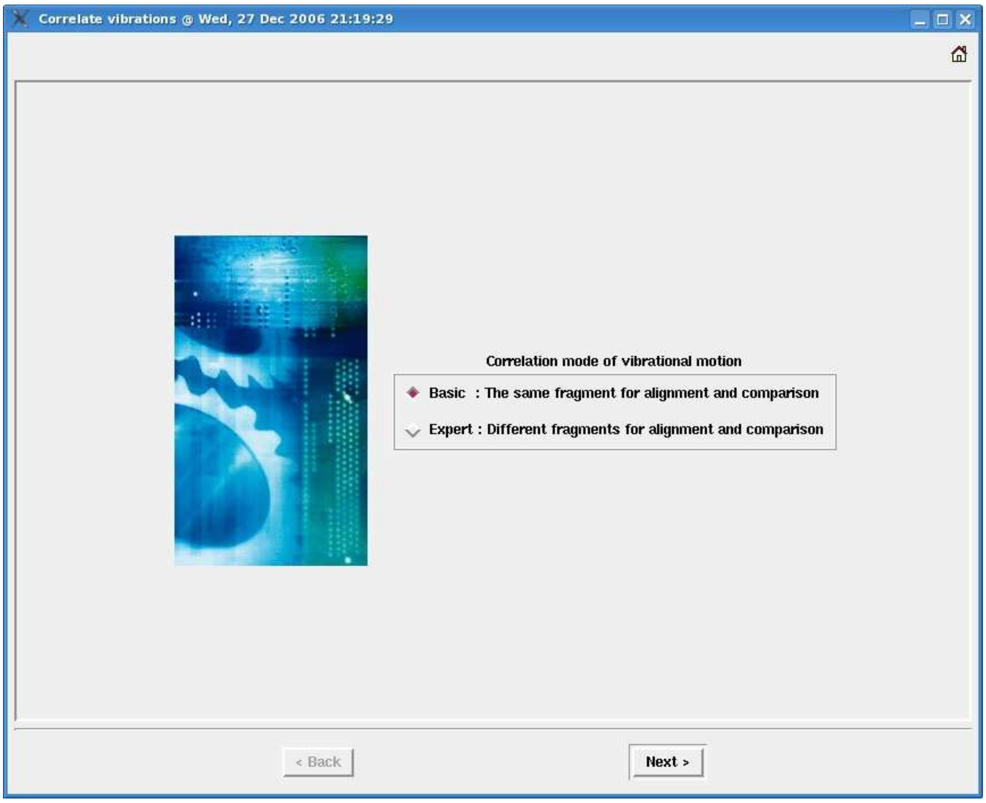
4.8 Correlate vibrations interface

The interface is invoked by pressing the button on the button toolbar of the main window of PyVib2, a molecule window or a window, where spectra for several molecules are plotted. It is implemented as a wizard, which guides the user through several steps. The navigation is performed with the < **Back** and **Next** > buttons.

4.8.1 Wizard

Step 1

In the first step, one has to select the correlation mode of vibrational motion :



Correlate vibrations @ Wed, 27 Dec 2006 21:19:29

Correlation mode of vibrational motion

◆ Basic : The same fragment for alignment and comparison

◇ Expert : Different fragments for alignment and comparison

Figure 30. First step of the wizard.

There are two options available :

- **Basic**

  The geometrical alignment and comparison of vibrational motion are performed on the same fragment.

- **Expert**

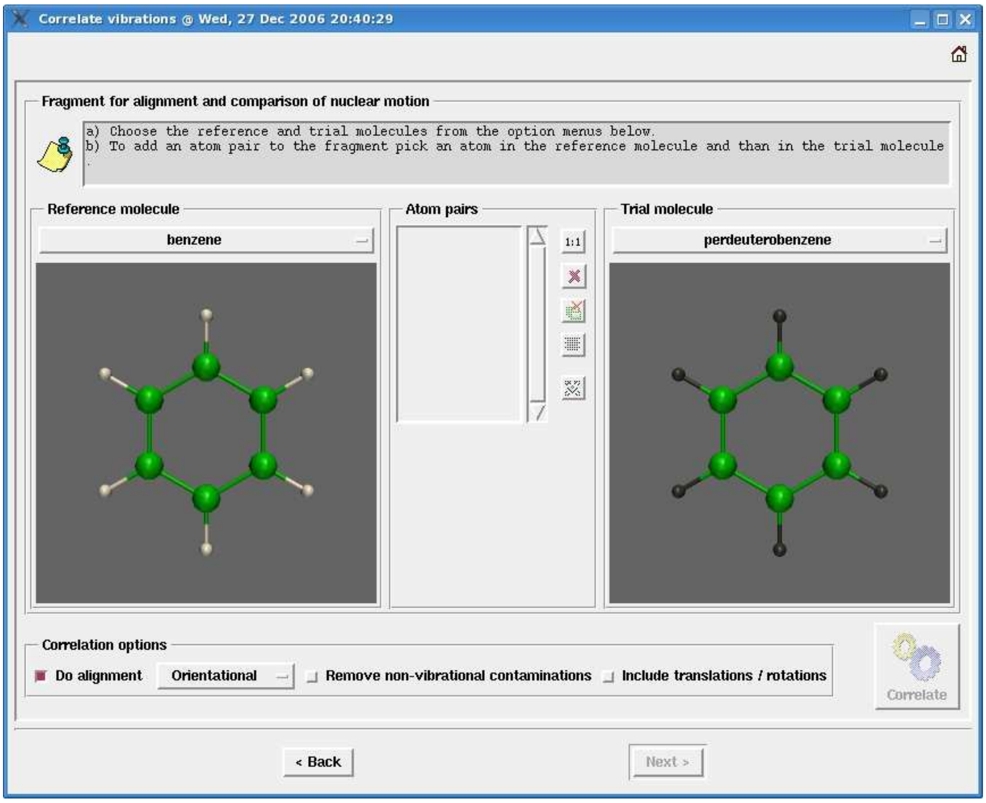
  The geometrical alignment and comparison of vibrational motion are performed on different fragments.

Step 2

The GUI depends on the mode chosen in the first step.

a) **Basic** mode

The user in prompted to select a fragment for the geometrical alignment and comparison of vibrational motion and set up options for the correlation. This is the last step in the basic mode.


Correlate vibrations @ Wed, 27 Dec 2006 20:40:29

Fragment for alignment and comparison of nuclear motion

a) Choose the reference and trial molecules from the option menus below.
b) To add an atom pair to the fragment pick an atom in the reference molecule and than in the trial molecule

Reference molecule: benzene

Trial molecule: perdeuterobenzene

Correlation options

☒ Do alignment: Orientational

☐ Remove non-vibrational contaminations

☐ Include translations / rotations

Figure 31. Second step of the wizard in the basic mode.

For the correlation of vibrational motions, the user has to specify which two molecules are to be considered, on which fragment the orientational alignment is to be performed and on which fragment vibrational motions are to be compared. For convenience, lets us denote by reference the first molecule and by trial the second molecule, for which there are two panels in the middle part of the window shown on figure 31. Each of them consists of an option menu at the top, from which a molecule can be chosen, and of a 3D render widget, where the molecule is shown. In the basic mode, the fragment for the orientational alignment is the same as the fragment for comparison of vibrational motions (in contrary to the expert mode). The procedure of specifying any of the them is the same :

1. Click on an atom in the reference molecule.
2. Click on the correspondent atom in the trial molecule.
3. Repeat 1 and 2 until the fragment is completely constructed.

The added atom pairs appear in a list box, located between the panels of the reference and trial molecules. A vertical button toolbar allows to perform actions related to the fragment :

Button	Explanation
1:1	Use the 1:1 correspondence between the number of atoms to define the fragment.
✘	Remove the selected atom pair(s) from the fragment.
☒	Remove all atom pairs from the fragment.
≣	Perform the geometrical alignment of the fragment.
⌘	Synchronize the rotation and zooming in both reference and trial molecules.

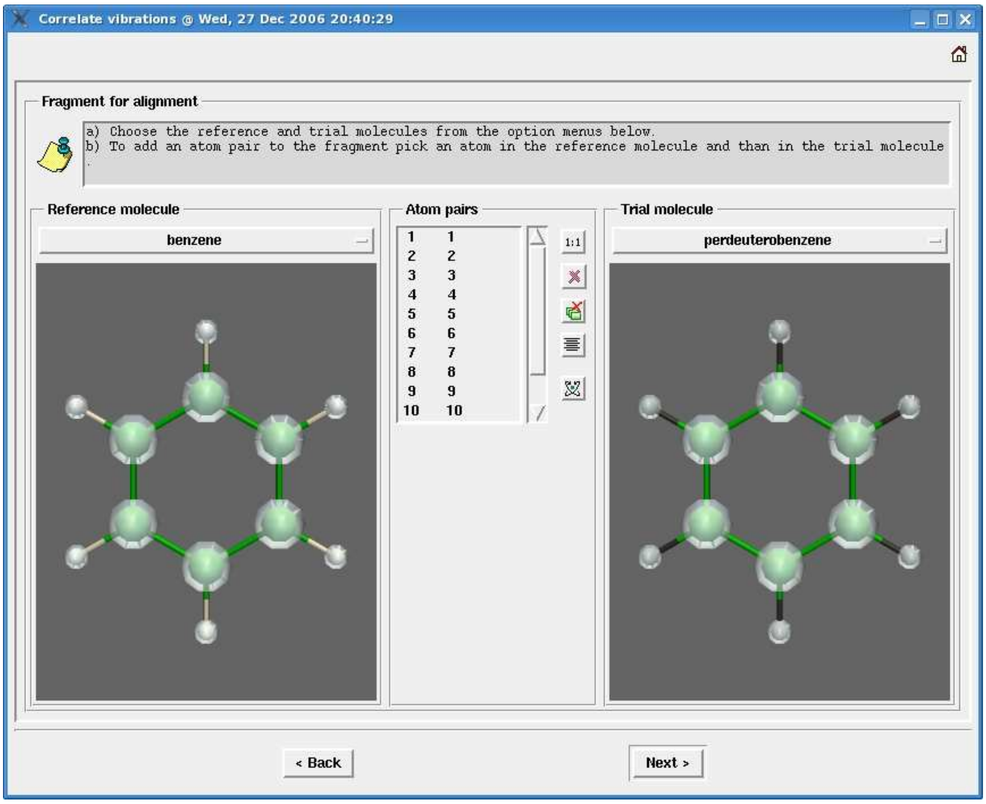
A panel at the bottom of the window shown on figure 31 allows to set up the correlation options :

- **Do alignment** check box and associated option menu
  Whether perform or not the geometrical alignment.
- **Remove non-vibrational contaminations** check box
  Whether remove or not the translational and rotational contaminations on the fragment to compensate the violation of the Eckart-Sayvetz conditions.
- **Include translations / rotations** check box
  Whether perform or not the correlation of the true normal modes with the translational and rotational modes.

After at least two atoms were added to the fragment, the **Correlate** ⚙ button becomes enabled and the user can start the correlation. For description of the results see section 4.8.2.

b) **Expert** mode

In the second step in the expert mode the user has to select a fragment for the geometrical alignment.



Correlate vibrations @ Wed, 27 Dec 2006 20:40:29

Fragment for alignment

a) Choose the reference and trial molecules from the option menus below.
b) To add an atom pair to the fragment pick an atom in the reference molecule and than in the trial molecule.

Reference molecule: benzene

Trial molecule: perdeuterobenzene

Atom pairs

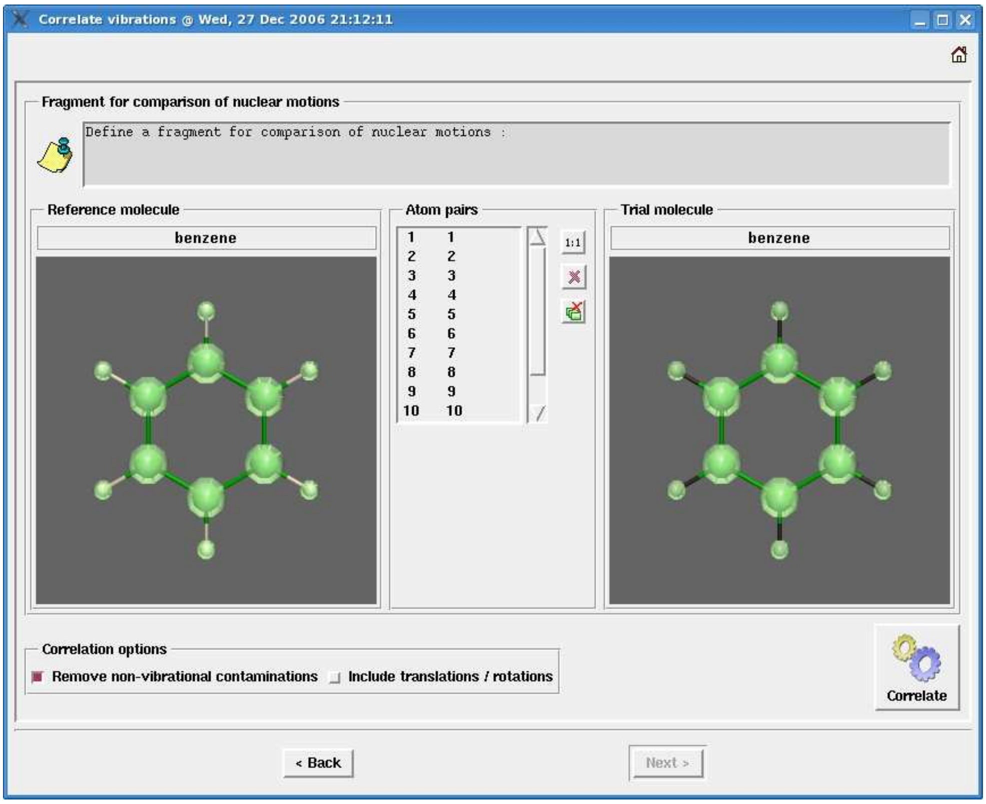
1	1
2	2
3	3
4	4
5	5
6	6
7	7
8	8
9	9
10	10

Figure 32. Second step of the wizard in the expert mode.

The specification of the reference and the trial molecules as well as of the fragment is performed in the same way as in the basic mode. To complete the wizard go step 3.

Step 3

In the final step (expert mode), a fragment for comparison of vibrational motion has to be selected. The user cannot change the reference or trial molecule, since this choice was already made in the second step.



Correlate vibrations @ Wed, 27 Dec 2006 21:12:11

Fragment for comparison of nuclear motions

```
Define a fragment for comparison of nuclear motions :
```

Reference molecule: benzene

Trial molecule: benzene

Atom pairs

1	1
2	2
3	3
4	4
5	5
6	6
7	7
8	8
9	9
10	10

Correlation options

■ Remove non-vibrational contaminations ☐ Include translations / rotations

Figure 33. Third step of the wizard in the expert mode.

The specification of the fragment is performed in the same way as described in the step 2 of the basic mode. After at least two atoms were added to the fragment, the **Correlate** button becomes enabled and the user can start the correlation. For description of the results see section 4.8.2.

4.8.2 Correlation results window

Results of a correlation are two matrices of the overlaps and similarities of the normal modes of the reference and trial molecules. By convention, the rows of the matrices correspond to the normal modes of the reference molecule, while the columns correspond to the normal modes of the trial molecule. The matrices can be depicted as tables of numerical values or as circles, the area of which is proportional to the values. Since the overlaps and similarities take values between 0 and 1., the biggest circle corresponds to a value of 1.

Top panel

The top panel of the window with the correlation results contains the following informations :

- **Reference/trial range from** and **to** counters

  Allows to restrict the representation of the normal modes of the reference/trial molecule to a given range.

- **Reset the reference/trial range** buttons

  Set the reference/trial range to be from the first to the last available vibration.

- **Range of the reference/trial wavenumbers** read-only labels

  Show the wavenumbers for the chosen reference/trial range.

- **Precision** counter

  Specify the order of magnitude for the overlaps and similarities, below which their values are considered to be 0.

- **Mark overlaps/simililarities** >= check boxes and associated entry fields

  Overlaps/similarities above or equal to the specified value will be marked in the overlaps/similarities table with yellow.

- **Refresh** button

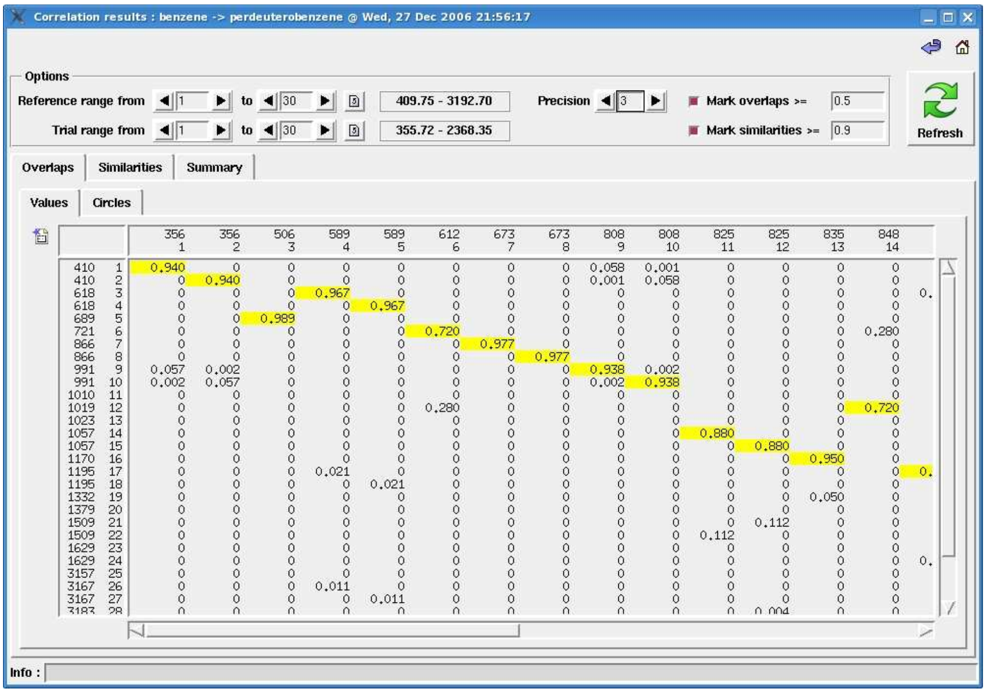
  Apply the above described settings.

