

(continued from previous page)

```

#
# input for simulation of absorption and resonance Raman spectra
# using experimental values of transition energy and displacement
# parameters corresponding to the strongly allowed 1-1Ag 1-1Bu transition
# in trans-1,3,5-hexatriene
#
%sim
  Model IMDHO

  AbsRange      38000.0,   48000.0
  NAbsPoints    2000
  AbsScaleMode  Rel

  # resonance Raman intensities will be calculated
  # for all vibrational states with excitation number
  # up to RamanOrder:
  RamanOrder    4

  # excitation energies (cm**-1) for which rR spectra will be calculated:
  RRSE 39500, 39800, 41400

  # full width half maximum of Raman bands in rR spectra (cm**-1):
  RRS_FWHM 10

  RSRange 0, 5000 # spectral range for simulation of rR spectra (cm**-1)
  NRRSPoints 5000 # number of points to simulate rR spectra (cm**-1)

end

$el_states
1
  1 39800.0      150.00    0.0      1.0    0.0    0.0

$vib_freq_gs
9
  1      354.0
  2      444.0
  3      934.0
  4     1192.0
  5     1290.0
  6     1305.0
  7     1403.0
  8     1581.0
  9     1635.0

$sdnc
9 1
      1
  1      0.55
  2      0.23
  3      0.23
  4      0.82
  5      0.485
  6      0.00
  7      0.085
  8      0.38
  9      1.32

```

After the `orca_asa` run the following files will be created:

- `example005abs.dat` contains the simulated absorption spectrum. It is shown in Fig. 5.38.
- `example005.o4.rrs.39500.dat`, `example005.o4.rrs.39800.dat` and `example005.o4.rrs.41400.dat` contain the simulated rR spectra for excitation energies at 39500, 39800 and 41400  $\text{cm}^{-1}$ , respectively. The suffix “o4” stands for the order of Raman scattering specified in the input by keyword `RamanOrder=4`. The rR spectra are shown in Fig. 5.39.
- `example005.o4.rrs.39500.stk`, `example005.o4.rrs.39800.stk` and `example005.o4.rrs.41400.stk` provide Raman shifts and intensities for each vibrational transition. Corresponding vibrational states are specified by the quantum numbers of excited modes.

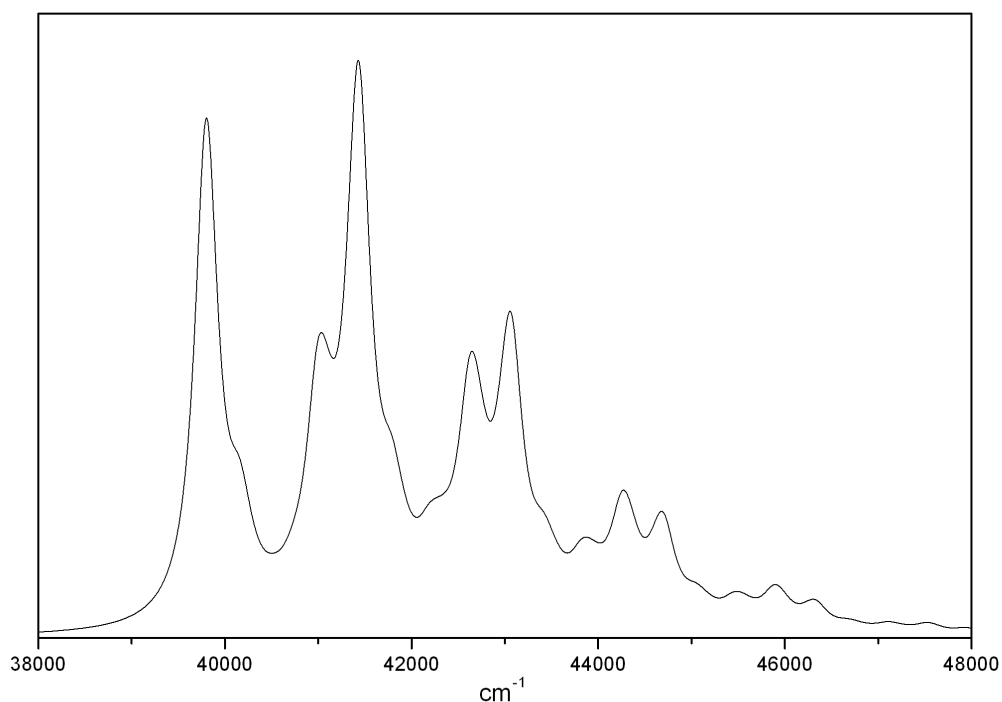


Fig. 5.38: Absorption spectrum corresponding to  $1-^1A_g \rightarrow 1-^1B_u$  transition in *trans*-1,3,5-hexatriene generated after `orca_asa` run on the file `example005.inp`.

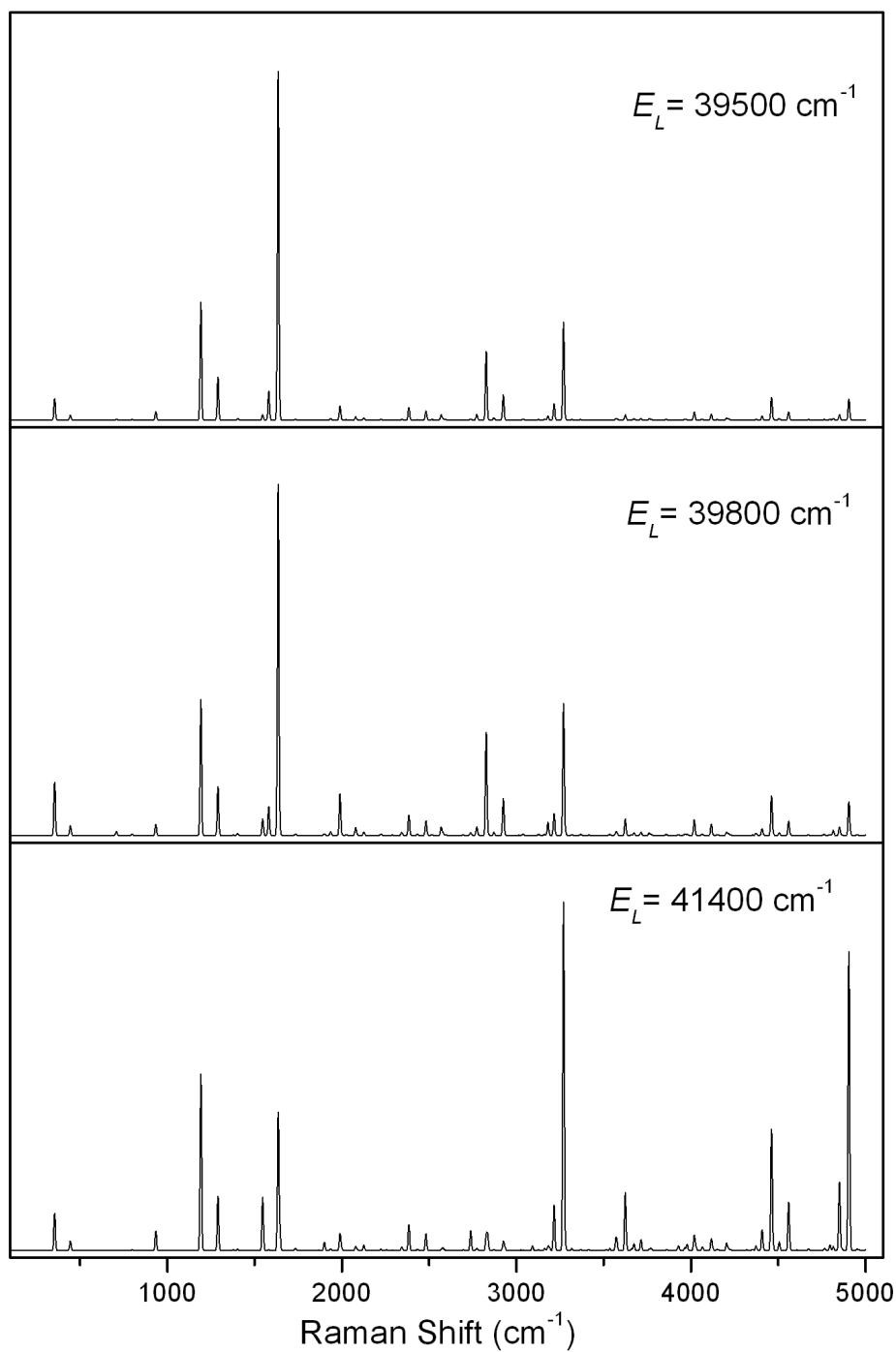


Fig. 5.39: Resonance Raman spectra for 3 different excitation energies which fall in resonance with  $1 \rightarrow 1$   $A_g \rightarrow B_u$  transition in *trans*-1,3,5-hexatriene.

**Note**

- By default the program provides rR spectra on an arbitrary scale since only relative rR intensities within a

single rR spectrum are of major concern in most practical cases. However, one can put rR spectra corresponding to different excitation energies on the same intensity scale by providing the keyword `RSISM=ASR` in `%sim` block (`RSISM` – Raman Spectra Intensity Scaling Mode; `ASR` – All Spectra Relative). By default `RSISM=SSR` (`SSR` – Single Spectrum Relative) for which each rR spectrum is normalized so that the most intense band in it has intensity 1.0. The relative intensities of bands in rR spectra measured for different excitation energies can be compared if they are appropriately normalized relative to the intensity of a reference signal (e.g. Raman band of the solvent). We also keep in mind the possibility to extend our methodology in order to provide the absolute measure of rR intensities in terms of the full or differential cross-sections.

- Within the harmonic model, for a single electronic state neither relative rR intensities nor absorption band-shapes in the case of `AbsScaleMode=Rel` do depend on the values of the electronic transition dipole moment (unless it is precisely zero).

In the example above resonance Raman spectra have been generated for all vibrational transitions with total excitation number up to the value specified by the parameter `RamanOrder`. It is also possible to make explicit specification of vibrational states corresponding to various fundamental, overtone and combination bands via the `$rr_vib_states` block. In such a case rR spectra involving only these vibrational transitions will be generated separately.

```
$rr_vib_states 5 # total number of vibrational transitions
1
  modes 1
  quanta 1; # final vibrational state for the fundamental band corresponding to
↪mode 1
2
  modes 9
  quanta 1; # final vibrational state for the fundamental band corresponding to
↪mode 9
3
  modes 3, 4
  quanta 1, 1; # final vibrational state for the combination band involving
↪single
                                # excitations in modes 3 and 4
4
  modes 5
  quanta 3; # final vibrational state for the second overtone band corresponding
↪to
                                # mode 5
5
  modes 1, 5, 9
  quanta 1, 2, 1; # final vibrational state for the combination band involving
↪single
                                # excitations in modes 1 and 2, and double excitation in mode 5
```

Each vibrational transition is specified via the subblock which has the following structure:

```
k
  modes m1,m2,...mn
  quanta q1,q2,...qn;
```

This means that the  $k$ -th transition is characterized by excitation numbers  $q_i$  for modes  $m_i$  so that corresponding Raman shift is equal to  $\nu = \sum q_i \nu_i$ , where  $\nu_i$  is vibrational frequency of the mode  $m_i$ .

After the `orca_asa` run the following files will be created in addition:

- `example005.us.rrs.39500.dat`, `example005.us.rrs.39800.dat` and `example005.us.rrs.41400.dat` contain the simulated rR spectra involving only vibrational transitions specified in the `$rr_vib_states` block, for excitation energies at 39500, 39800 and 41400  $\text{cm}^{-1}$ , respectively. The suffix “us” stands for “User specified vibrational States”.
- `example005.us.rrs.39500.stk`, `example005.us.rrs.39800.stk` and `example005.us.rrs.41400.stk`

us.rrs.41400.stk provide Raman shifts and intensities for each vibrational transition specified in the \$rr\_vib\_states block.

### Example: Modelling of Absorption Spectrum and Resonance Raman Profiles for the $1^{-1}A_g \rightarrow 1^{-1}B_u$ Transition in *trans*-1,3,5-Hexatriene

The following example illustrates an input for simulation of absorption bandshape and resonance Raman profiles (RRP):

```
#
# example006.inp
#
# input for simulation of absorption and resonance Raman profiles
# using experimental values of transition energy and displacement
# parameters corresponding to the strongly allowed 1-1Ag 1-1Bu transition
# in trans-1,3,5-hexatriene
#

%sim
  Model IMDHO

  AbsRange      38000.0,    48000.0
  NAbsPoints    2000
  AbsScaleMode  Rel

  RRPRange      38000.0, 48000.0 # spectral range for simulation of
                                # rR profiles (cm**1)

  NRRPPoints    2000 # number of points for simulation of rR profiles
  CAR 0.8

  RamanOrder 2
end

$el_states
1
  1  39800.0      150.00    0.0      1.0    0.0    0.0

$vib_freq_gs
9
  1      354.000000
  2      444.000000
  3      934.000000
  4     1192.000000
  5     1290.000000
  6     1305.000000
  7     1403.000000
  8     1581.000000
  9     1635.000000

$sdnc
9 1
      1
  1      0.55
  2      0.23
  3      0.23
  4      0.82
  5      0.485
  6      0.00
  7      0.085
  8      0.38
```