At the bottom of the window there is a status bar, which provides the information on where the mouse pointer is.

Overlaps and Similarities tabs

The correspondent matrix is shown as a table (**Values** tab) and as circles (**Circles** tab). For theoretical explanation see section 5.2.

- **Values** tab



Correlation results : benzene -> perdeuterobenzene @ Wed, 27 Dec 2006 21:56:17

Options

Reference range from 1 to 30 409.75 - 3192.70

Trial range from 1 to 30 355.72 - 2368.35

Precision 3

Mark overlaps >= 0.5

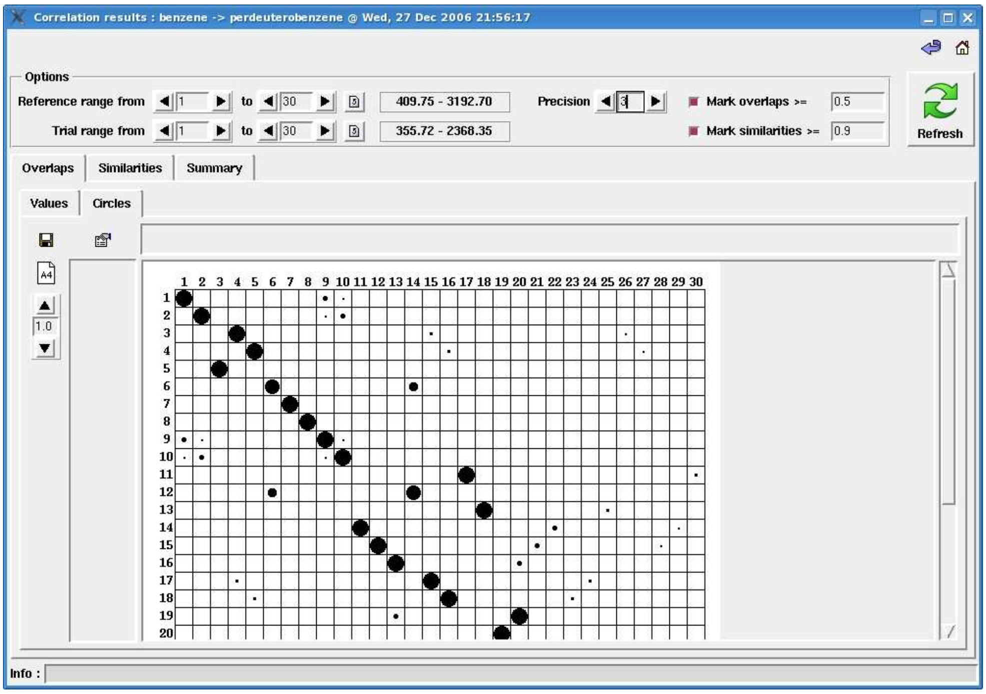
Mark similarities >= 0.9

		356 1	356 2	506 3	589 4	589 5	612 6	673 7	673 8	808 9	808 10	825 11	825 12	835 13	848 14	
410	1	0.940	0	0	0	0	0	0	0	0.058	0.001	0	0	0	0	
410	2	0	0.940	0	0	0	0	0	0	0.001	0.058	0	0	0	0	
618	3	0	0	0	0.967	0	0	0	0	0	0	0	0	0	0	0.
618	4	0	0	0	0	0.967	0	0	0	0	0	0	0	0	0	
689	5	0	0	0.989	0	0	0	0	0	0	0	0	0	0	0	
721	6	0	0	0	0	0	0.720	0	0	0	0	0	0	0	0.280	
866	7	0	0	0	0	0	0	0.977	0	0	0	0	0	0	0	
866	8	0	0	0	0	0	0	0	0.977	0	0	0	0	0	0	
991	9	0.057	0.002	0	0	0	0	0	0	0.938	0.002	0	0	0	0	
991	10	0.002	0.057	0	0	0	0	0	0	0.002	0.938	0	0	0	0	
1010	11	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
1019	12	0	0	0	0	0	0.280	0	0	0	0	0	0	0	0.720	
1023	13	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
1057	14	0	0	0	0	0	0	0	0	0	0	0.880	0	0	0	
1057	15	0	0	0	0	0	0	0	0	0	0	0	0.880	0	0	
1170	16	0	0	0	0	0	0	0	0	0	0	0	0	0.950	0	
1195	17	0	0	0	0.021	0	0	0	0	0	0	0	0	0	0	0.
1195	18	0	0	0	0	0.021	0	0	0	0	0	0	0	0	0	
1332	19	0	0	0	0	0	0	0	0	0	0	0	0	0.050	0	
1379	20	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
1509	21	0	0	0	0	0	0	0	0	0	0	0	0.112	0	0	
1509	22	0	0	0	0	0	0	0	0	0	0	0.112	0	0	0	
1629	23	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
1629	24	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.
3157	25	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
3167	26	0	0	0	0.011	0	0	0	0	0	0	0	0	0	0	
3167	27	0	0	0	0	0.011	0	0	0	0	0	0	0	0	0	
3183	28	0	0	0	0	0	0	0	0	0	0	0	0.004	0	0	

Figure 34. Overlap matrix represented as a table.

The user can save the matrix in the Comma Separated Values (CSV) format by pressing the 🗎 button, located to the left of the table.

- **Circles** tab



Correlation results : benzene -> perdeuterobenzene @ Wed, 27 Dec 2006 21:56:17

Options

Reference range from 1 to 30 409.75 - 3192.70

Trial range from 1 to 30 355.72 - 2368.35

Precision 3

Mark overlaps >= 0.5

Mark similarities >= 0.9

Figure 35. Overlap matrix represented as circles.

The following additional GUI elements are available in the **Circles** tab :

→ 💾 button

Save the canvas in the PostScript (PS), Encapsulated PostScript (EPS) or Portable Document Format (PDF) formats (for the latter ps2pdf is required).

→ A4 button

Switch to the overview mode, in which the maximum size of the squares is chosen reasonably small so that the table encompasses all the available vibrations.

→ **Scale factor** counter

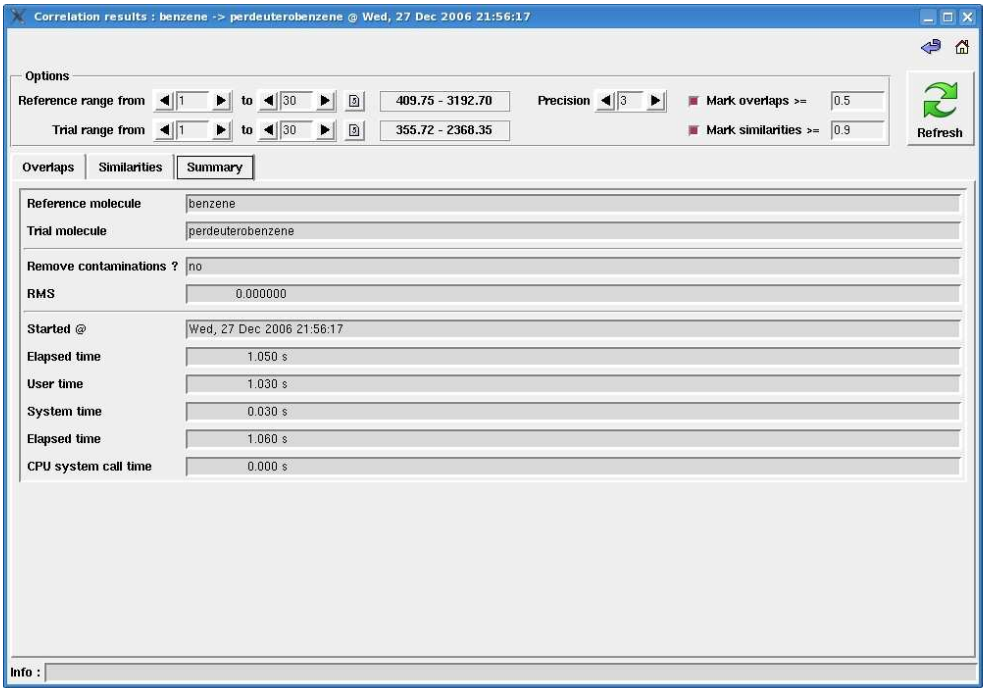
In the overview mode, the maximum size of the squares will be multiplied with this number.

→ 📋 button

See the Canvas settings dialog subsection.

Summary tab

The details of the correlation are provided here.



Correlation results : benzene -> perdeuterobenzene @ Wed, 27 Dec 2006 21:56:17

Options

Reference range from 1 to 30 409.75 - 3192.70 Precision 3 ☑ Mark overlaps >= 0.5

Trial range from 1 to 30 355.72 - 2368.35 ☑ Mark similarities >= 0.9

Reference molecule: benzene

Trial molecule: perdeuterobenzene

Remove contaminations ?: no

RMS: 0.000000

Started @: Wed, 27 Dec 2006 21:56:17

Elapsed time: 1.050 s

User time: 1.030 s

System time: 0.030 s

Elapsed time: 1.060 s

CPU system call time: 0.000 s

Info :

Figure 36. Summary tab.

Canvas settings dialog

The user can set up several options of the canvas :

Circles canvas settings

☑ Grid on ☑ Labels on ☐ Bounding box

Figure 37. Settings of the circles canvas.

- **Grid on** check box

Whether the grid is to be rendered.

- **Labels on** check box

  Whether the number of the vibrations are to be rendered.

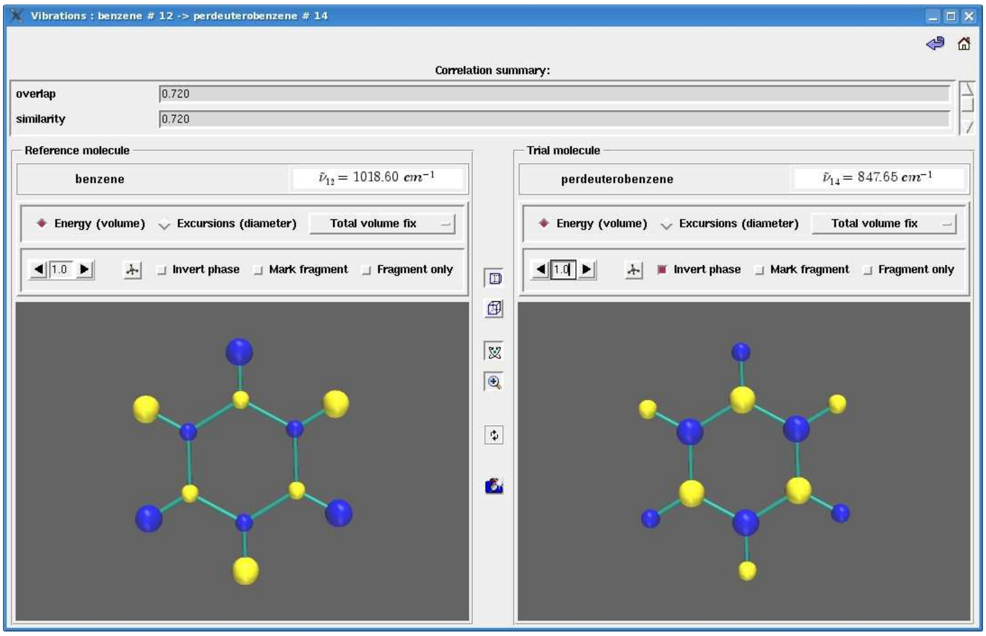
- **Bounding on** check box

  If checked, a rectangle which bounds all the squares on the canvas is rendered.

Upon clicking on an element of the table or on a circle of the canvas, the two selected vibrations will be shown in a separate window. See section 4.5.3.

4.8.3 Simultaneous window for two vibrations

The window allows to explore two vibrations simultaneously.



Vibrations : benzene # 12 -> perdeuterobenzene # 14

Correlation summary:

overlap 0.720

similarity 0.720

Reference molecule

benzene $\tilde{\nu}_{12} = 1018.60\ cm^{-1}$

● Energy (volume) ○ Excursions (diameter) Total volume fix

1.0 ☐ Invert phase ☐ Mark fragment ☐ Fragment only

Trial molecule

perdeuterobenzene $\tilde{\nu}_{14} = 847.65\ cm^{-1}$

● Energy (volume) ○ Excursions (diameter) Total volume fix

1.0 ☑ Invert phase ☐ Mark fragment ☐ Fragment only

Figure 38. Simultaneous window for two vibrations.

The top panel shows the overlap and similarity of the vibrations as well as whether the non-vibrational contaminations were removed. The bottom part of the window consists of two molecule panels for the reference and trial molecules and a button toolbar, located between them.

Molecule panel

The molecule panel has the following elements :

- Name of the molecule read-only label

  Name of the molecule.

- Vibration information

  Shows the number of the vibration and its wavenumber in cm^{-1}.

- **Energy (volume)** and **Excursions(diameter)** radio box with the associated option menu

  Options for representation of vibrational motion. See section 4.7.4.

- **Scale factor** counter

  A number with which the amplitudes of vibrational motion are multiplied.

- button
  Allows to toggle between the rendering of the structure and of vibrational motion.
- **Invert phase** check box
  Invert the phase of vibrational motion. In praxi, the colors of the hemispheres are interchanged.
- **Mark fragment** check box
  Whether the fragment, on which vibrational motion were compared, is to be marked with semitransparent grey spheres.
- **Fragment only** checkbox
  If checked, then vibrational motion on the fragment only is shown.

The following keyboard shortcuts are associated with the above described elements :

- m
  Toggle the **Mark fragment** check box.
- f
  Toggle the **Fragment only** checkbox.

Button toolbar

The button toolbar allows to perform some actions with the 3D render widgets :

Button	Explanation
	Instruct the camera to do a perspective projection.
	Instruct the camera to do an orthogonal projection.
	Enable a synchronized rotation in both 3D render widgets.
🔍	Enable a synchronized zooming in both 3D render widgets.
🔄	Restore the initial camera position.
	Show the Raman/ROA spectra of the molecules. See section 4.11.4.
📷	Make a snapshot of both 3D render widgets.

Note : button is present on the toolbar only if the Raman/ROA data are available for *both* molecules.

4.9 Raman / ROA generation interface

The interface is invoked from the **Molecule|Raman / ROA generation** menu of a molecule's thumbnail or from the **Tools|Raman / ROA generation** menu of a molecule window or by clicking the button on the button toolbars of windows described in section 4.11. The user can visualize nuclear and group coupling matrices (NCMs and GCMs), atomic and group contribution patterns (ACPs and GCPs). For theoretical explanation see section 5.

The GUI consists of a top panel, a vertical button toolbar at the right side of the window and a notebook with several tabs in the middle.

4.9.1 Top panel

The top panel contains the following elements :

- Navigation panel
  Allows to select a vibration. See section 4.7.4.
- **Mode** radio box
  Two possible choices are :
  - → **single atoms**

Show nuclear coupling matrices.

→ **groups**

Show group coupling matrices. Use ● button to define groups. Remains disabled until the groups are defined.

- ● button

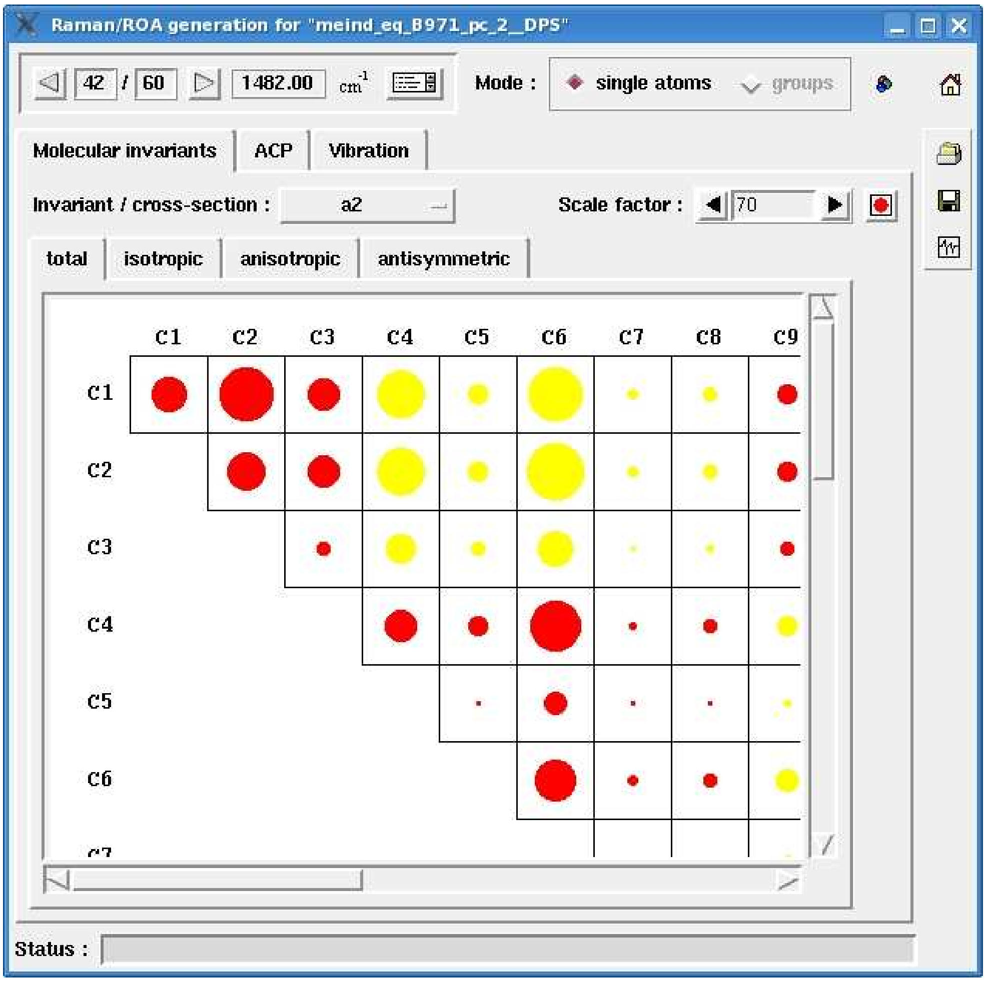
  Define groups. See section 4.9.6.