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```
9          1.32
$rr_vib_states 5 # total number of vibrational transitions
1
  modes 1
  quanta 1;
2
  modes 9
  quanta 1;
3
  modes 3, 4
  quanta 1, 1;
4
  modes 5
  quanta 3;
5
  modes 1, 5, 9
  quanta 1, 2, 1;
```

The keyword `RamanOrder=2` will invoke generation of rR profiles for all vibrational transitions with total excitation number up to 2 in the range of excitation energies specified by the keywords `RRPRange` and `NRRPPoints`. Likewise, rR profiles for the vibrational states given in the `$rr_vib_states` block will be generated separately. Since in most cases only relative rR intensities are important, and one would be interested to compare absorption bandshape and shapes of individual rR profiles, the keyword `CAR = 0.8` is used to scale rR profiles for all vibrational transitions by a common factor in such a way that the ratio of the maximum of all rR intensities and the maximum of absorption band is equal to 0.8.

After the `orca_asa` run the following files will be created:

- `example006.abs.dat` contains the simulated absorption spectrum (Fig. 5.40).
- `example006.o1.rrp.dat` and `example006.o2.rrp.dat` contain rR profiles for vibrational transitions with total excitation numbers 1 and 2, respectively. RR profiles for all fundamental bands (from the file `example006.o1.rrp.dat`) are shown in Fig. 5.40.
- `example006.o1.info` and `example006.o2.info` contain specification of vibrational transitions with total excitation numbers 1 and 2, respectively, as well as corresponding Raman shifts.
- `example006.us.rrp.1.dat`–`example006.us.rrp.5.dat` contain rR profiles for vibrational transitions 1–5 specified in the `$rr_vib_states` block.

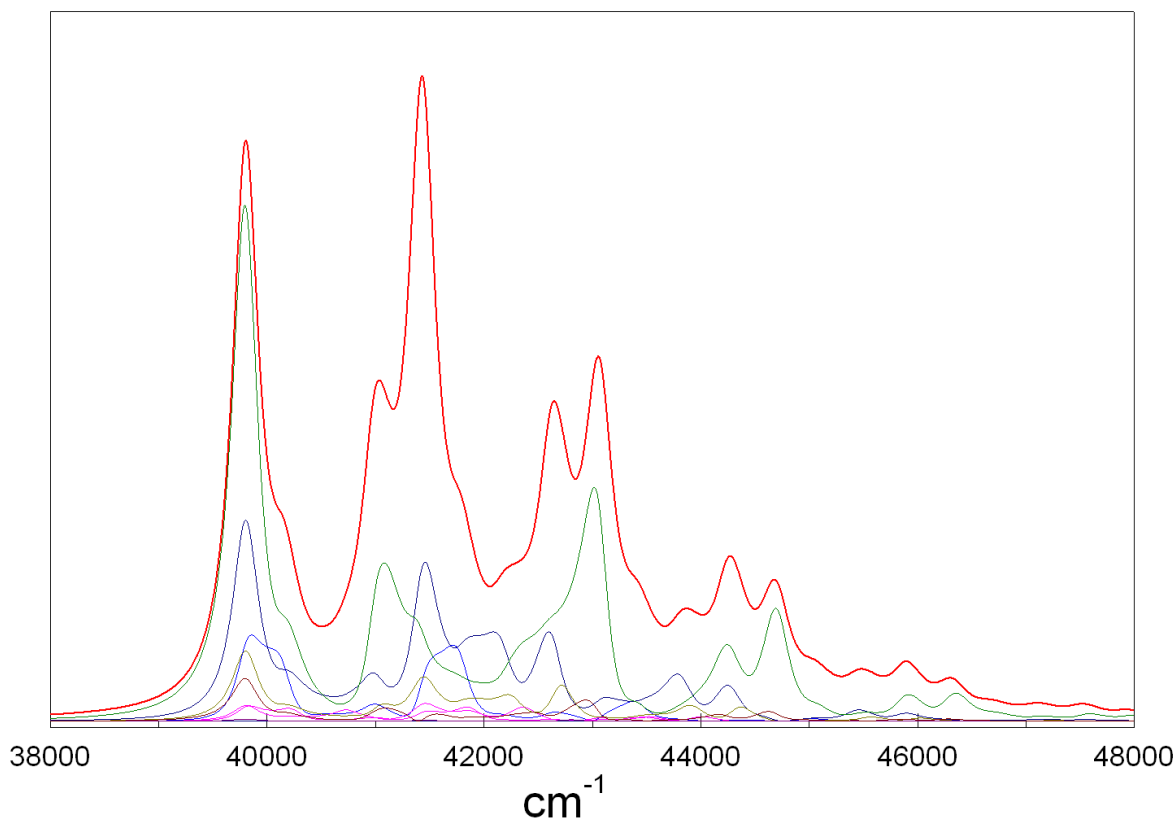


Fig. 5.40: Absorption spectrum and resonance Raman profiles of fundamental bands corresponding to  $1^{-1} A_g \rightarrow 1^{-1} B_u$  transition in *trans*-1,3,5-hexatriene.

### 5.16.3 Fitting of Experimental Spectra

#### Example: Gauss-Fit of Absorption Spectrum

An absorption spectrum basically consists of a number of absorption bands. Each absorption band corresponds to a transition of the ground electronic state to an excited electronic state. In molecules such transitions are usually considerably broadened. In many cases there will be overlapping bands and one would need to deconvolute the broad absorption envelope into contributions from individual transitions. Within the “Simple model” the `orca_asa` program enables fit of an absorption spectrum with a sum of standard lineshape functions (Gaussian, Lorentzian) or more general Voigt functions. In most cases, one simply performs a “Gauss-Fit”. That is, it is assumed that the shape of each individual band is that of a Gaussian function. Then one applies as many (or as few) Gaussians as are necessary for an accurate representation of the absorption envelope. In order to explain the fitting procedures within the “Simple model” let us consider an experimental absorption spectrum in Fig. 5.41:

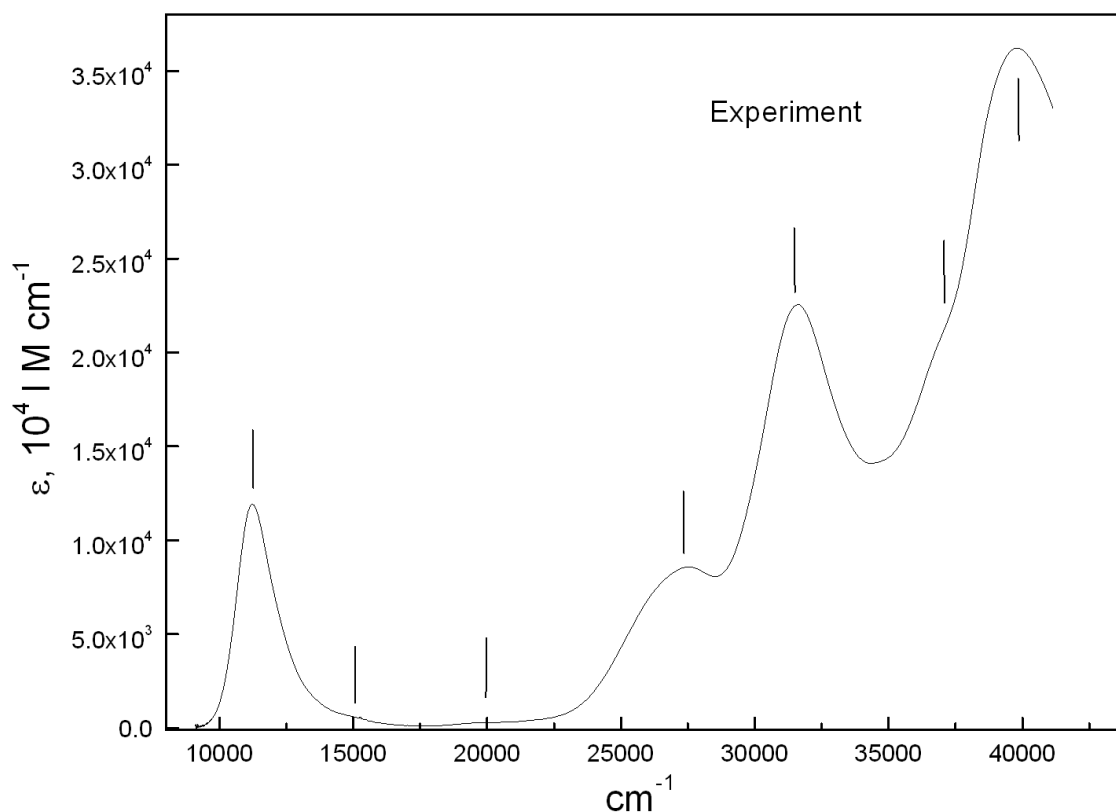


Fig. 5.41: Experimental absorption spectrum. Bars indicate transition energies which were used for the initial guess in the input for spectral fitting.

As shown in Fig. 5.41 one can identify roughly 7 electronic bands. The initial estimates of transition energies corresponding to the maxima and shoulders in the absorption spectrum (indicated by bars in Fig. 5.41) and rather approximate values of inhomogeneous broadening and transition dipole moment components are specified in the `$el_states` block of the input file for the spectral fitting:

```
# example007.inp
#
# Input file for fitting of experimental absorption spectrum
#

%sim
    model Simple
end

%fit
    Fit true                # Global flag to turn on the fit
    AbsFit true             # Flag to include absorption into the fit
    method Simplex
    WeightsAdjust true

    AbsRange 0.0, 100000.0 # absorption spectral range to be included in the
    fit;                  # in the present case all experimental points
                        # will be included

    AbsName "absexp.dat"   # name of the file containing experimental
                        # absorption spectrum in a simple two-column
                        # ASCII format
```

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```

ExpAbsScaleMode Ext      # This keyword indicates that the experimental
                          # absorption intensity is given in terms of
                          # the extinction coefficient. This is important
                          # for the proper fitting of transition dipole
                          # moments and oscillator strengths

NMaxFunc 10000           # maximum number of function evaluations in simplex
                          # algorithm

MWADRelTol 1e-5          # Relative Tolerance of the Mean Weighted Absolute
                          # Difference (MWAD) function which specifies the
                          # convergence criterion

E0Step 500.00            # initial step for the transition energies
                          # in the simplex fitting

TMStep 0.5               # initial step for the transition dipole moments
                          # in the simplex fitting

E0SDStep 500.0           # initial step for the inhomogeneous linewidth (Sigma)
                          # in the simplex fitting

end

# ! Parameters specified in the $el_states block
#   are used as initial guess in the fit

#-----
# Transition      Gamma      Sigma Transition Dipole Moment (atomic unit)
# Energy (cm**-1) (cm**-1) (cm**-1)      Mx      My      Mz
#-----
$el_states
7
  1 11270          0.0      1000.00      1.0000      0.0000      0.0000
  2 15100          0.0      1000.00      1.0000      0.0000      0.0000
  3 20230          0.0      1000.00      1.0000      0.0000      0.0000
  4 27500          0.0      1000.00      1.0000      0.0000      0.0000
  5 31550          0.0      1000.00      1.0000      0.0000      0.0000
  6 37070          0.0      1000.00      1.0000      0.0000      0.0000
  7 39800          0.0      1000.00      1.0000      0.0000      0.0000

# the integer values specified in $el_states_c block indicate parameters
# in the $el_states block to be varied
$el_states_c
7
  1  1          0          1          1          0          0
  2  2          0          2          2          0          0
  3  3          0          3          3          0          0
  4  4          0          4          4          0          0
  5  5          0          5          5          0          0
  6  6          0          6          6          0          0
  7  7          0          7          7          0          0

```

The functionality of the constraint block `$el_states_c` should be understood as follows: 1) 0 flag indicates that the corresponding parameter in the `$el_state` block will not be varied in the fitting; 2) if the number corresponding to a certain parameter coincides with the number of the corresponding electronic state this parameter will be varied independently. Thus, the block `$el_states_c` in the input indicates that all transition energies, inhomogeneous

geneous linewidths and x-components of the transition electric dipole moment will be varied independently, while homogeneous linewidths, y- and z-components of the transition dipole moment will be fixed to their initial values.

The following considerations are important:

- Since in conventional absorption spectroscopy one deals with the orientationally averaged absorption cross-section, the signal intensity is proportional to the square of the transition electric dipole moment  $|\mathbf{M}|^2$ . Thus, the intensities do not depend on the values of the individual components of  $\mathbf{M}$  as long as  $|\mathbf{M}|^2 = \text{const.}$  Therefore, we have allowed to vary only  $M_x$  components. Otherwise there can be problems in convergence of the fitting algorithm.
- The sum of the weights of experimental points which enter the mean absolute difference function employed in the minimization is always kept equal to the number of experimental points. In the case of equidistant experimental photon energies all weights are assumed to be equal. However, in experimental electronic spectra the density of spectral points can increase significantly upon going from high- to low-energy spectral regions, which is due to the fact that experimental absorption spectra are initially acquired on the wavelength scale. In such a case the quality of the fit can be noticeably biased towards low-energy spectral region. Therefore, it is advisable to adjust relative weights of experimental points according to their density which is controlled by the keyword `WeightsAdjust` in the `%fit` block. Although this parameter is not crucial for the present example, in general, it will provide a more balanced fit.
- The parameters `E0Step`, `TMStep`, `E0SDStep` in the `%fit` block specify the initial dimension of the simplex in the space of  $E_T$ ,  $\mathbf{M}$ ,  $\sigma$  and should roughly correspond to the expected uncertainty of initial guess on these parameters in the `$el_states` block relative to their actual values. The quality of the fit can noticeably deteriorate if the parameters specifying initial steps are too low or too high.

The fit run of `orca_asa` on file `example007.inp` will converge upon approximately 3600 function evaluations (for `MWADRelTol=1e-5`). The results of the fit will be stored in file `example007.001.inp` which has the same structure as the input file `example007.inp`. Thus, if the fit is not satisfactory and/or it is not fully converged it can be refined in a subsequent `orca_asa` run upon which file `example007.002.inp` will be created, and so on. Some model parameters in intermediate files can be additionally modified and/or some constraints can be lifted or imposed if so desired. The output file `example007.001.inp` will contain fitted model parameters stored in the `$el_states` block:

```
$el_states
7
1 11368.24      0.00  732.50      1.6290  0.0000  0.0000
2 15262.33      0.00  495.17     -0.2815  0.0000  0.0000
3 19500.08      0.00 1023.39      0.2300  0.0000  0.0000
4 26969.01      0.00 1832.30      1.4089  0.0000  0.0000
5 31580.41      0.00 1440.87      1.8610  0.0000  0.0000
6 35769.07      0.00 1804.02      1.5525  0.0000  0.0000
7 39975.11      0.00 1909.38      2.4745  0.0000  0.0000
```

The overall quality of the fit is determined by the parameter `MWAD` which upon convergence reaches the value of  $\approx 0.009$  (`MWAD` stands for Mean Weighted Absolute Difference).

After the `orca_asa` run files `absexp.fit.dat` and `absexp.fit.as.dat` will be created. Both files contain the experimental and fitted spectra which are shown in Fig. 5.42. In addition, the file `absexp.fit.as.dat` will contain individual contributions to the absorption spectrum corresponding to different excited states.

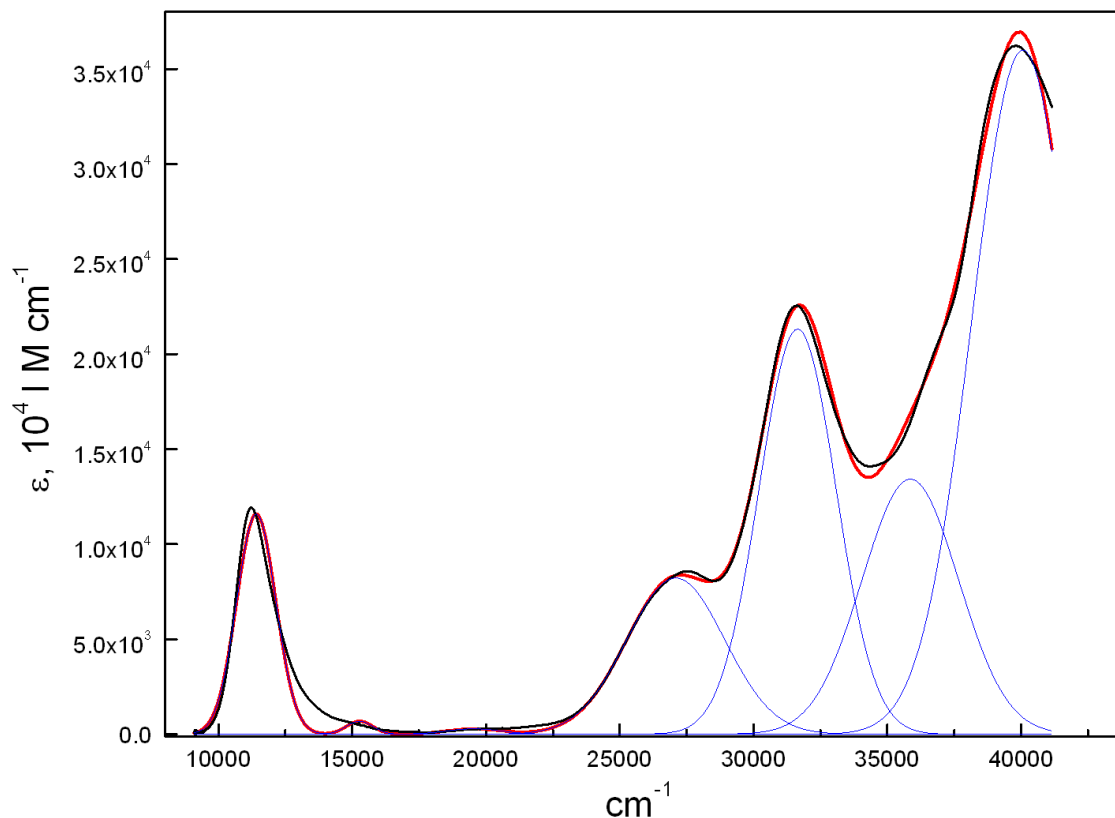


Fig. 5.42: Comparison of the experimental (black curve) and fitted (red) absorption spectra corresponding to the fit run of `orca_asa` on the file `example007.inp`. Blue curves represent individual contributions to the absorption spectrum from each state.