4.9.2 Button toolbar

Button	Explanation
🗗	Create a clone of the window.
💾	Save the active canvas.
📈	Plot Raman/ROA/Degree of circularity spectra for the molecule. See section 4.11.1.

4.9.3 Molecular invariants tab

Visualize nuclear or group coupling matrices for a particular molecular invariant or cross-section.



Raman/ROA generation for "meind_eq_B971_pc_2__DPS"

42 / 60   1482.00 cm^{-1}

Mode : ◆ single atoms ◇ groups

Invariant / cross-section : a2

Scale factor : 70

Figure 39. Molecular invariants tab of the Raman/ROA generation interface.

The GUI elements are :

- **Invariant / cross-section** option menu

List of the available molecular invariants and Raman/ROA differential cross-sections. For theoretical explanation see section 5.3.

→ **a2**

→ **b2**

→ **aG**

→ **b2G**

→ **b2A**

- **Scale factor** counter

  Defines a number with which the radii of the circles in the canvas are multiplied.

- ▣ button

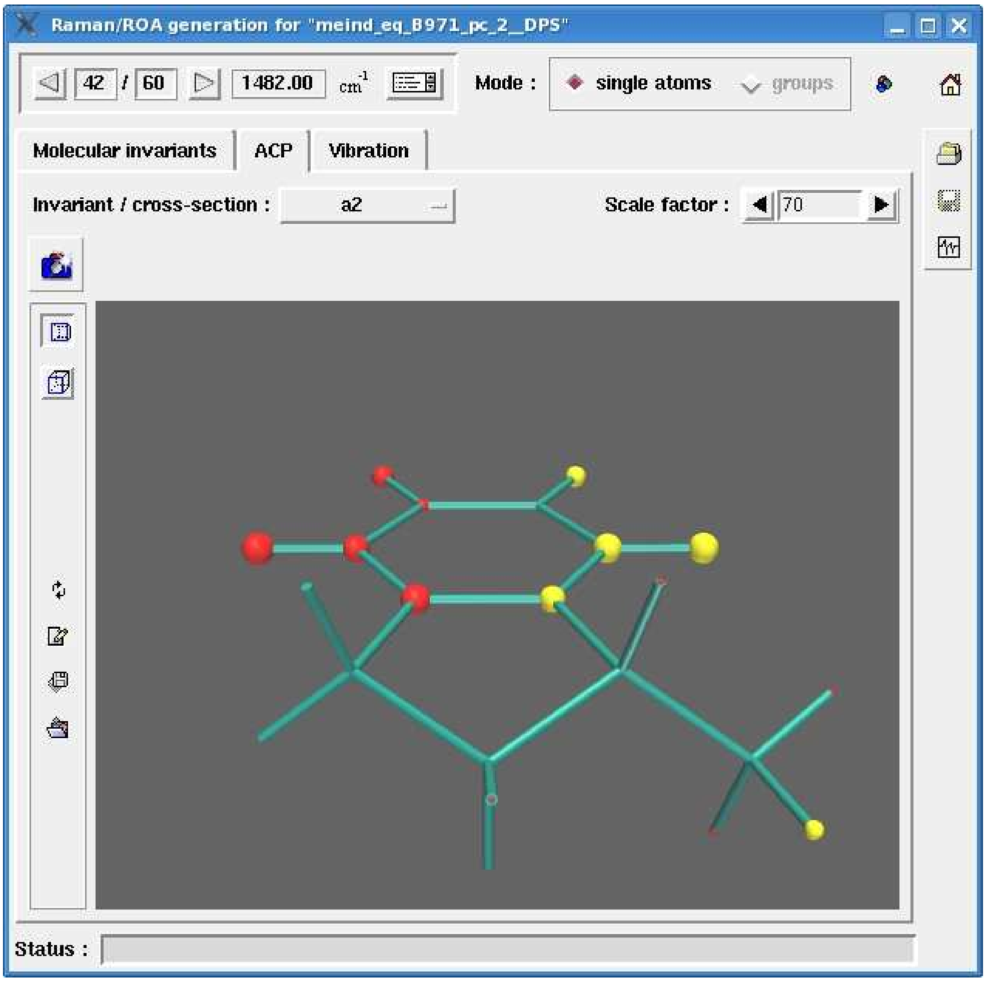
  Calculate the optimal scale factor for representation of the selected molecular invariant or cross-section.

- **total, isotropic, anisotropic** and **antisymmetric** tabs

  Canvas with the total or local isotropic , anisotropic or antisymmetric contributions of the selected molecular invariant or cross-section represented as circles.

4.9.4 ACP tab

Visualize atomic or group contribution patterns. For theoretical explanation see section 5.4.


Raman/ROA generation for "meind_eq_B971_pc_2_DPS"

42 / 60 1482.00 cm^{-1}

Mode : ◆ single atoms ◇ groups

Invariant / cross-section : a2

Scale factor : 70

Status :

Figure 40. ACP tab of the Raman/ROA generation interface.

The meaning of the **Invariant / cross-section** option menu and the **Scale factor** counter is the same as in the **Molecular invariants** tab. The navigation toolbar to the left side of the 3D render widget was already described in section 4.7.5. 📷 button allows to make a snapshot of the 3D render widget.

4.9.5 Vibration tab

Show the current vibration. The GUI elements are the same as in a 2 Vibration window, see section 4.5.3.

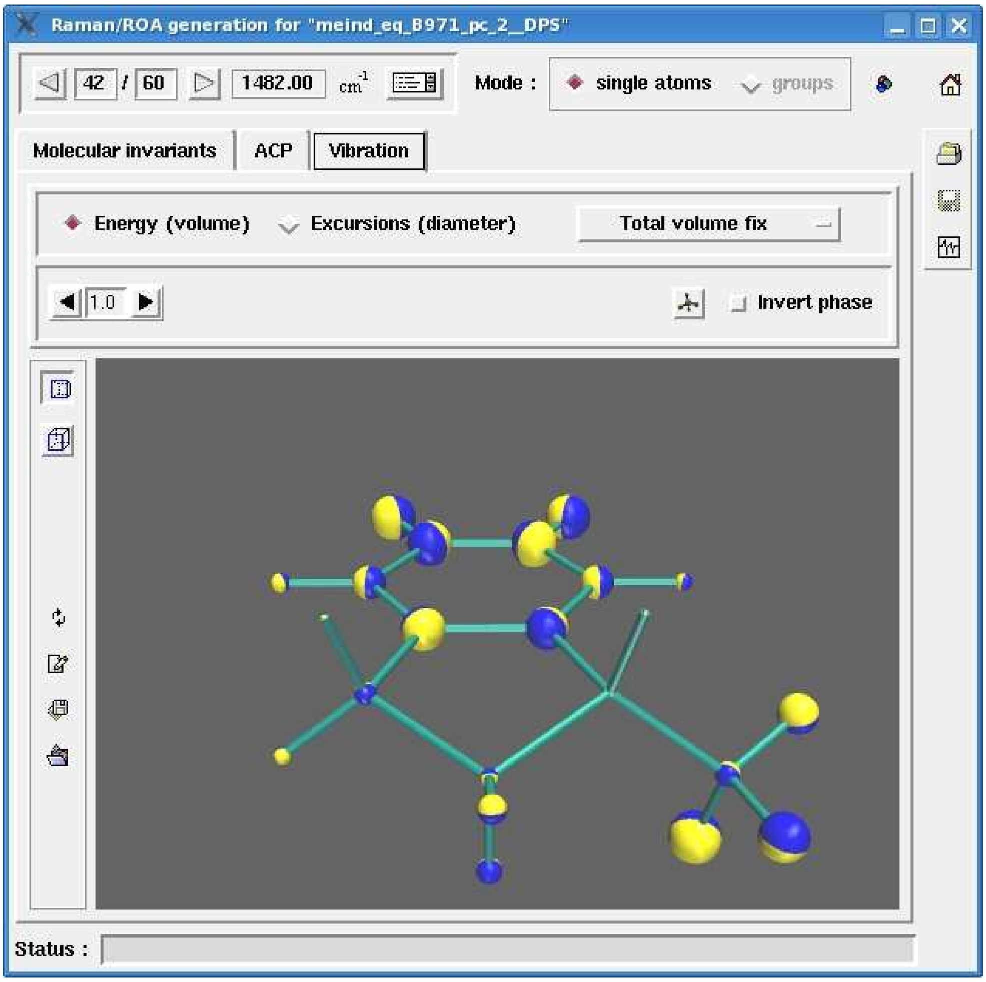
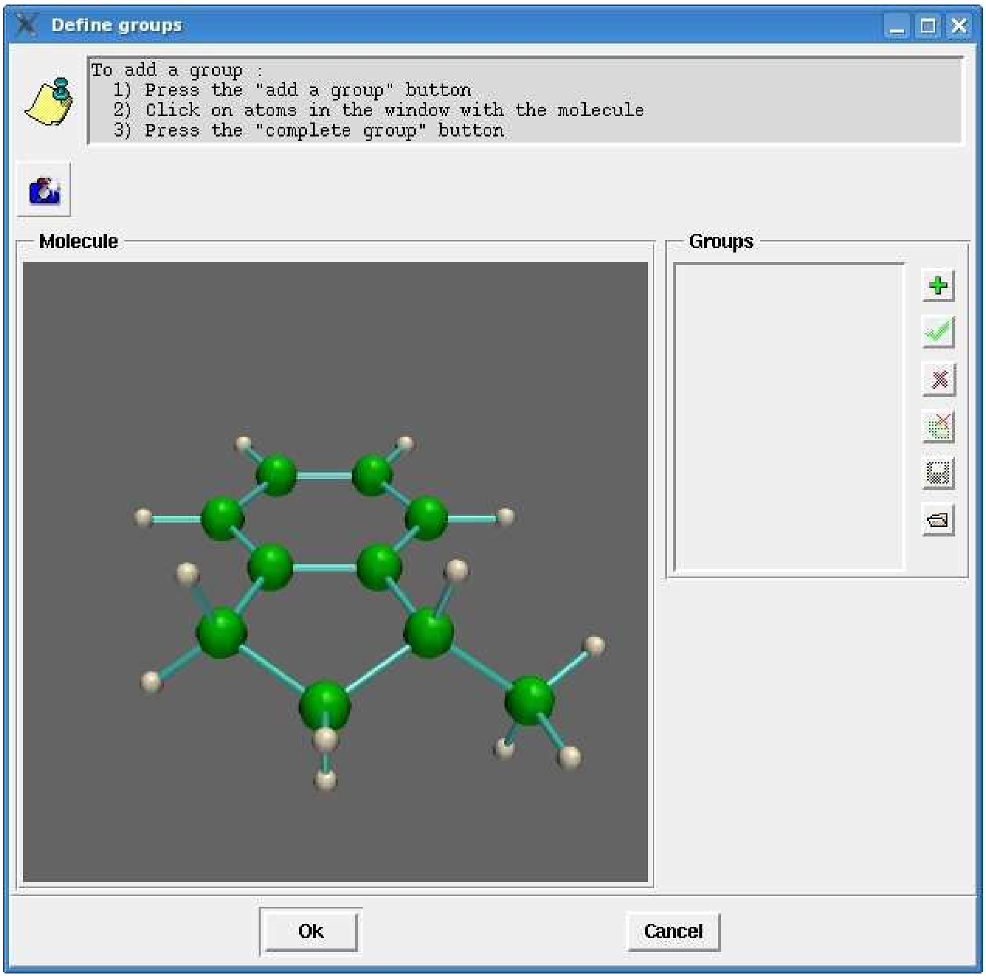


Figure 41. Vibration tab of the Raman/ROA generation interface.

4.9.6 Define groups dialog

The dialog is invoked by pressing the button on the button toolbar. It allows to define groups for visualizing group coupling matrices and group contribution patterns.



```
To add a group :
  1) Press the "add a group" button
  2) Click on atoms in the window with the molecule
  3) Press the "complete group" button
```

Figure 42. Define groups dialog without any groups.

The single button on the button toolbar at the top allows to make a snapshot of the 3D render widget.

Molecule panel

It consists of a 3D render widget where the molecule and defined groups are shown.

Groups panel

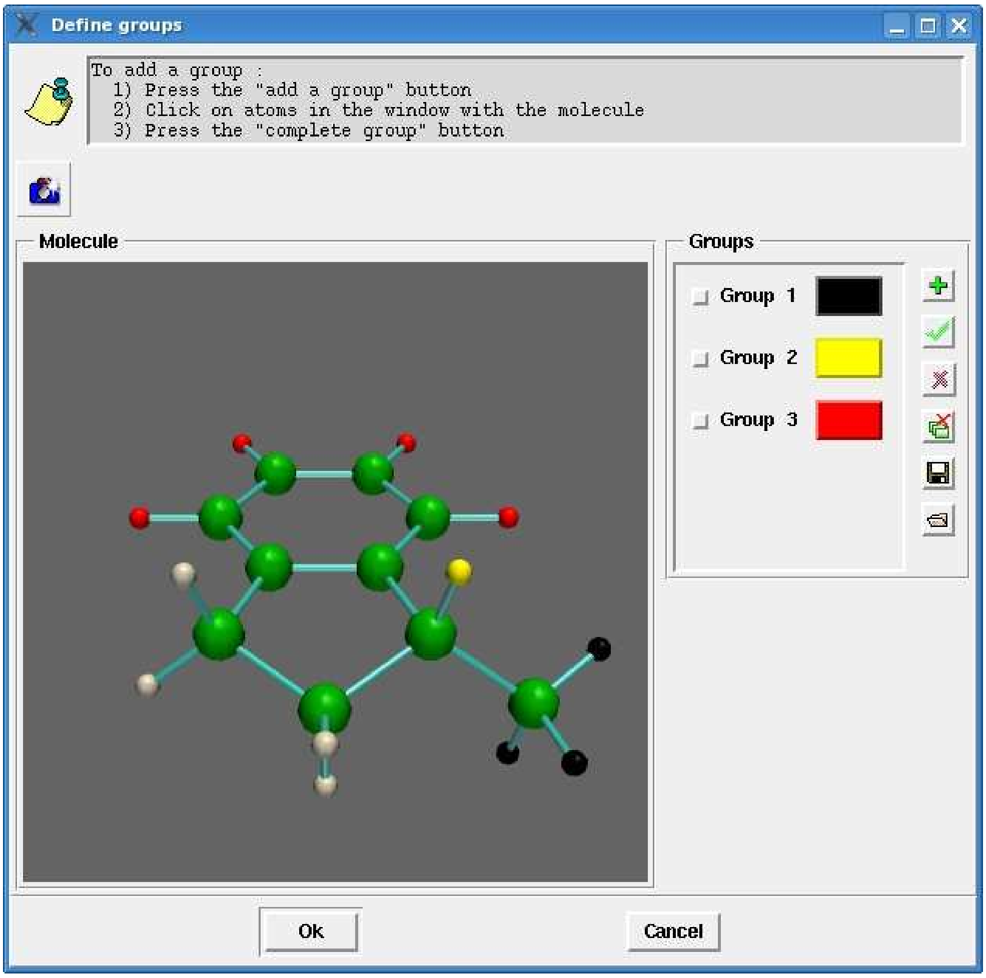
It consists of a list box with groups and a vertical button toolbar for manipulating groups. The functionalities of the latter are summarized in the following table :

Button	**Explanation**
✚	Start adding a new group.
✓	Complete the current group.
✘	Remove group(s) selected in the list box.
💾	Save the currently defined groups to a file.
📂	Load groups from a file.

To add a group :

1. Press the ✚ button.
2. Click on atoms constituting the group in the 3D render widget.
3. Press the ✓ button to complete the group. After that, the added group appears in the list box.

Figure 43 shows an example :



```
To add a group :
  1) Press the "add a group" button
  2) Click on atoms in the window with the molecule
  3) Press the "complete group" button
```

Figure 43. Define groups dialog with three groups.

Pressing the **Ok** button will enable the **groups** radio button in the top panel of the **Raman/ROA generation interface**. After that the user can visualize group coupling matrices for molecular invariants, cross-sections as well as group contribution patterns. For instance, the group coupling matrix for the three groups defined above is given on figure 44. The correspondent group contribution pattern is given on figure 45. The spheres which represent the contributions of the groups are located in their centers of gravity.