Since there is a noticeable discrepancy between the fitted and experimental spectra around  $13000\text{ cm}^{-1}$  (Fig. 5.42) it is worthwhile to refine the fit after adding parameters for a new state in the file `example007.001.inp`:

```
$sel_states
8
  1 11368.24    0.00  732.50    1.6290  0.0000  0.0000
... ..
  8 13280.00    0.00 1000.00    1.000  0.0000  0.0000

$sel_states_c
8
  1    1    0    1    1    0    0
... ..
  8    8    0    8    8    0    0
```

Actually, the character of the discrepancy in the present case is very similar to that in Fig. 5.39 (section *Example: Modelling of Effective Broadening, Effective Stokes Shift and Temperature Effects in Absorption and Fluorescence Spectra within the IMDHO Model*) where a vibronically broadened absorption spectrum was fitted with a Gaussian lineshape. Thus, the poor fit in the region around  $1300\text{ cm}^{-1}$  is most likely due to the essentially asymmetric character of the vibronic broadening rather than to the presence of another electronic band.

As shown in Fig. 5.43 the refined fit leads to much better agreement between the experimental and fitted absorption spectra (MWAD=0.0045).

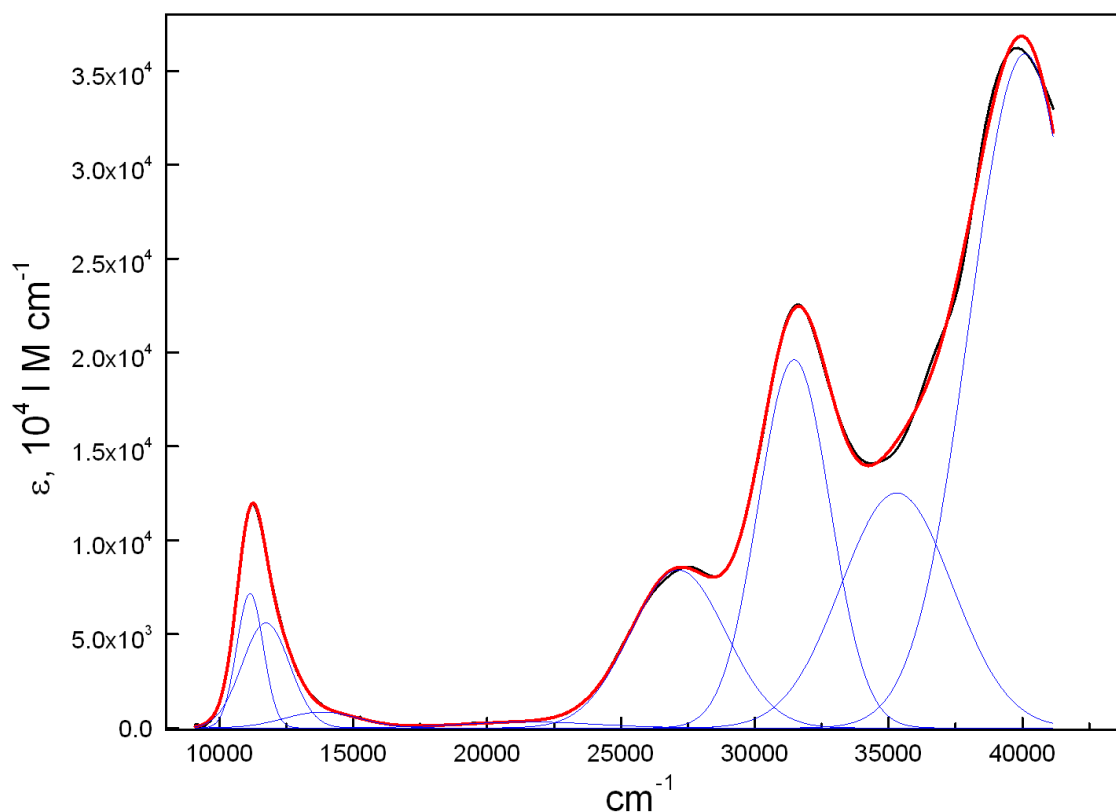


Fig. 5.43: Comparison of the experimental (black) and fitted (red) absorption spectra corresponding to the fit run of `orca_asa` on the file `example007.001.inp`. Blue curves represent individual contributions to the absorption spectrum from each state.

Due to some peculiarities of the simplex algorithm for function minimization, you can still refine the fit by rerunning `orca_asa` on the file `example007.002.inp`! This leads to an even lower value of the parameter `MWAD`=0.0038, and therefore to better agreement of experimental and fitted spectra (even though the previous run has been claimed to be converged).

It is also possible to perform a fit using the same value of inhomogeneous linewidth for all electronic states. For this purpose one needs to choose as a guess the same linewidth parameters in the `$el_states` block:

```
$el_states
8
 1 11118.58    0.00 1000.0    1.0687    0.0000    0.0000
 2 13673.38    0.00 1000.0   -0.5530    0.0000    0.0000
 3 21267.40    0.00 1000.0    0.3675    0.0000    0.0000
 4 27024.71    0.00 1000.0    1.4041    0.0000    0.0000
 5 31414.74    0.00 1000.0    1.7279    0.0000    0.0000
 6 35180.77    0.00 1000.0    1.6246    0.0000    0.0000
 7 39985.52    0.00 1000.0    2.5708    0.0000    0.0000
 8 11665.01    0.00 1000.0    1.2332    0.0000    0.0000
```

In addition the constraint block should be modified as follows:

```
$el_states_c
8
 1 1 0 1 1 0 0
 2 2 0 1 2 0 0
 3 3 0 1 3 0 0
 4 4 0 1 4 0 0
 5 5 0 1 5 0 0
```

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6	6	0	1	6	0	0
7	7	0	1	7	0	0
8	8	0	1	8	0	0

The constraint parameters for the inhomogeneous broadening were chosen to be 1, which means that formally  $\sigma_1$  corresponding to the first state is varied independently while the linewidths  $\{\sigma_i\}$  for other bands are varied in such a way that the ratios  $\sigma_i/\sigma_1$  are kept fixed to their initial values, whereby the same linewidth parameter will be used for all states.