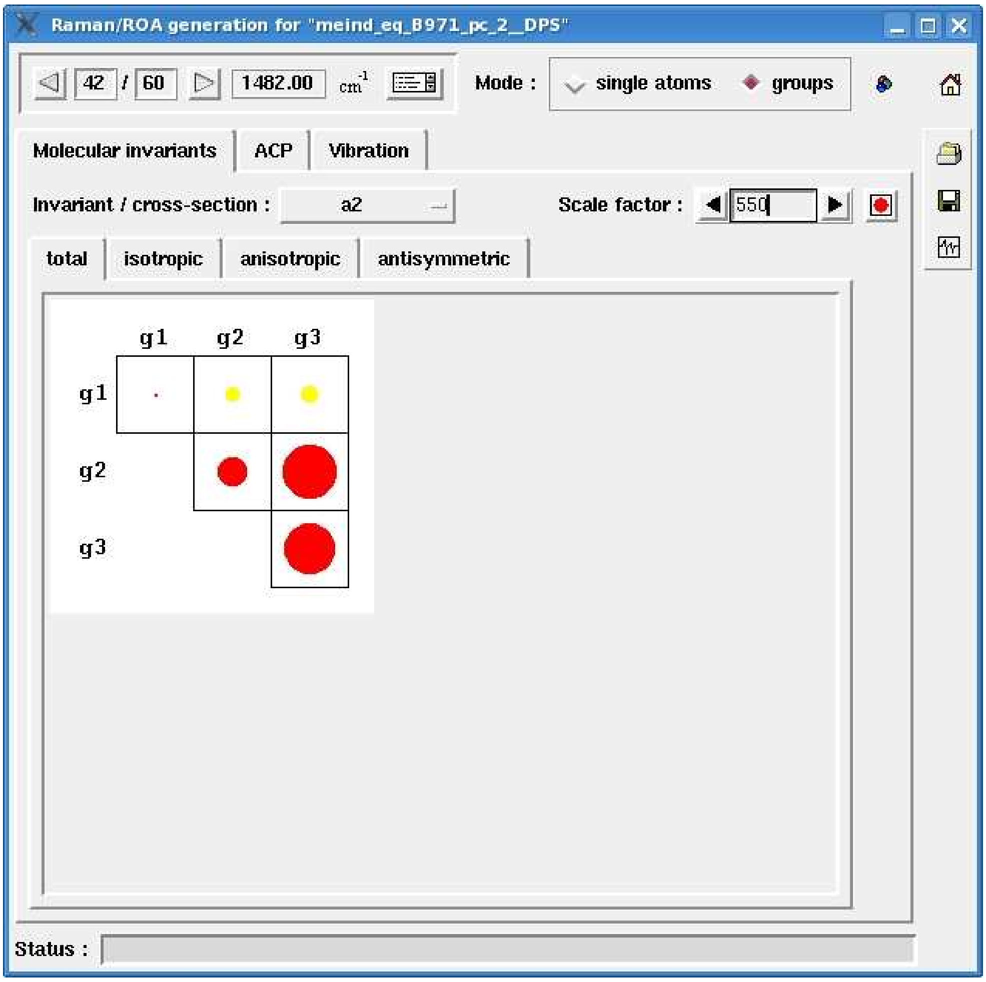


Figure 44. Group coupling matrix for three groups.

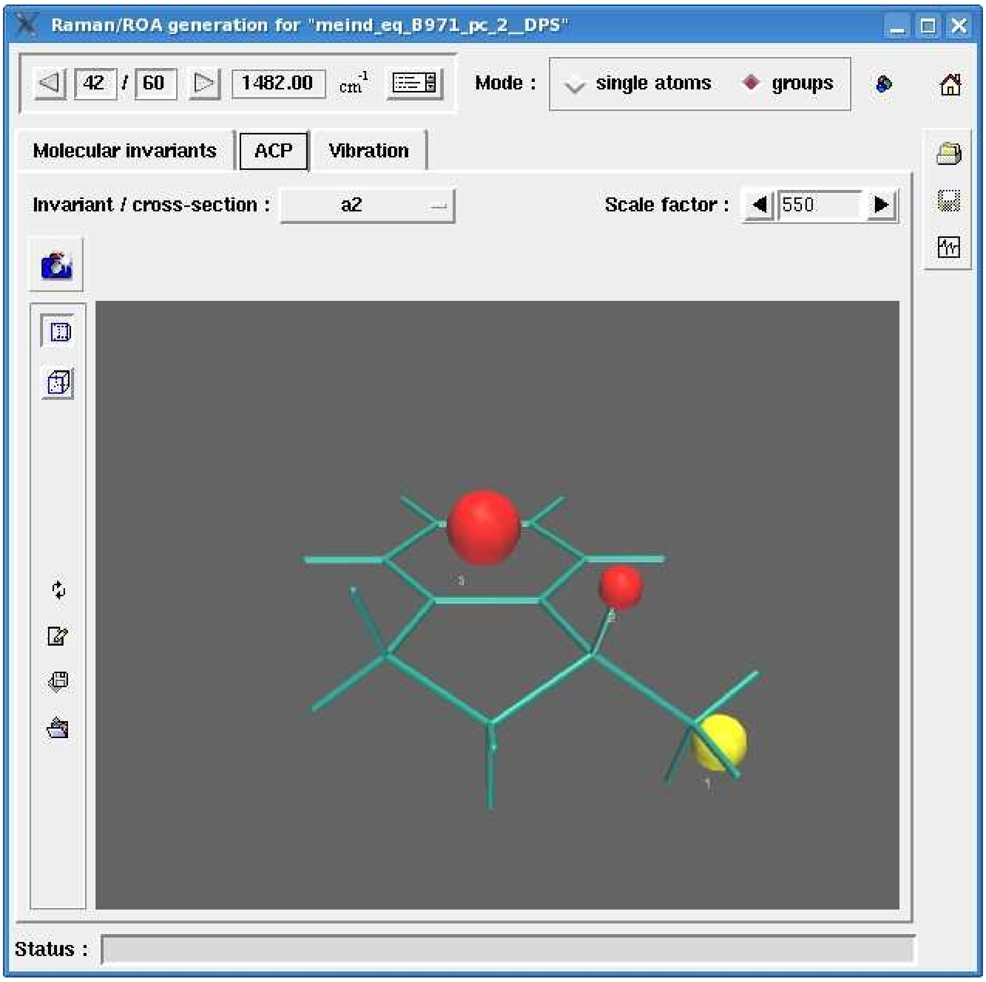


Figure 45. Group contribution pattern for three groups. The spheres are located in the centers of gravity of the groups.

4.10 IR / VCD generation interface

To be completed in a future version of PyVib2.

4.11 Plotting Spectra

The user can plot Raman, ROA, Degree of circularity, IR, VCD and g spectra in the curve and stick representation.

4.11.1 Raman / ROA / Degree of circularity spectra for a single molecule

This window is invoked from the **Molecule|Spectra|Raman / ROA / Degree of circularity** menu of a molecule's thumbnail or from the **Spectra|Raman / ROA / Degree of circularity** menu of a molecule window or by pressing the button on the button toolbar of the **Raman / ROA generation interface**. The GUI window consists of a top panel, vertical button toolbar at the right side of the window, a spectra canvas and a status bar, which shows where the mouse pointer is.

Top panel

Allows to choose the scattering and representation type. The GUI elements are :

- **Scattering option** menu

  Available choices are :

  → **Backward**

    Backward scattering in a scattered circular polarization (SCP) experiment.

  → **Forward**

    Forward scattering in a SCP experiment.

- **Representation** option menu

  → **Curves**

    Plot the spectra in the curves representation.

→ **Stick**

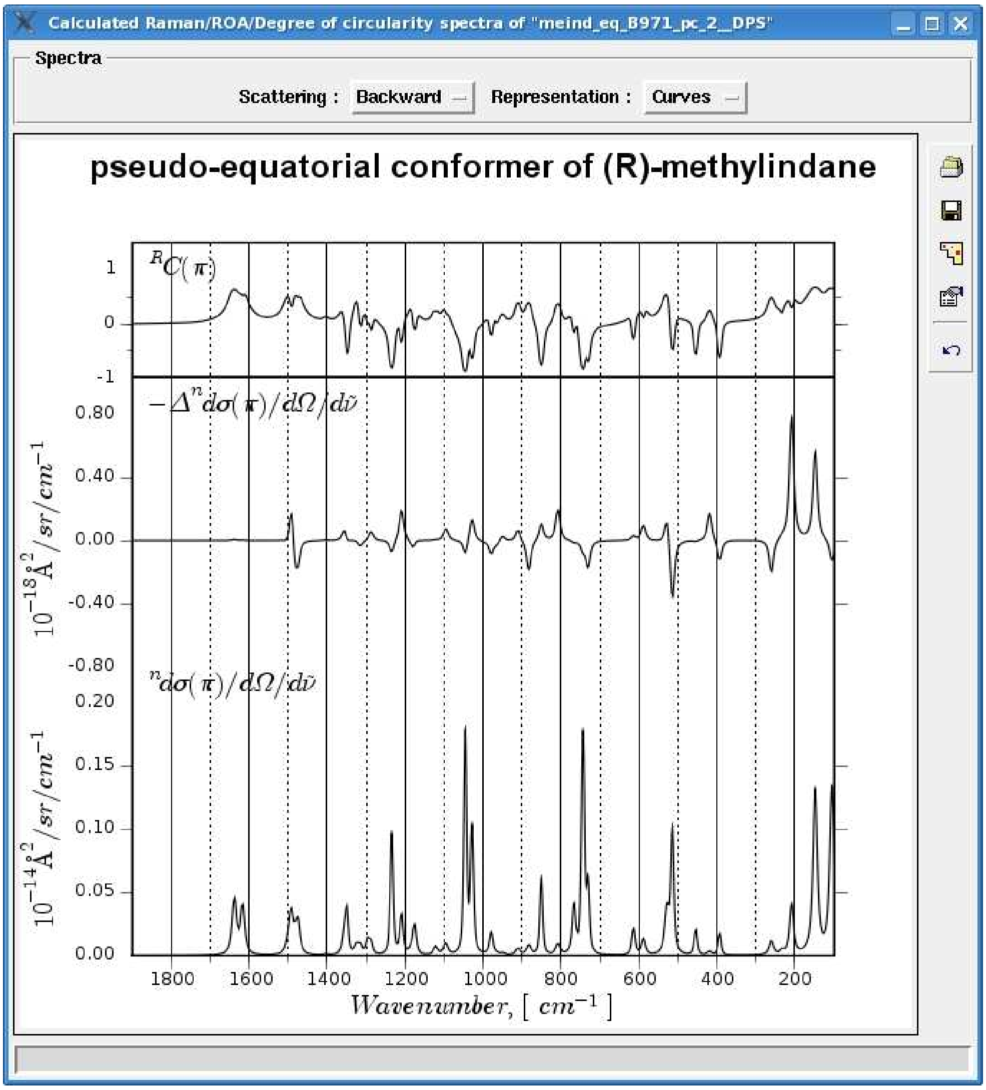
Plot the stick spectra.

Button toolbar

Button	Explanation
🗗	Create a clone of the window.
💾	Save the spectra in the PS, EPS or PDF (ps2pdf is required) formats.
▦	Start the Raman/ROA generation interface. See section 4.9.
📋	Spectra settings. See section 4.11.2.
↶	Restore the previous plotting region.

Spectra canvas

Examples of spectra in the curve and stick representations are shown on figures 46 and 47.



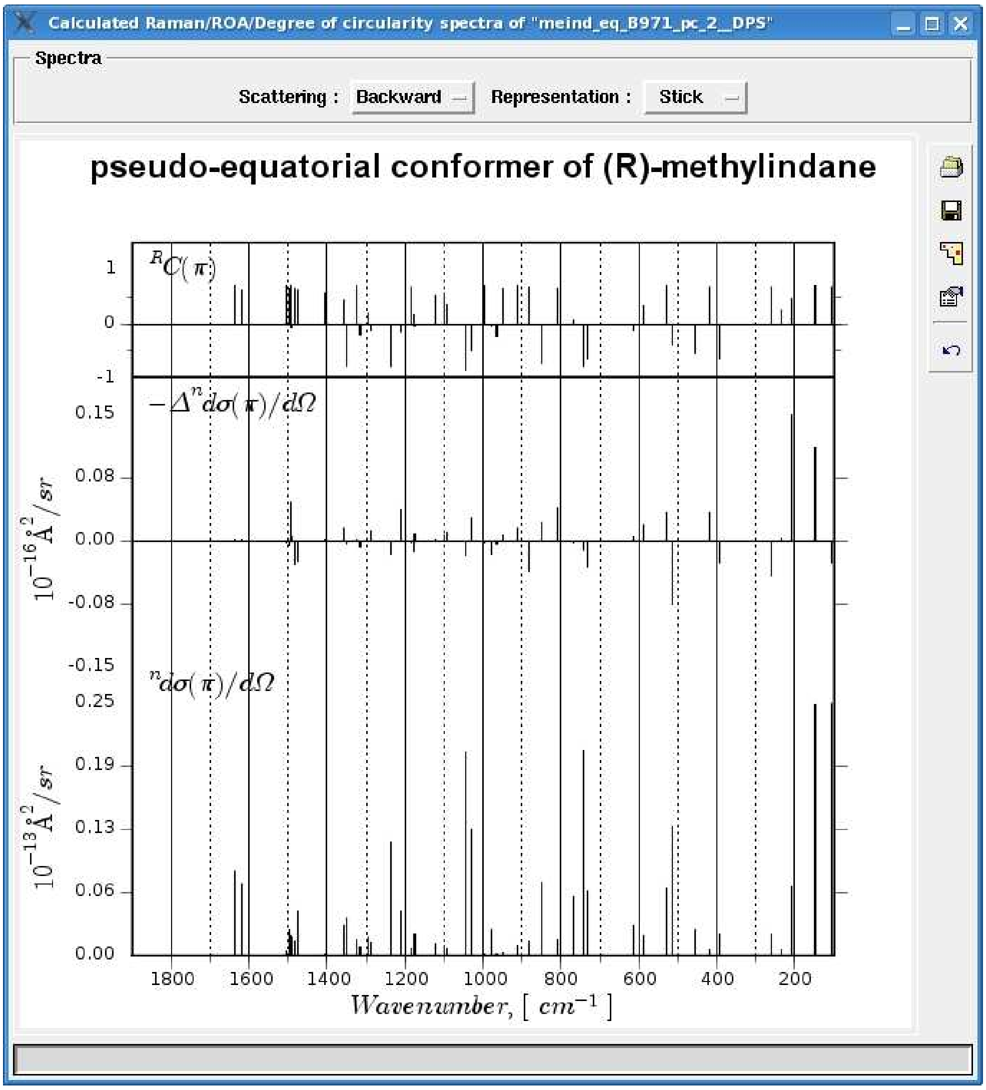
Calculated Raman/ROA/Degree of circularity spectra of "meind_eq_B971_pc_2__DPS"

Spectra

Scattering : Backward

Representation : Curves

Figure 46. Raman/ROA/Degree of circularity spectra in the curve representation.



Calculated Raman/ROA/Degree of circularity spectra of "meind_eq_B971_pc_2__DPS"

Spectra

Scattering : Backward

Representation : Stick

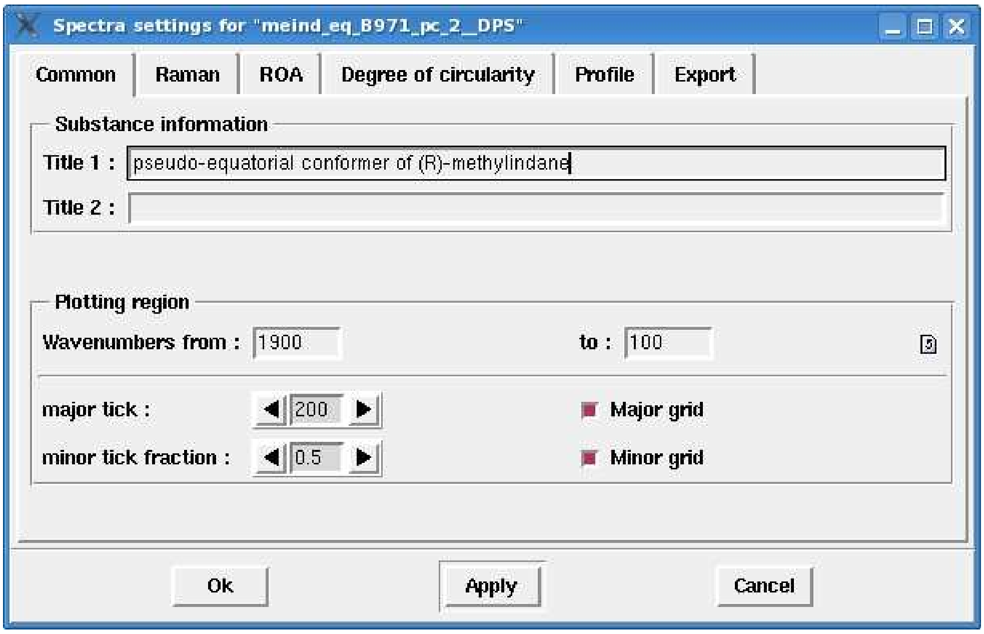
Figure 47. Raman/ROA/Degree of circulartiry spectra in the stick representation.

Clicking within the spectra canvas pops up a window with a vibration, closest to the current position of the mouse pointer, see section 4.11.3. There are two possibilities of zooming : zooming in the x direction (wavenumbers) and in both x and y directions, y is the y axis of the axes over which the mouse pointer is. To zoom in the x direction, press the left mouse button and drag until the desired region of wavenumbers is covered. A red rectangle is shown during the dragging. To zoom in both x and y direction use the right mouse button instead. A blue rectangle is then shown. Pressing ↶ on the button toolbar allows to return to the previous plotting region.

4.11.2 Spectra settings dialog (single molecule, see section 4.11.1)

The dialog is invoked by pressing the 📝 button on the toolbar of a window with spectra for a single molecule.

Common tab



Title 1 : pseudo-equatorial conformer of (R)-methylindane

Title 2 :

Wavenumbers from : 1900 to : 100

major tick : 200

minor tick fraction : 0.5

☑ Major grid

☑ Minor grid

Figure 48. Common tab of the Raman/ROA/Degree of circularity spectra settings dialog for a single molecule.

The GUI elements are :

- **Substance information** panel
  - → **Title 1**

    Text at the top of the spectra.

  - → **Title 2**

    Text unter the Title1 in a smaller font.

- **Plotting region** panel

    → **Wavenumbers from** and **to** entry fields

    Start and end of the wavenumbers interval.

    → 🗎 button

    Set the wavenumbers interval to be equal to (1900, 100).

    → **major tick** (grid) counter and the associated check box

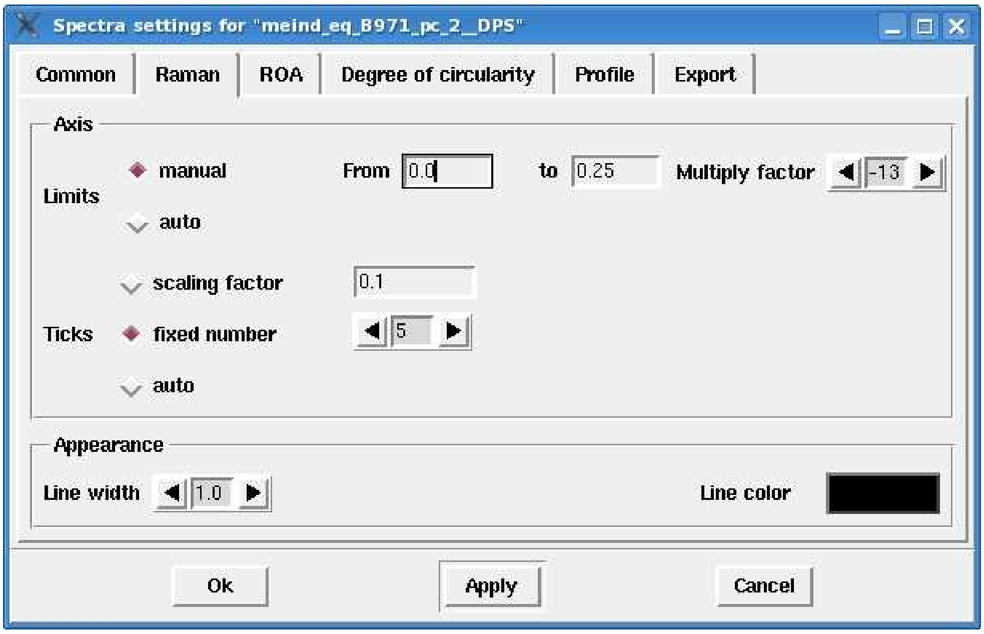
    Whether or not the major ticks should be rendered with a specified step.

    → **minor tick** (grid) counter and the associated check box

    Whether or not the minor ticks should be rendered with the step defined as a fraction of the major stick step.

Raman, ROA and Degree of circularity tabs

These tabs are of the same kind. One can adjust the settings of the correspondent axes.



Spectra settings for "meind_eq_B971_pc_2__DPS"

Axis

Limits ● manual From 0.0 to 0.25 Multiply factor -13

○ auto

Ticks ○ scaling factor 0.1

● fixed number 5

○ auto

Appearance

Line width 1.0

Line color

Figure 49. Raman tab of the Raman/ROA/Degree of circularity spectra settings dialog for a single molecule.

The GUI elements are :

- **Axis** panel

    → **Limits** radio box

    – **manual**

    Set the y limits of the axis manually. Enter these values together with the multiply factor to the correspondent controls.

    – **auto**

Automatic normalization to the biggest peak.

→ **Ticks** radio box

  – **scaling factor**

    Set the scaling factor of the y axis manually.

  – **fixed number**

    Render a fixed number of the ticks.

  – **auto**

    The render engine decides how to perform the rendering of the ticks.

- **Appearance** panel

  → **Line width** counter

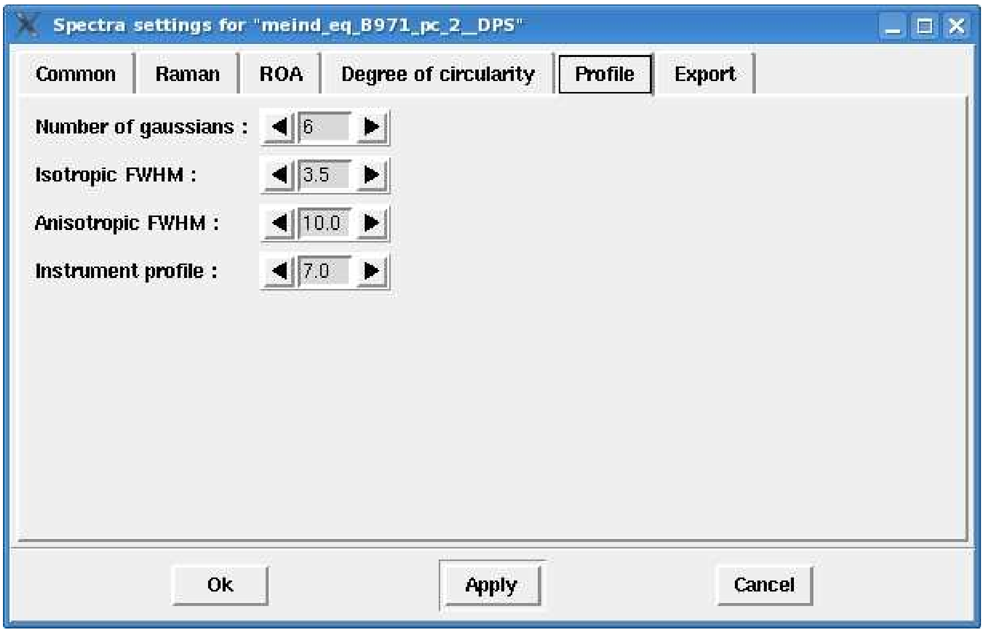
  Set the line width.

  → **Line color** button

  Set the line color using the standard color choosing dialog (specific to the user's operating system).

Profile tab

Set up options for the profiles of the curves. The profile of the calculated bands is considered to be Lorentz, which is approximated as a linear combination of a fixed number of Gauss functions. The profile of the instrument is considered to be Gauss. The approximated Lorentz profile is convoluted then with the instrument profile. This technique is described in detail in [10].



Spectra settings for "meind_eq_B971_pc_2__DPS"

Number of gaussians : 6

Isotropic FWHM : 3.5

Anisotropic FWHM : 10.0

Instrument profile : 7.0

Figure 50. Profile tab of the Raman/ROA/Degree of circularity spectra settings dialog for a single molecule.

The GUI elements are :

- **Number of gaussians** counter

  Number of gauss functions for approximating a Lorentz curve.

- **Isotropic FWHM** counter

  Full width at half maximum (FWHM) for the contributions of the isotropic invariants.

- **Anisotropic FWHM** counter

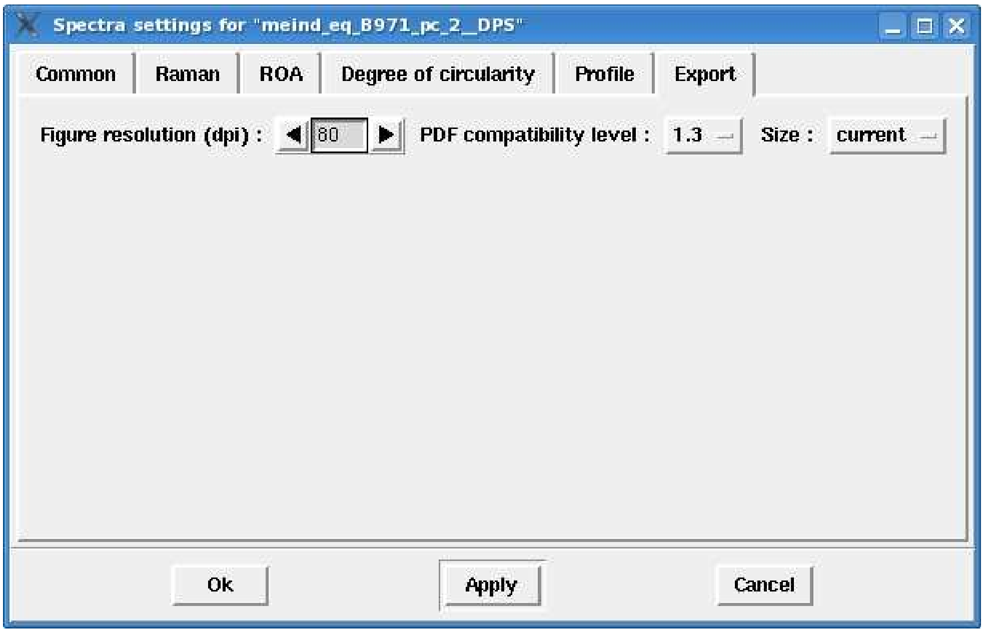
  FWHM for the contributions of the anisotropic invariants.

- **Instrument profile** counter

  FWHM of the Gauss profile of the instrument.

Export tab

Set up options for exporting the spectra canvas.



Spectra settings for "meind_eq_B971_pc_2__DPS"

Figure resolution (dpi) : 80

PDF compatibility level : 1.3

Size : current

Figure 51. Export tab of the Raman/ROA/Degree of circularity spectra settings dialog for a single molecule.

The GUI elements are :

- **Figure resolution (dpi)** counter

  The resolution in dots per inch.

- **PDF compatibility level** option menu

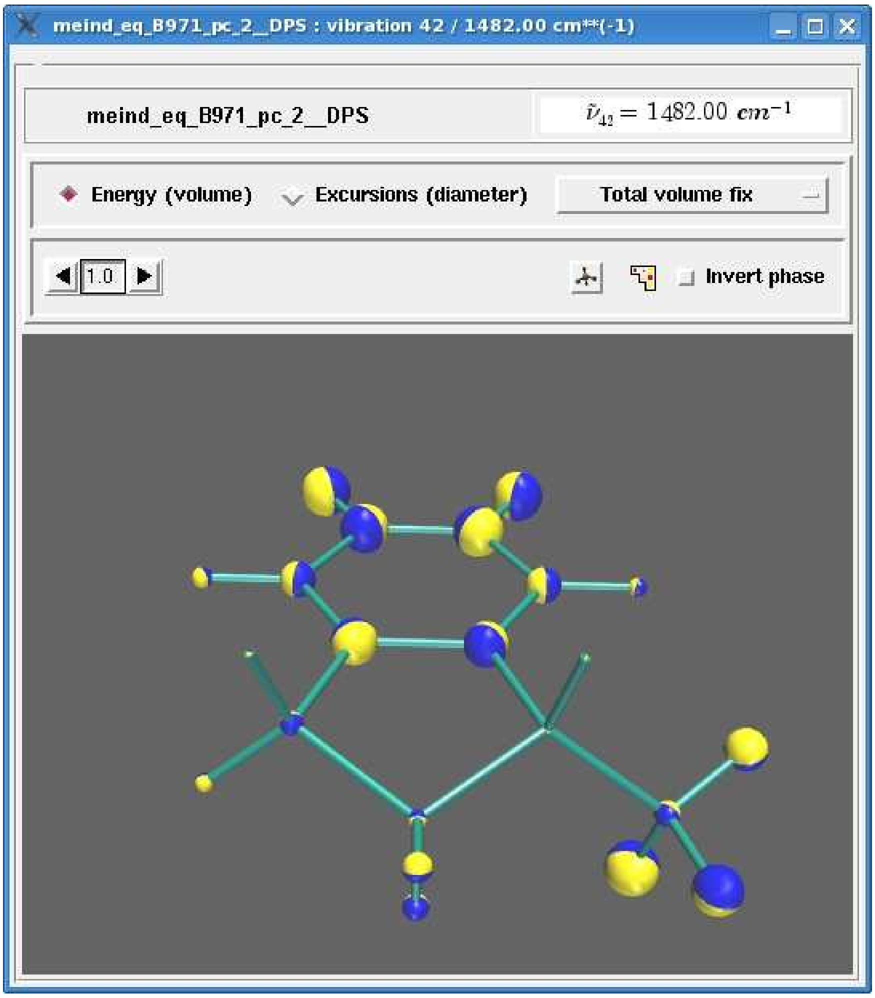
  PDF encryption level. See the manual page of ps2pdf.

- **Size** option menu

  Specifies whether the current size of the spectra canvas or the size of an A4 page should be used.

4.11.3 Single vibration window

The window is popped up when one clicks on a band of a spectrum.



meind_eq_B971_pc_2__DPS : vibration 42 / 1482.00 cm**(-1)

meind_eq_B971_pc_2__DPS

$\tilde{\nu}_{42} = 1482.00\ cm^{-1}$

◆ Energy (volume) ◇ Excursions (diameter) Total volume fix

1.0

☐ Invert phase

Figure 52. Single vibration window.

The following elements make up the GUI :

- Molecule name read-only label

  Molecule name.

- Vibration information widget

  Shows the number of the vibration and its wavenumber in cm^{-1}.

- **Energy (volume)** and **Excursions(diameter)** radio box with the associated option menu

  Options for representation of vibrational motion. See section 4.7.4.

- **Scale factor** counter

  A number with which the amplitudes of vibrational motion are multiplied.

- ⊹ button

  Show the structure of the molecule.

- ▦ button

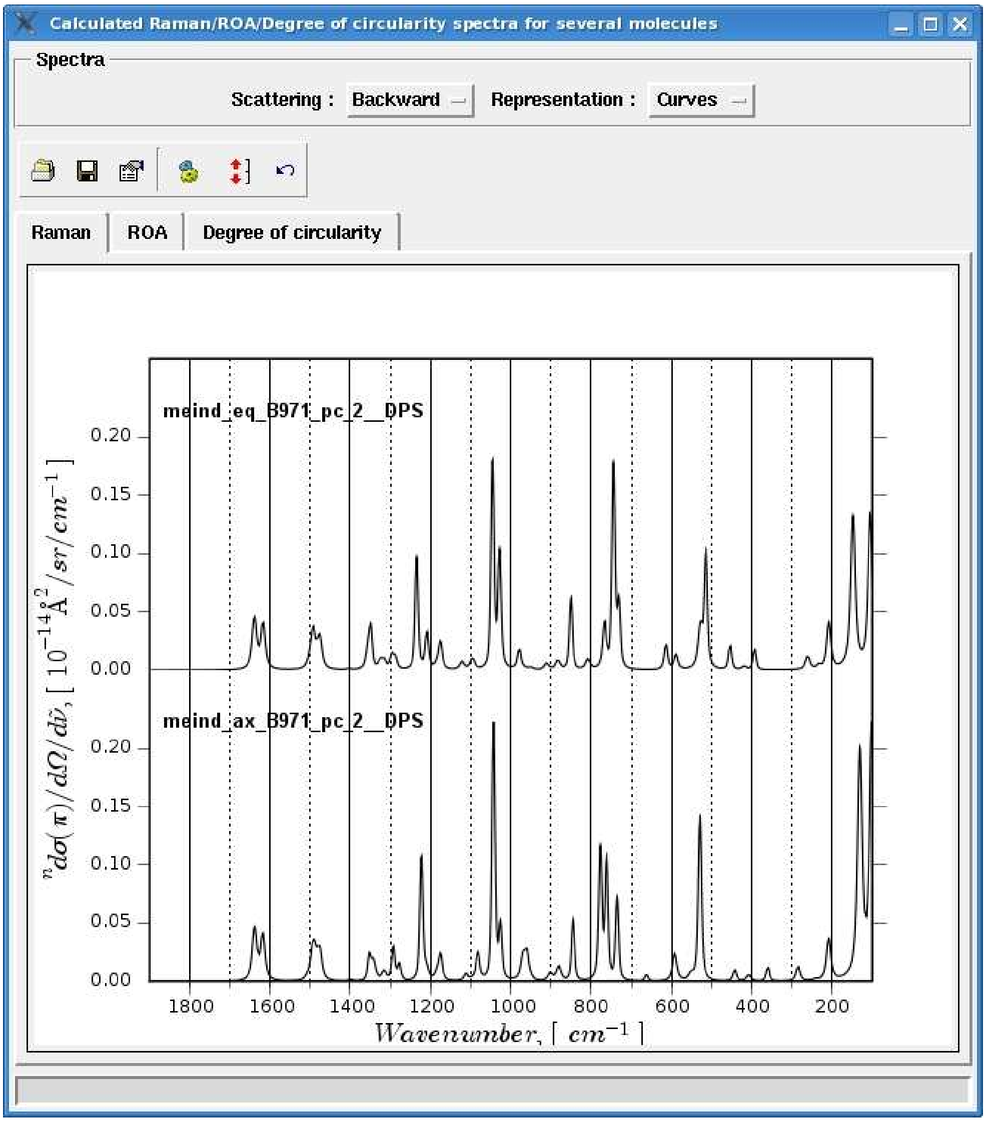
Start the **Raman/ROA generation interface**. See section 4.9.

- **Invert phase** check box

  Invert the phase of vibrational motion. In praxi, the colors of the hemispheres are interchanged.

4.11.4 Raman / ROA / Degree of circularity spectra for several molecules

The window is invoked by pressing the button on the button toolbar of the main application window (at least two thumbnails with the Raman/ROA data must be checked).



Scattering : Backward

Representation : Curves

Figure 53. Raman tab of the window.

Top panel

Allows to choose the scattering and representation type of the spectra as was already described in section 4.11.1.

Button toolbar

Button	Explanation
🖨	Make a clone of the window.
💾	Save the active spectra in PS, EPS or PDF (ps2pdf is required) formats.
📝	Spectra settings. See section 4.11.5.
⚙	Correlate vibrational motion of the molecules the spectra of which are plotted.
↕]	Adjust the y-scale of the active spectra.
↶	Restore the previous plotting region.

Spectra canvas

The spectra of the single molecules plotted under each other are on the three tabs. Within one tab the spectra have the same y-scale.