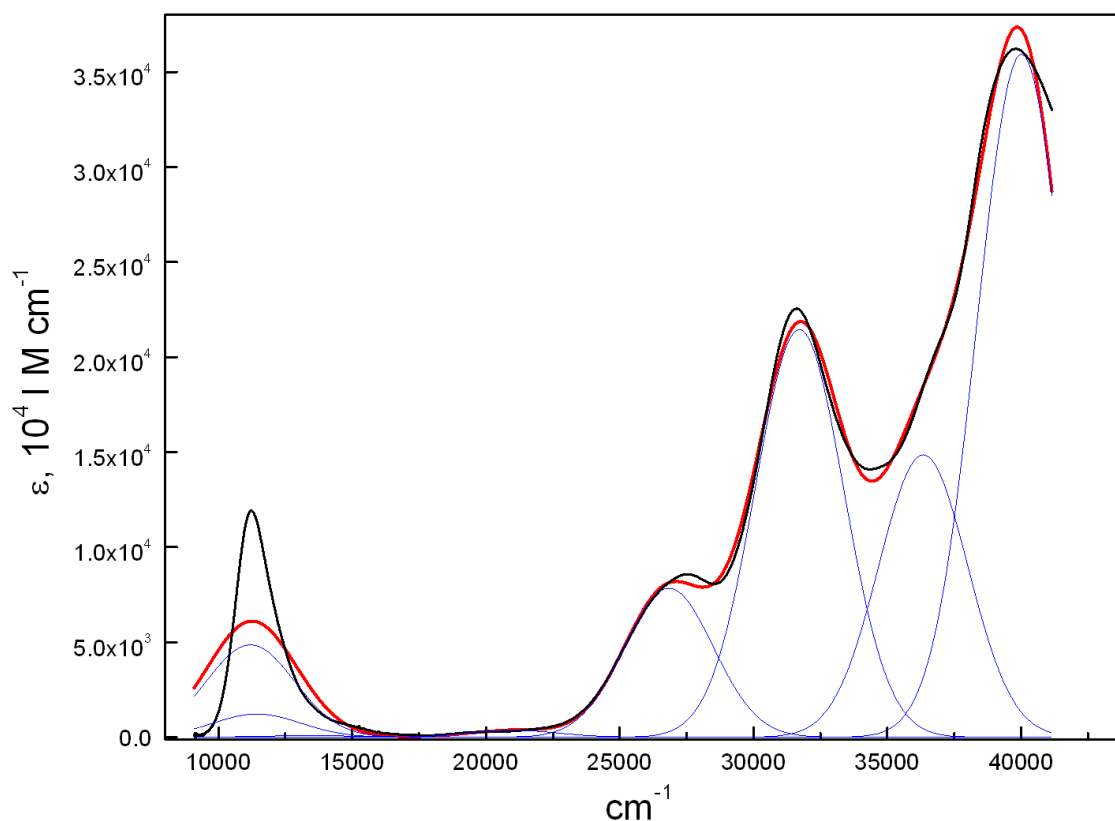


Fig. 5.44: Comparison of the experimental (black) and fitted (red) absorption spectra corresponding to the fit run of `orca_asa` on the file `example007.002.inp` in which equal broadening was assumed for all electronic bands. Blue curves represent individual contributions to the absorption spectrum from each state.

One can see (Fig. 5.44) that the assumption of equal linewidths for all electronic bands leads to a rather pronounced deterioration of the quality of the fit in the low-energy spectral range (MWAD=0.017). Apparently, this discrepancy can be fixed assuming more electronic states at higher energies.

#### NOTE

- The homogeneous linewidth parameters can also be included in the fit in a similar way. However, one can see that in most cases they appear to be much smaller than corresponding Gaussian linewidth parameters.
- Gauss-fit of absorption spectra is coventionally performed assuming the same linewidth parameters for all bands. However, since a large portion of Gaussian broadening is mainly due to the unresolved vibronic structure in the spectra which can significantly vary depending on the nature of transition, the assumption of unequal Gaussian bandwidths seems to be a physical one.

### Example: Fit of Absorption and Resonance Raman Spectra for $1^{-1}A_g \rightarrow 1^{-1}B_u$ Transition in *trans*-1,3,5-Hexatriene

Below we provide an example of the fit of the lineshape parameters and  $\{\Delta_m\}$  corresponding to the strongly dipole-allowed  $1^{-1}A_g \rightarrow 1^{-1}B_u$  transition in hexatriene. It is known that the most intense bands in rR spectra correspond to the most vibronically active in absorption spectrum. For the IMDHO model this correlation is determined by the values of  $\{\Delta_m\}$ . Thus, the larger  $\Delta$ , the larger is the rR intensity of a given mode and the more pronounced is the progression in the absorption spectrum corresponding to this mode. In principle, if all vibrational transitions in absorption are well resolved it is possible to determine  $\{\Delta_m\}$  by a fit of the absorption spectrum alone. In practice this task is ambiguous due to the limited resolution of the experimental absorption spectra. The observation of a rR spectrum enables the identification of the vibrational modes that are responsible for the progression in the absorption spectrum, as well as a quantitative analysis in terms of  $\{\Delta_m\}$ . The file `example006.inp` provides a brute-force example on how to approach the fit employing the minimal possible experimental information: 1) An absorption spectrum; 2) relative rR intensities of fundamental bands for a given excitation energy. The rR spectrum upon the excitation in resonance with the 0-0 vibronic band at  $39809\text{ cm}^{-1}$  is shown in Fig. 5.33.

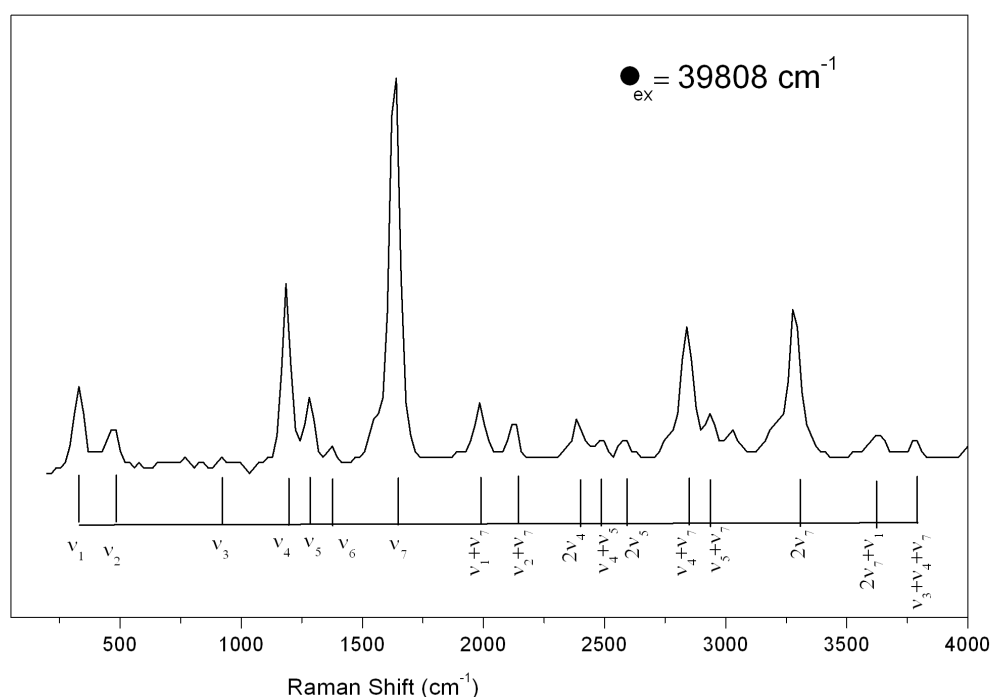


Fig. 5.45: Experimental Resonance Raman spectrum corresponding to  $1^{-1}A_g \rightarrow 1^{-1}B_u$  transition in *trans*-1,3,5-hexatriene.