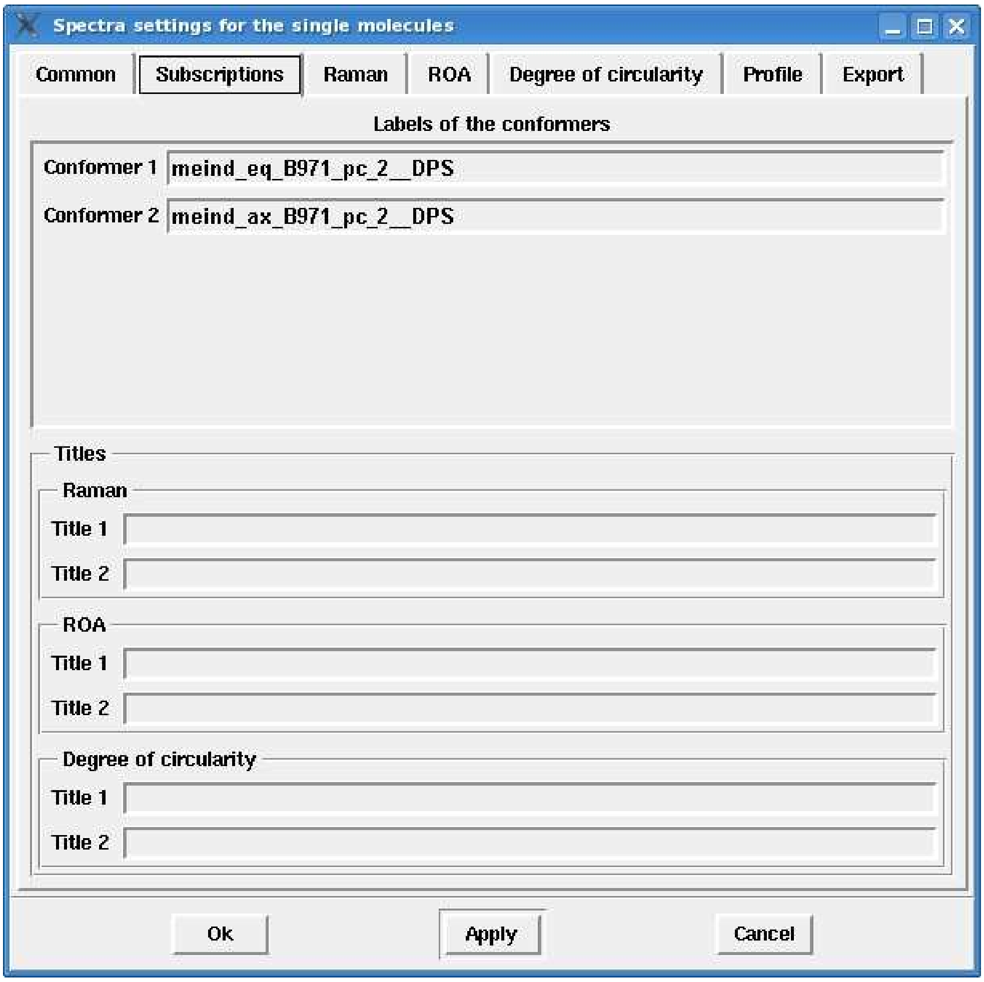
4.11.5 Spectra settings (several molecules, see section 4.11.4)

The dialog is invoked by pressing the 📝 button on the toolbar of a window with spectra for several molecules.

Common tab

See section 4.11.2.

Subscriptions tab



Conformer 1 meind_eq_B971_pc_2__DPS

Conformer 2 meind_ax_B971_pc_2__DPS

Figure 54. Subscriptions tab of the Raman/ROA/Degree of circularity spectra settings dialog for several molecules.

The user can change the labels for the molecules and the titles on all the tabs.

Raman, ROA, Degree of circularity tabs

See section 4.11.2. The settings are applied to all the spectra plotted on the correspondent tab.

Profile tab

See section 4.11.2.

Export tab

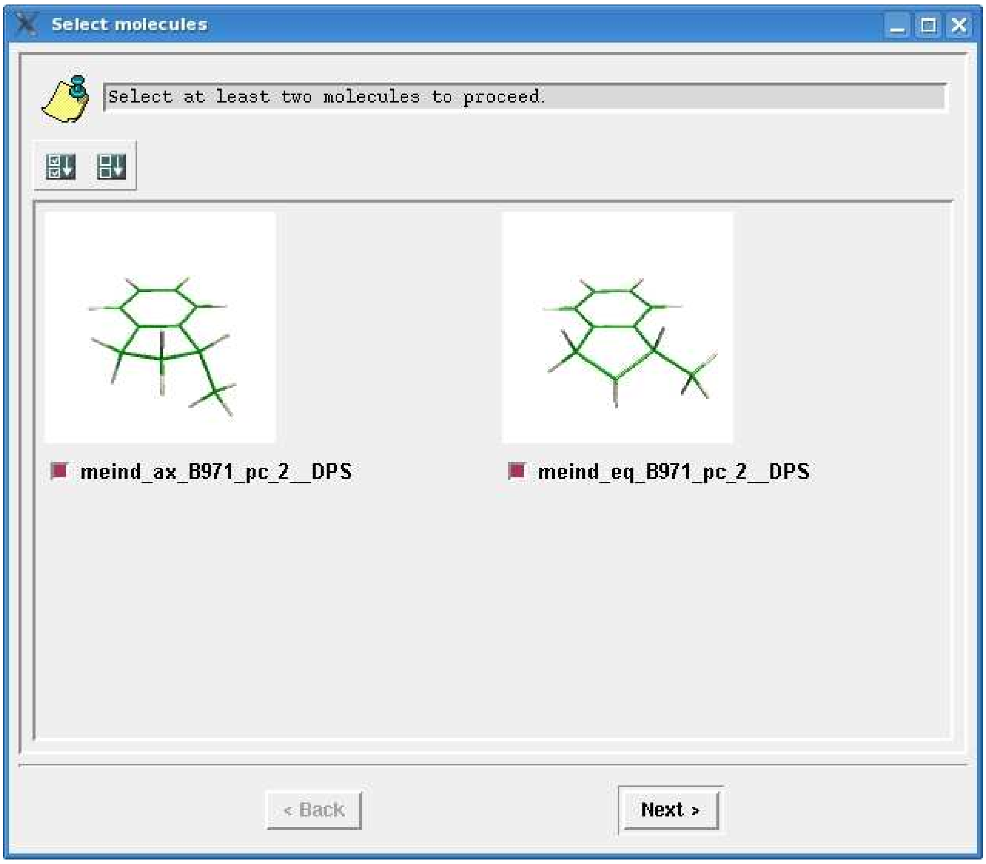
See section 4.11.2.

4.11.6 Raman / ROA / Degree of circularity spectra of a mixture of conformers

This window is invoked by pressing the button on the button toolbar of the main window of PyVib2. The user must select at least two conformers the spectra of which are to be “mixed”. It is assumed that the composition of the mixture of the conformers is determined through their Gibbs energies according to the Boltzmann energy distribution at a temperature of 298.15 K. In praxis, the user can select arbitrary molecules, for which the Boltzmann distribution does not make physical sense. That is why the term “molecule” is used bellow. The GUI is implemented as a wizard with two steps.

Step 1

In a first step, one has to select the molecules. They are represented exactly in the same way as in the thumbnails pane of the main window of PyVib2.



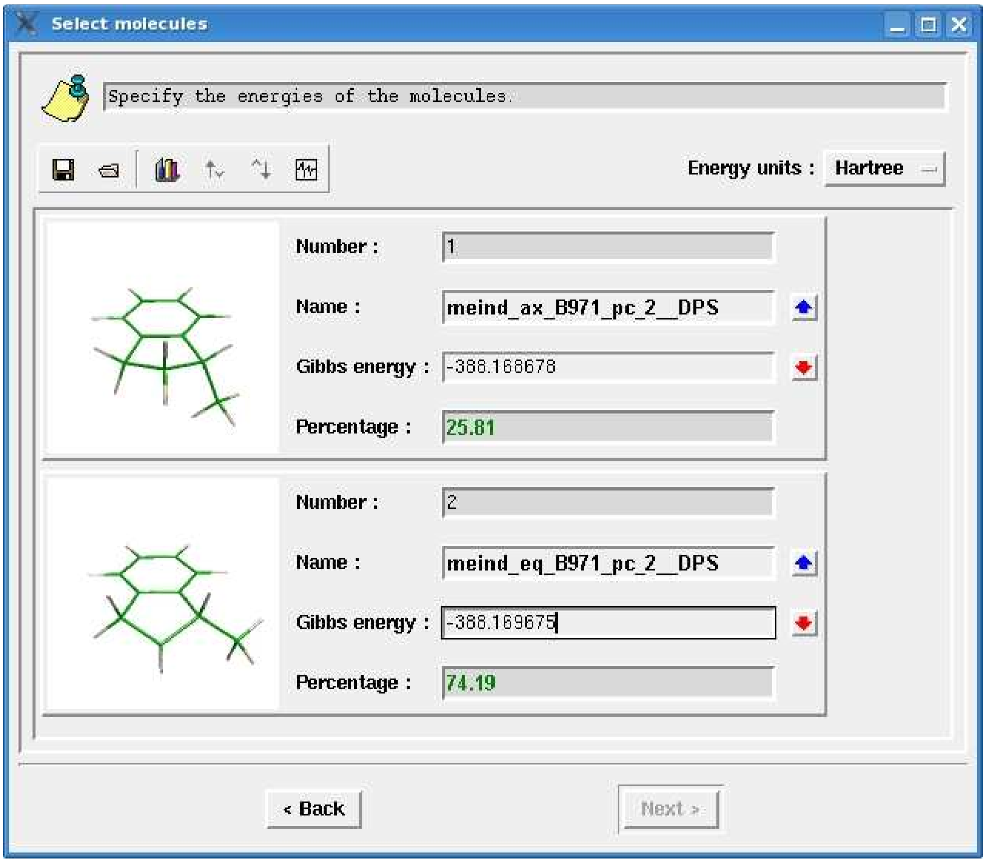
Select at least two molecules to proceed.

Figure 55. Step 1 of the wizard.

The button toolbar at the top allows the selection (leftmost button) or deselection (rightmost button) of all the molecules.

Step 2

In a second step, the energies of the selected molecules can be specified.



Select molecules

Specify the energies of the molecules.

Energy units : Hartree

Number : 1
Name : meind_ax_B971_pc_2__DPS
Gibbs energy : -388.168678
Percentage : 25.81

Number : 2
Name : meind_eq_B971_pc_2__DPS
Gibbs energy : -388.169675
Percentage : 74.19

Figure 56. Step 2 of the wizard.

Significance of the buttons on the button toolbar at the top :

Button	Explanation
💾	Save the energies of the molecules in a file.
📂	Load the energies of the molecules from a file.
📊	Show a bar chart with the percentages of the molecules.
⇅	Sort the molecules by percentage in ascending order.
⇵	Sort the molecules by percentage in descending order.
📈	Plot the spectra of the mixture.

The **Energy units** option menu allows to choose between Hartree and kJ/mol. The distination of the remaining GUI elements is self-explainary. Finally, press ⎍ on the toolbar to plot the spectra of the mixture.

Spectra of the mixture

On the first tab of this window the spectra of the mixture (according to the Boltzmann energy distribution) are shown in the same way as for a single molecule, see section 4.11.1. On the remaining tabs the spectra of the single molecules are shown, see section 4.11.4.

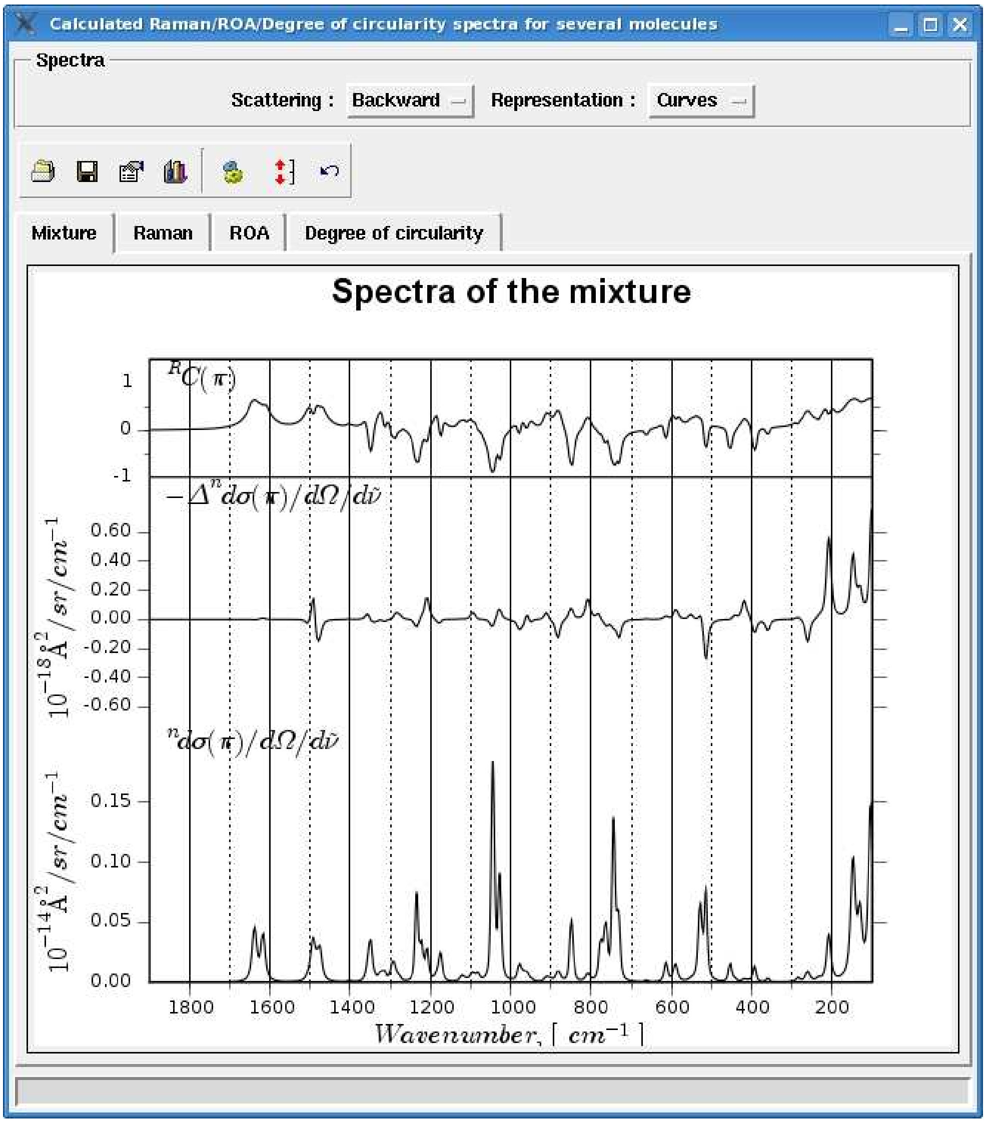


Figure 57. Raman/ROA/Degree of circulartiry spectra of the mixture in the curve representation.

4.11.7 IR / VCD spectra for a single molecule

This window is invoked from the **Molecule|Spectra|IR / VCD** menu of a molecule's thumbnail or from the **Spectra|IR / VCD** menu of a molecule window. The GUI is built exactly in the same was as for the Raman/ROA/Degree of circularity spectra for a single molecule, see section 4.11.1. The quantities being plotted are the molar and integrated absorption coefficients as well as the dimensionless g-values (anisotropy ratio). In the curve representation we plot the molar absorption coefficients, while in the stick representation - the integrated absorption coefficients. For theoretical explanation refer to section 5.5.

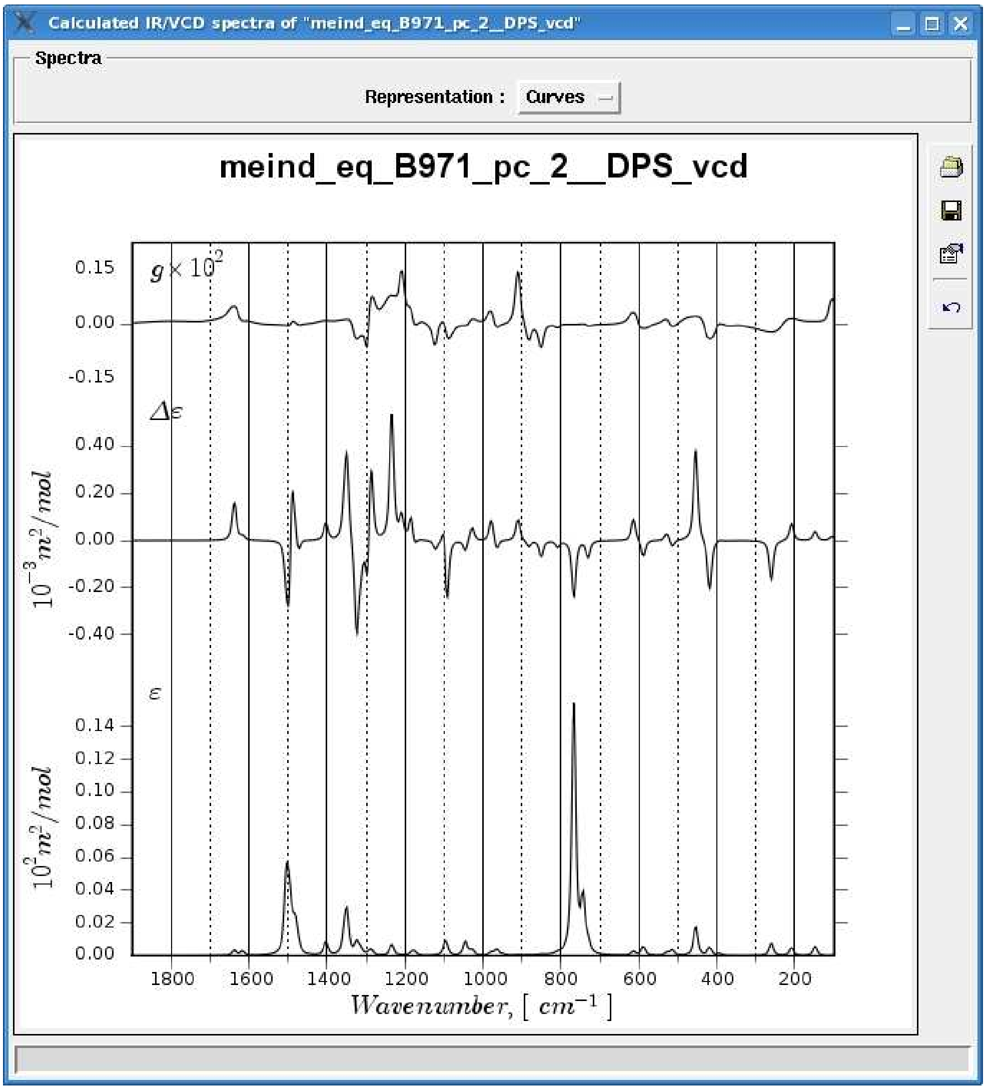
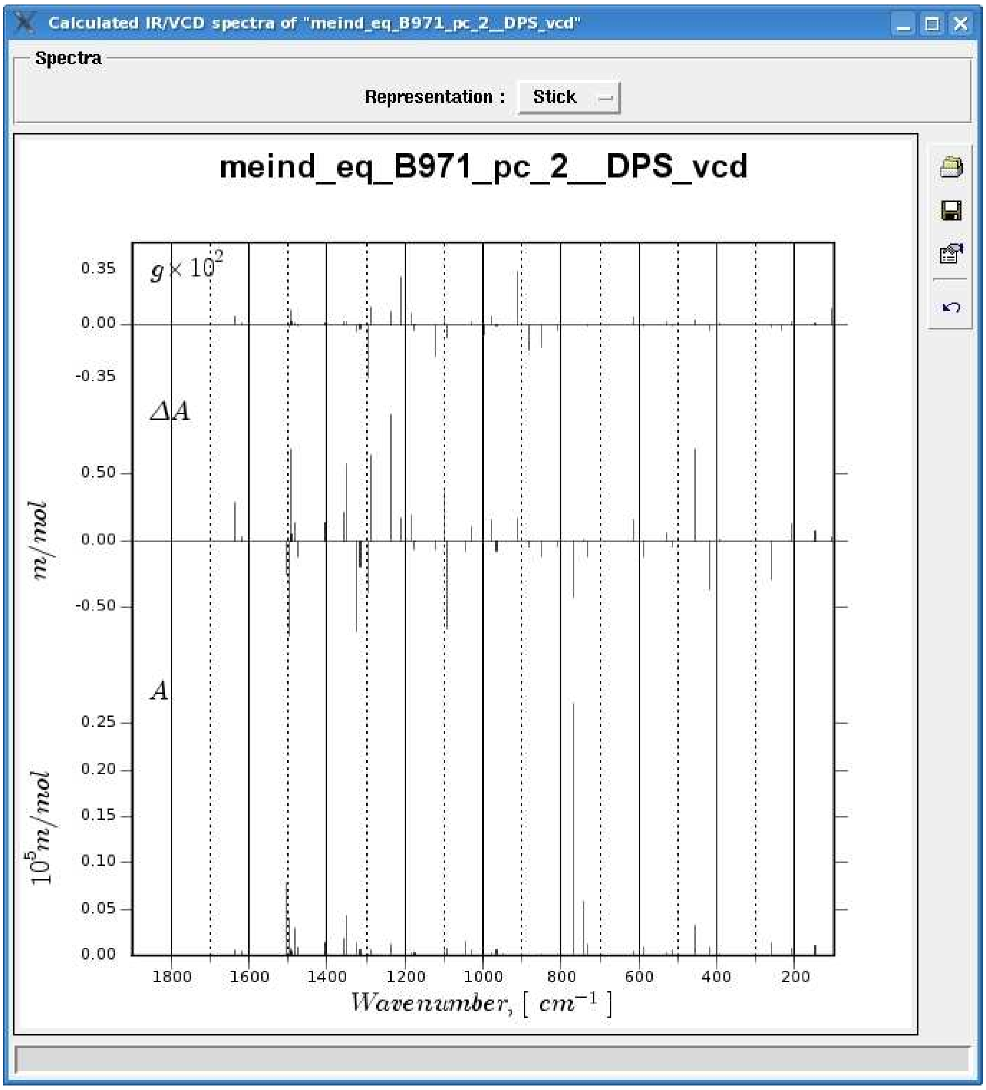


Figure 58. IR/VCD spectra in the curve representation.



Calculated IR/VCD spectra of "meind_eq_B971_pc_2__DPS_vcd"

Representation : Stick

Figure 59. IR/VCD spectra in the stick representation.

4.11.8 Spectra settings dialog (single molecule, see section 4.11.7)

The dialog is invoked by pressing the button on the toolbar of a window with the IR/VCD spectra for a single molecule.

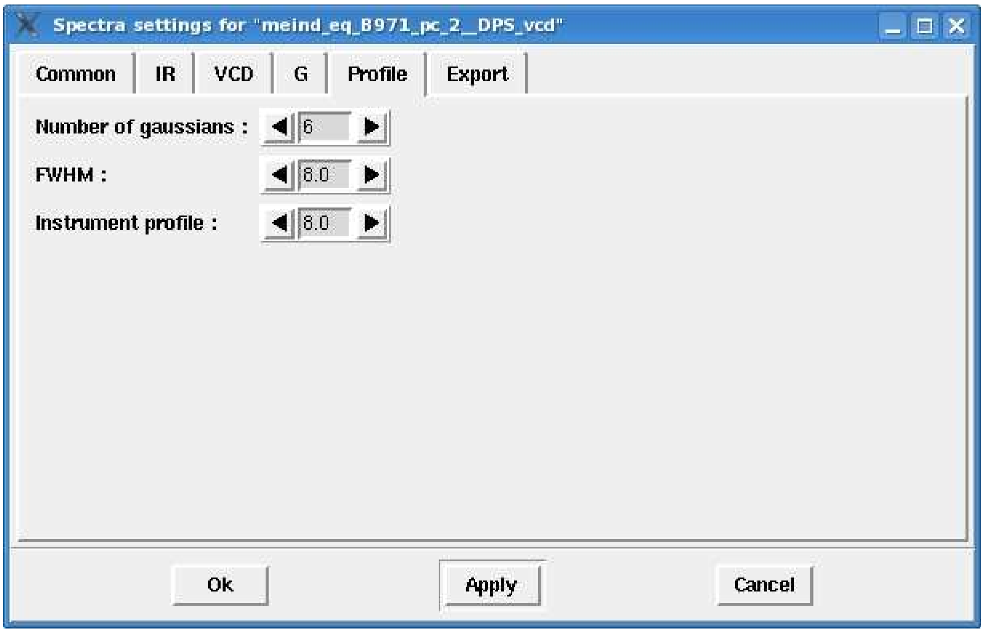
Common tab

See section 4.11.2.

IR, VCD, G tabs

These tabs are built exactly in the same way as the Raman, ROA, Degree of circularity tabs described in section 4.11.2.

Profile tab



Spectra settings for "meind_eq_B971_pc_2__DPS_vcd"

Number of gaussians : 6

FWHM : 8.0

Instrument profile : 8.0

Figure 60. Profile tab of the IR/VCD spectra settings dialog for a single molecule.

The GUI elements are :

- **Number of gaussians** counter
  Number of gauss functions for approximating a Lorentz curve.
- **FWHM** counter
  FWHM of the Lorentz profile of the calculated bands.
- **Instrument profile** counter
  FWHM of the Gauss profile of the instrument.

Export tab
See section 4.11.2.

4.11.9 IR / VCD spectra for several molecules

To be completed in a future version of PyVib2.

4.11.10 Spectra settings dialog (several molecules, see section 4.11.9)

To be completed in a future version of PyVib2.

4.11.11 IR / VCD spectra of a mixture of conformers

To be completed in a future version of PyVib2.

4.12 The pyviblib class library

Apart from the graphical user interface of PyVib2, one can use the functionalities of the program via the class library.

4.12.1 Overview

A short description of the packages is provided below :

pyviblib.
Root package of the class library.

pyviblib.io.
Modules for reading and writing files in different formats.

pyviblib.calc.
Calculation routines e.g. for computing vibrational motion, Raman/ROA as well as IR/VCD tensors.

pyviblib.util.
Help modules for physical constants used throughout the program, the chemical elements and their isotopes (see sections 4.13.1 and 4.13.2) etc.

pyviblib.gui.
Classes comprising the GUI of PyVib2, graphical resources etc.

For a comprehensive description of all the modules refer to the web site of the program. This documentation was automatically generated with pydoc (in the HTML format).

For the data storage and manipulation numpy is used. Array (ndarray) indices are one-based for convenience. See the next subsection for details.

4.12.2 Example session

As an illustration, it will be shown here how to use the pyviblib class library in an interactive Python session. Start a Python shell in order to follow the instructions bellow. For that, type *`python`* in the command prompt or use e.g. the IDLE Python shell.

First, one has to instantiate an appropriate parser object passing the file name as an argument. During the creation of the object the data are extracted from the file and their validity is checked. Let us parse a DALTON output file, where the Raman optical activity of the pseudo-equatorial conformer of (R)-methylindane was calculated. For brevity the full path to the file is omitted.

```
>>> from pyviblib.io import parsers
>>> parser_obj = parsers.DaltonOutputParser('pro_meind_eq_B971_pc_2__DPS.out')
```

After the parser object is created, one can access the data via properties. To retrieve the number of atoms :

```
>>> print parser_obj.Natoms
22
```

The cartesian coordinates (in angstroms) of the molecule are stored as the *`coords`* property. It represents a two-dimensional ndarray whose indices start at one, as was already mentioned in the previous subsection. The first index identifies an atom while the second one relates to the x, y or z coordinate (1, 2 or 3 respectively) of that atom.

```
>>> print parser_obj.coords[6, 1:] # the coordinates of the sixth atom
[-0.80511717 -1.46511648 -0.1721069 ]
>>> print parser_obj.coords[10, 2] # the y coordinate of the tenth atom
-1.52580691892
```

The user might be interested in such classes, defined in the *`pyviblib.io.parsers`* module, as *`FCHKFileParser, MOLDENFileParser, XMolXYZFileParser`* etc.

In a next step, one should create an instance of the *`pyviblib.molecule.Molecule`* class by passing the parser object as an argument to the constructor of the class. It contains all the data which a molecule possesses. It calculates the bonds in the molecule from the cartesian coordinates and examines which data are supplied in the passed parser object. It defines common properties such as *`coords`* or *`masses`* and serveral specific ones, e.g. if the normal modes are available, the *`NFreq`*, *`freqs`*, *`L`* and *`Lx`* properties are set, being the number of vibrations, array with the wavenumbers sorted in ascending order, mass-weighted and cartesian excursions, respectively. If the ROA data are available, the *`raman_roa_tensors`* property is an instance of the *`pyviblib.calc.spectra.RamanROATensors`* class. In our example, the normal modes along with the ROA data are available and so can be accessed as follows :

```
>>> from pyviblib import molecule
>>> mol = molecule.Molecule(parser_obj)
>>> print mol.NFreq # number of vibrations
60
>>> print mol.freqs[1:5] # wavenumbers of the first four vibrations
[ 104.8 147.93 208.47 233.2 ]
>>> print mol.raman_roa_tensors
<pyviblib.calc.spectra.RamanROATensors object at 0xb50ca50c>
```

In such a way the data manipulation with the class library is performed. For details on the usage of certain classes or functions refer to the HTML documentation (**Help|pyviblib Class Library Reference** menu of the main window of PyVib2 or http://pyvib2.sourceforge.net/doc/pydoc/pyviblib.html). As a last example, let us save the data for our test molecule in the MOLDEN format. For that, we will use the *`pyviblib.io.writers`* module :

```
>>> from pyviblib.io import writers
>>> writer_obj = writers.MOLDENFileWriter('meind_eq_B971_pc_2__DPS.mol',
...molecule=mol)
>>> writer_obj.write()
```

4.13 PyVib2 resources

The program stores informations about the chemical elements in two files, located in the util subdirectory of the pyviblib package directory. Should a syntax error be found in these files, the program won't start. Some user specific default settings are saved in ~/.pyvib2rc.

4.13.1 pse.dat

In the pse.dat file a common information about the chemical elements is stored. The format of the file is quite straightforward. Each line describes an element and consists of a number of obligatory and optional fields. Lines starting with # or empty lines are ignored. The six obligatory fields are :

Atomic number (integer).
Atomic number of the element.

Symbol (string).
Symbol of the element (one or two characters).

Standard atomic weight (float).
Standard atomic weight of the element.

Covalent radius (float).
Covalent radius of the element in angstroms.

Van der Waals radius (float).
Van der Waals radius of the element in angstroms.

Diffuse color (string).
Diffuse color of the element in the HTML format e.g. *`#FF0000`* for the red color.

The remaining two optional fields specify the specular and the ambient colors (in the HTML format). The default values for them are white and black, respectively. The default data for hydrogen atoms are :

```
1   H   1.00794   0.37   1.20   #D3D3D3
```

The file can be edited to extend the list of recognized elements or to modify the properties of the existing ones (e.g. the colors). Such properties as the covalent radii can be taken e.g. from http://www.webelements.com/.

4.13.2 isotopes.dat

The isotopes for the elements, specified in the pse.dat file, must be listed in the isotopes.dat file. Each non-empty line, which does not start with #, must contain the atomic number of an element followed by a list of its known isotopes. E.g. for the hydrogen atom :

```
1   1.007825   2.014102   3.016049
```

4.13.3 .pyvib2rc

This file contains some user specific default settings, read by PyVib2 at startup and written when exiting the program. The structure of the file is similar on what one would find on Microsoft Windows INI files. It consists of sections, led by a “[section]” header and followed by “key: value” or ‘’key=value‘‘ entries. At the time being, there are two sections with the following keys :

- **DEFAULT**

  lastdir.
  Last visited directory. The initial directory for the File Open dialog.

  recentfiles.
  A list of recently opened files, shown in the **File|Recent Files** menu of the main window (at most 13 files).

- **Rendering**

  resolution.
  Default VTK resolution. See section 4.6.5.

An example content of the file is shown below :

```
[DEFAULT]
lastdir = /home/fedorovsky/pyviblib/test
recentfiles = ['/home/fedorovsky/pyviblib/test/pro_meind_eq_B971_pc_2__DPS.out',
'/home/fedorovsky/pyviblib/test/1-PE/pro_1_PE_R_B971_pc_2__DPS.dat']

[Rendering]
resolution = 10
```

Note : The program remains silent on errors found in .pyvib2rc.

5 Theoretical background

A brief compendium of the most important concepts and formulae is provided in this section. The informations are taken essentially from [11] [12].

5.1 Vibrational motion

In a molecule with N nuclei there are 3N normal modes Q_p, which represent the true vibrations along with the translations and rotations. The connection of Q_p with the 3N mass-weighted cartesian displacements $q_{\alpha,i}$ for the nuclei α with mass m_α is expressed through the following equations :

$$\mathbf{q} = \mathbf{L} \cdot \mathbf{Q} \tag{1}$$

$$q_{\alpha i} = \sqrt{m_\alpha}\, x_{\alpha i} \tag{2}$$

The transformation matrix $\mathbf{L}$ consists of the 3N eigenvectors $\mathbf{L}_p$ of the Hessian matrix. These vectors as well as the correspondent cartesian excursions $\mathbf{L}_p^x$ are normalized in the following way :

$$\sum_{\alpha=1}^{N} \mathbf{L}_{\alpha,p} \cdot \mathbf{L}_{\alpha,p} = \sum_{\alpha=1}^{N} m_\alpha \mathbf{L}_{\alpha,p}^x \cdot \mathbf{L}_{\alpha,p}^x = 1 \tag{3}$$

There are several possibilities of visualizing $\mathbf{L}_p$ and $\mathbf{L}_p^x$. The usual technique consists in rendering of an arrow on each nucleus α with the length of the arrow proportional to $|\mathbf{L}_{\alpha,p}^x|$. The same cartesian excursions are used to create animations of vibrations. Notwithstanding the clearness of this approach, it is problematically enough to gain simultaneously a good impression of the size and the direction of nuclear motion even for a medium-sized molecule. A proficient solution to this problem has been proposed by W. Hug [11]. The size of vibrational motion on a nucleus can be represented as a sphere centered on the nucleus with the radius depending on the magnitude of the motion. The sphere is to be shaded appropriately to indicate the direction of the motion. Depending on the context, it might be useful to represent $\mathbf{L}_p$ or $\mathbf{L}_p^x$ for a particular purpose.

1. Representation of $\mathbf{L}_p^x$ (cartesian excursions) :

   a) Standard normalization

   The radii of the spheres are proportional to $|\mathbf{L}_{\alpha,p}^x|$. The size of the surfaces of the spheres reflects the importance of nuclear motion for VCD absorption cross-sections but does not for vibrational absorption, Raman and ROA scattering cross-sections upon comparison of different vibrations. The size is strongly dependent on the mass of the nuclei, which leads to smaller contributions of heavier nuclei compared with ones of lighter nuclei.

   b) Zero-point

   The radii of the spheres are proportional to $\left|\mathbf{L}_{\alpha,p}^x\right| / \omega_p$, where $\omega_p = 200\pi c\tilde{\nu}_p$ with $\tilde{\nu}_p$ expressed in cm^{-1}. The size of the surfaces of the spheres reflects the importance of nuclear motion for vibrational absorption, Raman and ROA scattering cross-sections but does not for VCD absorption cross-sections upon comparison of different vibrations. This option has the same disadvantage with the masses as described in a). Additionally to it, low-frequecy vibrations can appear much bigger than high-frequency ones due to the dependence on the wavenumber.

   c) Total surface fix

   Cartesian excursions are renormalized so that $\sum_{\alpha=1}^{N} \mathbf{L}_{\alpha,p}^x \cdot \mathbf{L}_{\alpha,p}^x = 1$. The sum of the surfaces of the spheres is always constant and therefore one does not need to readjust the scale in graphical representations when comparing two arbitrary vibrations. On the other hand, one cannot compare the size of nuclear motion for them. For a given normal mode, the relative size of the surfaces of the spheres reflects the relative importance of nuclear motion for a particular cross-section. The latter is not the case when comparing different modes.

2. Representation of $\mathbf{L}_p$ (vibrational energy distribution) :

   a) Total volume fix

   The volume of the spheres is proportional to $\left|\mathbf{L}_{\alpha,p}\right|^2$. One can see the contribution of the single nuclei to the vibrational energy of a normal mode. This representation is most practical for finding out resemblances of nuclear motion for arbitrary vibrations.

b) Zero-point

The volume of the spheres is proportional to $|\mathbf{L}_{\alpha,p}|^2/\omega_p$. See 1b).