The experimental rR spectrum has enabled the identification of seven vibrational modes that give rise to the most intense resonance Raman bands. Therefore, they are expected to have the largest excited-state displacements and the most pronounced effect on the vibrational structure of the absorption spectrum. Their vibrational frequencies have been entered as input for the fit as shown below:

```
#
# example008.inp
#
# Input for fit of absorption and resonance Raman spectra
# corresponding to the strongly allowed 1-1Ag 1-1Bu transition
# in 1,3,5 trans-hexatriene.
```

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```

#
# Parameters to be varied:
# 1) adiabatic minima transition energy
# 2) homogeneous linewidth (Gamma)
# 3) dimensionless normal coordinate displacements of the
#    excited-state origin
#

%sim
    Model IMDHO
end

%fit

    Fit true      # boolean parameter to switch on the fit

    # boolean parameter to include experimental absorption
    # spectrum in the fit:
    AbsFit true

    # boolean parameter to include experimental rR spectra
    # specified in $rrs_exp block in the fit:
    RRSFit true

    AbsExpName "hex-abs.dat" # name of the file with experimental absorption
                           # spectrum

    # the following value of keyword ExpAbsScaleMode
    # indicates that only the shape of absorption band
    # but not its total intensity will be accounted in the fit:
    ExpAbsScaleMode Rel

    # the weight of absorption relative to the total weight of
    # rR intensities in the difference function to be minimized:
    CWAR 5.0

    NMaxFunc 1000 # maximum number of function evaluations in simplex
                  # algorithm

    MWADRelTol 1e-4 # Relative Tolerance of the Mean Weighted Absolute
                   # Difference (MWAD) function which specifies the
                   # convergence criterion

    SDNCStep 1.0

end

# The values specified in $el_states block serve as initial guess in the fit
$el_states
1
  1  40000.0      200.00    0.0      1.0    0.0    0.0

# the integer values specified in $el_states_c block indicate parameters
# in $el_states block to be varied
$el_states_c
1
  1      1          1          0          0          0          0

# 7 totally symmetric vibrations which give rise to the most
# intense bands in the rR spectra are included into analysis.

```

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```

# Experimental values of vibration frequencies are given:
$vib_freq_gs
7
  1      354.0
  2      444.0
  3      934.0
  4     1192.0
  5     1290.0
  6     1403.0
  7     1635.0

# Initial guess for the values of dimensionless normal
# coordinate displacements of the excited-state origin
$sdnc
7 1
      1
  1      0.0
  2      0.0
  3      0.0
  4      0.0
  5      0.0
  6      0.0
  7      0.0

# the integer values specified in $sdnc_c block indicate parameters
# in $sdnc block to be varied
$sdnc_c
7 1
      1
  1      1
  2      2
  3      3
  4      4
  5      5
  6      6
  7      7

# specification of vibrational transitions and their intensities
# in experimental rR spectra:
$rrs_exp
1      # number of rR spectra
1 1      # start of the block specifying the 1st rR spectrum
Ex 39809.0 # excitation energy for the first rR spectrum
NTr 7      # number of vibrational transitions for which intensities are
           # provided
1
  int  10.0  1.0
  modes 1
  quanta 1;
2
  int  5.0  1.0
  modes 2
  quanta 1;
3
  int  1.5  1.0
  modes 3
  quanta 1;
4
  int  21.0  1.0
  modes 4

```

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```

    quanta 1;
5
    int    7.5  1.0
    modes  5
    quanta 1;
6
    int    2.0  1.0
    modes  6
    quanta 1;
7
    int   46.0  1.0
    modes  7
    quanta 1;

```

The input of rR intensities for an arbitrary number of excitation energies follows the keyword `$rrs_exp` block:

```

$rrs_exp
1          # number of rR spectra
1 1

```

The first “1” in the last line denotes the number of the rR spectrum for which specification starts below. If the second number is the same as the number of the spectrum, then it means that only relative intensities for the first rR spectrum are meaningful in the fit. If several spectra are given in the input then the second number may have a different value, e.g.:

```

$rrs_exp
3          # number of rR spectra
1 2
...

```

This input is to be interpreted as indicating that 3 rR spectra are provided and the relative intensities for the first spectrum are given on the same scale as the second one that will be accounted for in the fit. The value of the excitation energies and the number of vibrational transitions specified are indispensable within the blocks specifying intensities for each rR spectrum.

Following the number of vibrational transitions given by the keyword `NTr` one has to specify each vibrational transition and its intensity. Thus, in the present case there are seven subblocks with the following structure:

```

k      int    I  W
      modes m1,m2,...mn
      quanta q1,q2,...qn;

```

This means that the  $k$ -th transition has intensity  $I$  and weight  $W$  in the mean absolute difference function that is used for the minimization ( $W$  is an optional parameter). The following 2 lines specify the vibrational transitions by providing excitation numbers  $q_i$  for modes  $m_i$  so that the corresponding Raman shift is equal to  $\nu = \sum_{q_i \nu_i}$ , where  $\nu_i$  is vibrational frequency of the mode  $m_i$ .

The parameters that are to be varied are specified within the constraint blocks `$el_states_c` and `$sdnc_c`. Both blocks have the same structure and number of parameters as `$el_states` and `$sdnc`, respectively. A parameter from the `$el_states` block is supposed to be independently varied if its counterpart from the `$el_states_c` block is equal to the number of the electronic state. Likewise, a parameter from the `$sdnc` block is supposed to be independently varied if its counterpart from the `$sdnc_c` block is equal to the number of the normal mode. Model parameters that are set to 0 in the corresponding constraint blocks are not varied in the fit. The values of the following parameters may be important for the quality of the fit:

- `CWAR` in the `%fit` block specifies the weight of absorption relative to the weight of rR intensities in the difference function to be minimized. If this parameter was not specified the fit would be almost insensitive to the rR intensities in the input, since typically the number of experimental absorption points is much larger than the number of rR transitions in the input. In most cases the value of `CWAR` in the range 1.0–5.0 is a good choice since the error in the measured experimental intensity is expected to be much smaller for absorption

than for resonance Raman.

- SDNCStep in the %fit block specifies the initial dimension of the simplex in the space of  $\{\Delta_m\}$  and should roughly correspond to the expected uncertainty of initial guess on  $\{\Delta_m\}$  in the \$sdnc block compared to their actual values. You can notice in the present example that if this parameter is too large (>2.0) or too small (<0.4) the quality of the fit may significantly deteriorate
- Although the default initial dimensions of the simplex have reasonable values for different types of parameters it may turn out to be helpful in some cases to modify the default values:

```
FREQGStep 10.0 # ground-state vibrational frequencies
  FREQEStep 10.0 # excited-state vibrational frequencies
  E0Step     300.0 # transition energies
  SSStep     20.0 # Stokes shift
  TMStep     0.5 # electronic transition dipole moment
  GammaStep  50.0 # homogeneous linewidth
  E0SDStep   50.0 # inhomogeneous linewidth
  SDNCStep   1.0 # origin shift along dimensionless normal coordinate
```

The fit run of orca\_asa on the file example008.inp will converge upon approximately 700 function evaluations (for MWADRelTol=1e-4). The results of the fit will be stored in file example008.001.inp which has the same structure as the input file example008.inp. Thus, if the fit is not satisfactory and/or it is not fully converged it can be refined in subsequent orca\_asa run upon which file example008.002.inp will be created, and so on. Some model parameters in intermediate files can be additionally modified and/or some constraints can be lifted if so desired. The output file example008.001.inp will contain fitted displacement parameters  $\{\Delta_m\}$  stored in the \$sdnc block:

```
$sdnc
7 1
      1
1      0.675000
2      -0.194484
3      -0.217527
4      0.811573
5      0.529420
6      -0.149991
7      1.314915
```

In the present example, these parameters are actually in very close agreement with those published for the hexatriene molecule!

The overall quality of the fit is determined by the parameter MWAD which upon convergence reaches the value of  $\approx 0.027$ . The fitted rR intensities are presented in the commented lines next to the experimental rR intensities in file example008.001.inp:

```
$rrs_exp
1
1 1 3.495285e+001
Ex 39809.00
NT 7
1
  Int 10.0 1.0 # simulated intensity: 1.000982e+001
  modes 1
  quanta 1;
2
  Int 5.0 1.0 # simulated intensity: 8.976285e-001
  modes 2
  quanta 1;
3
  Int 1.5 1.0 # simulated intensity: 1.255880e+000
  modes 3
  quanta 1;
```

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```

4
  Int 21.0 1.0 # simulated intensity: 1.761809e+001
  modes 4
  quanta 1;
5
  Int 7.5 1.0 # simulated intensity: 7.499749e+000
  modes 5
  quanta 1;
6
  Int 2.0 1.0 # simulated intensity: 6.014466e-001
  modes 6
  quanta 1;
7
  Int 46.0 1.0 # simulated intensity: 4.600071e+001
  modes 7
  quanta 1;

```

The file hex-abs.fit.dat will contain the experimental and fitted absorption spectra in ASCII format which can be plotted in order to visualize the quality of absorption fit (Fig. 5.46).