5.2 Overlaps and similarities of vibrational modes

In order to be able to qualitatively compare vibrational motion in molecules, we have introduced the notions of overlap and similarity of vibrational modes.

The overlap $O^F_{p'p}$ of mode p' with mode p on a fragment F is definied by the double contraction of the dyads of their $\mathbf{L}$-vectors on the nuclei of the fragment :

$$O^F_{p'p} = \mathbf{L}^F_{p'}\mathbf{L}^F_{p'} : \mathbf{L}^F_p\mathbf{L}^F_p \tag{4}$$

The similarity $S^F_{p'p}$ of the modes is definied as follows :

$$S^F_{p'p} = \frac{O^F_{p'p}}{|\mathbf{L}^F_{p'}\mathbf{L}^F_{p'}||\mathbf{L}^F_p\mathbf{L}^F_p|} = \frac{\mathbf{L}^F_{p'}\mathbf{L}^F_{p'} : \mathbf{L}^F_p\mathbf{L}^F_p}{\sqrt{\mathbf{L}^F_{p'}\mathbf{L}^F_{p'} : \mathbf{L}^F_{p'}\mathbf{L}^F_{p'}}\sqrt{\mathbf{L}^F_p\mathbf{L}^F_p : \mathbf{L}^F_p\mathbf{L}^F_p}} \tag{5}$$

The overlap characterizes the common component of the modes while the similarity reflects the resemblance of their shapes. Both overlap and similarity are dimensionless quantities, which take values in the range between 0 and 1. If one compares vibrational motion on all the nuclei of two systems with the same number of nuclei, then the overlap is identically equal to the similarity, because of the normalization condition given by equation 3. Our procedure is aware of the fact that the Eckart-Sayvetz conditions are not, in general, satisfied for the fragment F in either of the compared modes. To compensate it, we can subtract out the translational and rotational contaminations from the dyads in equations 4 and 5. In this case we obtain the overlap of the vibrational components of the modes. Several illustrative examples of application of the method can be found in [12] [13] [14].

5.3 Nuclear and Group Coupling Matrices

According to the Placzek polarizability theory approach, calculated Raman and ROA intensities for a normal mode p are expressed as linear combinations of five molecular invariants of the form [11] :

$$J_p = \sum_{\alpha,\beta} J_{\alpha\beta,p} \tag{6}$$

$$J_{\alpha\beta,p} = \frac{\hbar}{400\pi c\Delta\tilde{\nu}_p}\mathbf{L}^x_{\alpha,p}\cdot\mathbf{V}_{\alpha\beta}\cdot\mathbf{L}^x_{\beta,p} \tag{7}$$

Each of the molecular invariants is given as a sum of its dinuclear terms definied by equation 7, where $\mathbf{V}_{\alpha\beta}$ is a dyadic composed of a combination of tensor elements depending on the invariant under consideration. We will limit our discussion here with the Raman and ROA intensities in a scattered circular polarization (SCP) experiment with the naturally polarized (n) incident light. The calculated Raman intensities, considered to be the circular sum differential scattering cross-sections per unit of solid angle of collected light, are expressed through the isotropic and anisotropic molecular invariants a^2 and β^2. For the backward and forward scattering one has :

$$^n d\sigma_{\mathrm{SCP}}(\pi)/d\Omega = {}^n d\sigma_{\mathrm{SCP}}(0)/d\Omega = K\left(90a^2 + 14\beta^2\right), \tag{8}$$

$$K = K_p = \frac{1}{90}\left(\frac{\mu_0}{4\pi}\right)^2\omega_p^3\omega_0 = \frac{10^7}{9}\pi^2\mu_0^2c^4\,\tilde{\nu}_p^3\tilde{\nu}_0, \tag{9}$$

where ω_0 and ω_p are the angular frequencies of the incident and scattered light respectively, μ_0 is the permeability of the vacuum. The calculated ROA intensities, considered to be the circular difference differential scattering cross-sections per unit of solid angle of collected light, are linear combinations of the remaining three molecular invariants aG', β_G^2 and β_A^2. The expressions for the backward and forward scattering are :

$$-\Delta^n d\sigma_{\mathrm{SCP}}(\pi)/d\Omega = \frac{4K}{c}\left(12\beta_G^2 + 4\beta_A^2\right) \tag{10}$$

$$-\Delta^n d\sigma_{\mathrm{SCP}}(0)/d\Omega = \frac{4K}{c}\left(90aG' + 2\beta_G^2 - 2\beta_A^2\right) \tag{11}$$

We use the sign convention for differences of scattering cross-sections because they are defined in agreement with the general sign convention in the field of optical actitivity left minus right circular. Since the involved cross-sections depend on the temperature at which a measurement is conducted, it is necessary to take into consideration the thermal population of vibrational states. To apply the correction, one multiplies all the intensities with the Boltzmann factor $1/\Big(1-e^{-100h\Delta\tilde{\nu}_p c/kT}\Big)$. The SI units of the Raman and ROA intensities are m^2/sr, but from practical reasons we use A^2/sr in PyVib2.

The dinuclear terms of the molecular invariants and of the differential cross-sections represent for a particular vibration a set of square $N \times N$ matrices with N being the number of atoms. We refer to them as *nuclear coupling matrices* (NCMs), which provide us the information on the size and the sign of coupling terms between single atoms. Since in sums of the form 6 only the symmetric part contributes, one can add the off-diagonal halves of the matrices and represent the result in triangular form. This still gives an enormous amount of information. To facilitate its interpretation, one can limit the consideration to several groups of atoms by separately adding up intra-group mono- and di-nuclear terms, and inter-group di-nuclear terms of that atoms. As a result, one obtains so called *group coupling matrices* (GCMs) of the dimension $N_{\mathrm{gr}} \times N_{\mathrm{gr}}$ with N_{gr} being the number of the definied groups.

5.4 Atomic and Group Contribution Patterns

Another possibility to get insight into Raman and ROA generation is the visualization of the contributions of individual atoms definied as :

$$J(\alpha)_p = \sum_{\beta} \left(J_{\alpha\beta,p}\, r(\alpha)_{\alpha\beta,p} + J_{\beta\alpha,p}\, r(\alpha)_{\beta\alpha,p}\right), \tag{12}$$

$$r(\alpha)_{\alpha\beta,p} = \frac{\left|\mathbf{L}^x_{\alpha,p}\cdot\mathbf{V}_{\alpha\beta}\right| + \left|\mathbf{L}^x_{\alpha,p}\cdot\mathbf{V}_{\alpha\alpha}\right|}{\left|\mathbf{L}^x_{\alpha,p}\cdot\mathbf{V}_{\alpha\beta}\right| + \left|\mathbf{L}^x_{\alpha,p}\cdot\mathbf{V}_{\alpha\alpha}\right| + \left|\mathbf{V}_{\boldsymbol{\alpha\beta}}\cdot\mathbf{L}^x_{\beta,p}\right| + \left|\mathbf{V}_{\boldsymbol{\beta\beta}}\cdot\mathbf{L}^x_{\beta,p}\right|} \tag{13}$$

$$r(\alpha)_{\beta\alpha,p} = \frac{\left|\mathbf{V}_{\boldsymbol{\beta\alpha}}\cdot\mathbf{L}^x_{\alpha,p}\right| + \left|\mathbf{V}_{\boldsymbol{\alpha\alpha}}\cdot\mathbf{L}^x_{\alpha,p}\right|}{\left|\mathbf{V}_{\boldsymbol{\beta\alpha}}\cdot\mathbf{L}^x_{\alpha,p}\right| + \left|\mathbf{V}_{\boldsymbol{\alpha\alpha}}\cdot\mathbf{L}^x_{\alpha,p}\right| + \left|\mathbf{L}^x_{\beta,p}\cdot\mathbf{V}_{\beta\alpha}\right| + \left|\mathbf{L}^x_{\beta,p}\cdot\mathbf{V}_{\beta\beta}\right|} \tag{14}$$

where $r(\alpha)_{\alpha\beta,p}$ are weighting coefficients for the dinuclear terms. We refer to the obtained quantitities $J(\alpha)_p$ as *atomic contribution patterns* (ACPs). The weighting coefficients in equtions 13 and 14 are based on the norms of vectors of the form $\mathbf{L}^x_{\alpha,p}\cdot\mathbf{V}_{\alpha\beta}$. The contribution of a single atom is rendered as a sphere centered on the atom with the surface of the sphere proportional to the absolute value of the contribution. For a group of atoms $\mathtt{A}$ one can add the contributions of the atoms comprising the group :

$$J(A)_p = \sum_{\alpha} J(\alpha)_p,\ \alpha \in A \tag{15}$$

We refer to the quantities $J(A)_p$, defined in equation 15, as *group contribution patterns* (GCPs). The contribution of a group is rendered as a sphere, placed in the center of gravity of the group with the surface of the sphere proportional to the absolute value of the contribution.

5.5 Spectra

The expressions for the Raman and ROA intensities were already discussed in the section 5.3. The degree of circularity C is the ratio of the intensity of the circularly polarized component to the total intensity of the scattered radiation defined as [15] :

$${}^{R}C(\pi) = \frac{{}^{R}I_R(\pi) - {}^{R}I_L(\pi)}{{}^{R}I_R(\pi) + {}^{R}I_L(\pi)} = -{}^{R}C(0) \tag{16}$$

and can be calculated from a^2 and β^2 as :

$${}^{R}C(\pi) = \frac{5\beta^2 - 45a^2}{7\beta^2 + 45a^2} \tag{17}$$

To plot infrared vibrational absorption and VCD spectra one has to calculate the molar absorption coefficient and the difference of the molar absorption coefficients for left and right circular light [10] [16] [17], respectively :

$$\varepsilon_p(\tilde{\nu}) = \frac{2\pi^2 N_A}{3\varepsilon_0 h\, c \ln(10)} \tilde{\nu}\, \langle m_p|Q_p|n_p\rangle D_p f_p(\tilde{\nu}_p, \tilde{\nu}), \tag{18}$$

$$\Delta\varepsilon_p(\tilde{\nu}) = \frac{8\pi^2 N_A}{3\varepsilon_0 h\, c^2 \ln(10)} \tilde{\nu}\, \mathrm{Im}\Big\{\langle m_p|Q_p|n_p\rangle \Big\langle m_p\Big|\hat{P}_p\Big|n_p\Big\rangle\Big\} R_p f_p(\tilde{\nu}_p, \tilde{\nu}), \tag{19}$$

$$D_p = \sum_{\alpha,\beta} \mathbf{L}^x_{\alpha,p} \cdot \boldsymbol{V}(D)_{\alpha\beta} \cdot \mathbf{L}^x_{\beta,p}, \tag{20}$$

$$R_p = \sum_{\alpha,\beta} \mathbf{L}^x_{\alpha,p} \cdot \boldsymbol{V}(R)_{\alpha\beta} \cdot \mathbf{L}^x_{\beta,p}, \tag{21}$$

where D_p and R_p are the reduced dipole and rotational strengths [10], ε_0 is the permittivity of the vacuum, N_A is Avogadro's number, $\tilde{\nu}_p$ is vibrational frequency, $f_p(\tilde{\nu}_p,\ \tilde{\nu})$ is a normalized band shape. The elements of the dyadics $\boldsymbol{V}_{\alpha\beta}$ are :

$$\boldsymbol{V}(D)_{\alpha i,\beta j} = \mathrm{Re}\left\{\sum_\mu \left(\frac{\partial \mu_\mu}{\partial x_i^\alpha}\right)_0 \left(\frac{\partial \mu_\mu}{\partial x_j^\beta}\right)_0\right\} = \mathrm{Re}\left\{\sum_\mu P^\alpha_{i\mu} P^\beta_{j\mu}\right\}, \tag{22}$$

$$\boldsymbol{V}(R)_{\alpha i,\beta j} = \mathrm{Re}\left\{\sum_\mu \left(\frac{\partial \mu_\mu}{\partial x_i^\alpha}\right)_0 \left(\frac{\partial m_\mu}{\partial \dot{x}_j^\beta}\right)_0\right\} = \mathrm{Re}\left\{\sum_\mu P^\alpha_{i\mu} M^\beta_{j\mu}\right\}, \tag{23}$$

where $\boldsymbol{\mu}$ stands for the electric and $\boldsymbol{m}$ for the magnetic dipole moment, $P^\alpha_{i\mu}$ and $M^\beta_{j\mu}$ are components of atomic polar tensors (APTs) and atomic axial tensors (AATs) [18][19], respectively.

The dimensionless anisotropy ratio, g_p, can be used to judge the measurability of VCD (should be $>10^{-5}$) [10]. It is defined as :

$$g_p = \frac{\Delta\varepsilon_p}{\varepsilon_p} \tag{24}$$

The integrated absorption coefficients, A_p and ΔA_p, correspond to the area under the plots of the molar absorption coefficient $\varepsilon_p(\tilde{\nu})$ and the difference of the molar absorption coefficients $\Delta\varepsilon_p(\tilde{\nu})$ against wavenumber [20], respectively :

$$A_p = \int_{\text{band}} \varepsilon_p(\tilde{\nu}) d\tilde{\nu} = \frac{2\pi^2 N_A}{3\varepsilon_0 h\, c \ln(10)} \tilde{\nu}_p \langle m_p|Q_p|n_p\rangle D_p \tag{25}$$

$$\Delta A_p = \int_{\text{band}} \Delta\varepsilon_p(\tilde{\nu}) d\tilde{\nu} = \frac{8\pi^2 N_A}{3\varepsilon_0 h\, c^2 \ln(10)} \tilde{\nu}_p\, \mathrm{Im}\Big\{\langle m_p|Q_p|n_p\rangle \Big\langle m_p\Big|\hat{P}_p\Big|n_p\Big\rangle\Big\} R_p \tag{26}$$

The SI units for the molar and integrated absorption coefficients are m^2/mol and m/mol respectively. The integrated absorption coefficient corresponds to the IR intensity calculated by DALTON (Vibrational Frequencies and IR Intensities section) and Gaussian (IR Inten field in the summary section) divided by ln(10).

6 Acknowledgements

The author is very grateful to Prof. Werner Hug for the scientific inspiration and many suggestions for the program. The following people have taken an active part in the testing stage : PhD students Dmytro Dudenko, Patric Oulevey. VOAView (Dr. Jacques Haesler) and pyVib (Dr. Mohamed Zerara) programs were very helpful during the development of PyVib2. Our research group is indebted to the DALTON team for the help in getting started with VROA calculations. The project was supported by the Swiss National Science Foundation under grants number 200020-103750/1 and 200020-112201/1.

Bibliography

[1] DALTON, a molecular electronic structure program, release 2.0. `http://www.kjemi.uio.no/software/dalton/dalton.html`, 2005.

[2] M. J. Frisch et al. Gaussian 03, Revision C.02. Gaussian, Inc., Wallingford, CT, 2004.

[3] J. Haesler. *Construction of a New Forward and Backward Scattering Raman and Raman Optical Activity Spectrometer and Graphical Analysis of Measured and Calculated Spectra for (R)-[$^2H_1$, $^2H_2$, $^2H_3$]-Neopentane*. PhD thesis, University of Fribourg, 2006.

[4] G. Schaftenaar and J.H. Noordik. *J. Comput. Aid. Mol. Des.*, 14(2):123–134, 2000.

[5] Xmol user guide. `http://www.kfa-juelich.de/zam/CompServ/software/graph/xmol/`. Minnesota Supercomputer Center, Inc.

[6] W. Hug, G. Zuber, A. Meijere, A.F Khlebnikov, and H.J. Hansen. *Helv. Chim. Acta*, 84:1–21, 2001.

[7] G. Zuber and W. Hug. *Helv. Chim. Acta*, 87:2208–2233, 2004.

[8] V. Liégeois, O. Quinet, B. Champagne, J. Haesler, G. Zuber, and W. Hug. *Vib. Spectrosc.*, 42:309–316, 2006.

[9] W. Hug, A. Kamatari, K. Srinivasan, H.J. Hansen, and H.R. Sliwka. *Chem. Phys. Lett.*, 76(3):469–474, 1980.

[10] W. Hug and J. Haesler. *Int. J. Quant. Chem.*, 104:695, 2005.

[11] W. Hug. *Chem. Phys.*, 264(1):53–69, 2001.

[12] W. Hug and M. Fedorovsky. *Theor. Chem. Acc.*, 2006. `http://dx.doi.org/10.1007/s00214-006-0185-2`.

[13] M. Fedorovsky. *Computing Letters*, 2(4):233–236, 2006.

[14] W. Hug. *Computing Letters*, 2(4):251–254, 2006.

[15] D.A. Long. *The Raman Effect*. John Wiley & Sons Ltd, Chichester, 2002.

[16] P.J. Stephens, F.J. Devlin, C.S. Ashvar, C.F Chabalowski, and M.J. Frish. *Faraday Discus.*, 99:103–119, 1994.

[17] P.J. Stephens. *J. Phys. Chem.*, 89:748, 1985.

[18] L.A. Nafie. *J. Chem. Phys.*, 79(10):4950–4957, 1983.

[19] L.A. Nafie. *J. Chem. Phys.*, 96(8):5687–5702, 1992.

[20] P.W. Atkins. *Physical Chemistry*. Oxford University Press, 1998.

Index

Glossary

GUI	graphical user interface	6
widget	part of a GUI that allows the user to interact with an application	6
rendering	process of generating an image from a model using computer technologies	6
menu bar	widget which manages a number of menu buttons and dropdown menus	17
dialog	enclosed area on the screen for presenting information or requesting input	20
option menu	single item selection widget	21
entry field	widget for entering or displaying a single line of text	21
check box	widget used to implement on/off selections	21
list box	widget for displaying a set of choices in a scrolled pane	22
VTK resolution	number which reflects the quality of rendering 3D objects	22
camera	viewport in the 3D world	24
counter	entry field with up and down arrow buttons usually used to modify a numeric value	31
image resolution	refers to the spacing of pixels in an image and is measured in dots per inch (dpi)	31
canvas	widget for rendering graphs, spectra etc	40
radio box	widget for displaying a set of choices usually shown as buttons with text	41