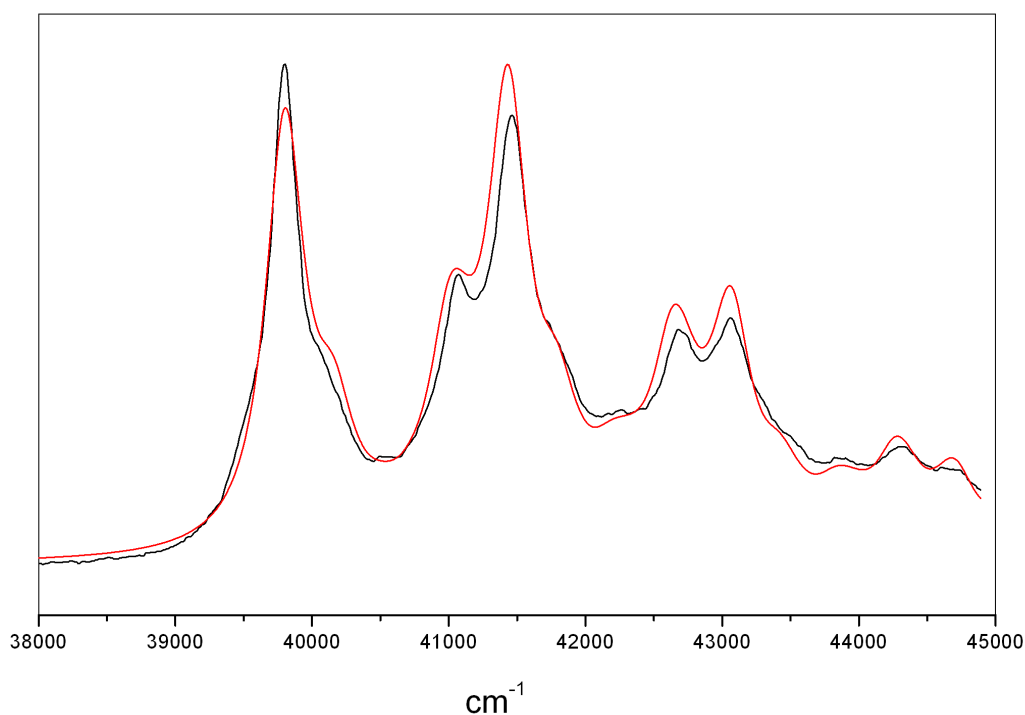


Fig. 5.46: Experimental (black) and fitted (red) absorption spectrum corresponding to  $1^{-1}A_g \rightarrow 1^{-1}B_u$  transition in 1,3,5 *trans*-hexatriene.

#### Note

- The more experimental rR intensities are included in the analysis the more reliable is the fit. In principle it is possible to obtain fully consistent results even if only a limited number of vibrational transitions is provided. However, in such a case it is desirable to include into analysis at least a single Raman transition

involving the mode for which  $\Delta$  is to be determined.

- The quality of the fit can be improved if the IMDHOFA model is invoked and excited-state vibrational frequencies are allowed to vary.
- Due to the initial guess and dimension of the simplex, as well as some peculiarities of the simplex algorithm for function minimization, you can still refine the fit by rerunning `orca_asa` on file `example008.001.inp` that may lead to an even lower value of the parameter  $MWAD = 0.021$ , and therefore to better agreement of experimental and fitted spectra (even though the previous run has been claimed to be converged).
- In this respect it appears to be wise to perform the fit in 3 steps:
  1. Fit the preresonance region below the 0-0 vibronic band with a single Lorentzian band, from which the adiabatic transition energy  $E_0$ , and homogeneous linewidth  $\Gamma$  are obtained. The range for fit of the absorption spectrum can be specified by the `AbsRange` keyword in the `%fit` block.
  2. Fix  $E_0$  and  $\Gamma$ , and optimize  $\{\Delta_m\}$  fitting the entire spectral range and rR intensities.
  3. Lift constraints on  $E_0$  and  $\Gamma$ , and reoptimize simultaneously all parameters.

### Example: Single-Mode Fit of Absorption and Fluorescence Spectra for $1^1A_g \rightarrow 1^1B_{2u}$ Transition in Tetracene

In this section we provide an example and discuss the most important aspects of joint fit of fluorescence and absorption spectra. Fig. 5.47 displays the experimental emission and absorption spectra corresponding to  $1^1A_g \rightarrow 1^1B_{2u}$  transition in tetracene.

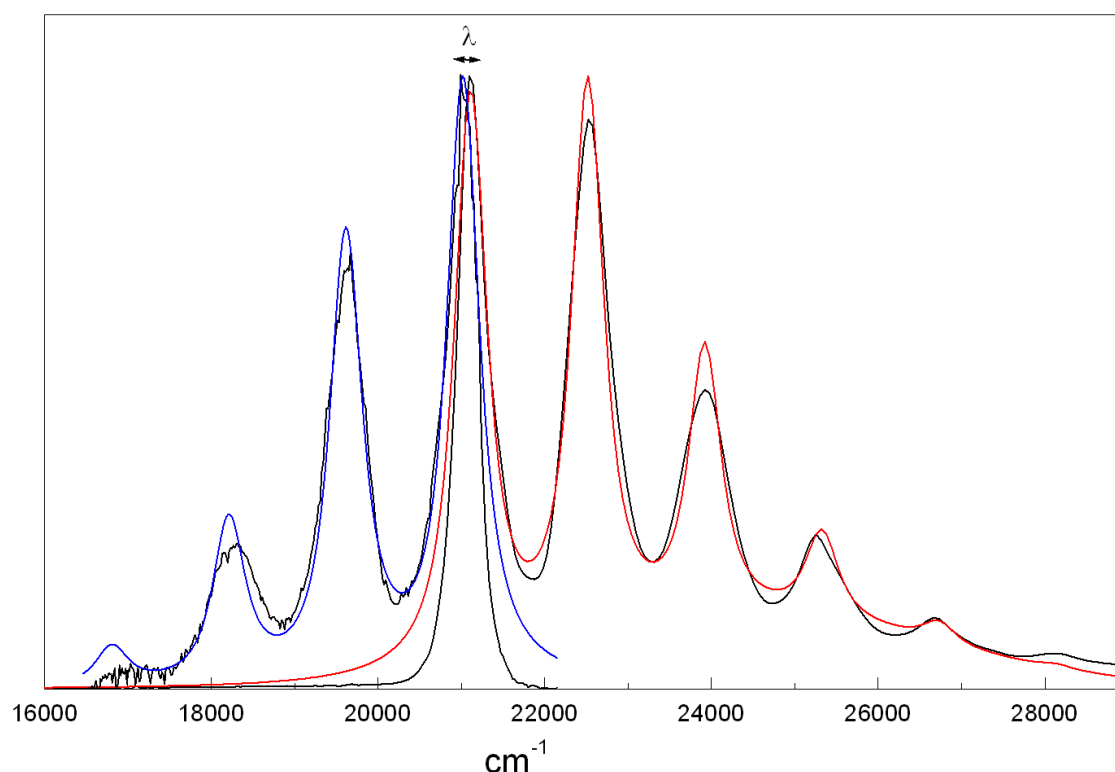


Fig. 5.47: Deconvoluted absorption (red) and fluorescence (blue) spectra of tetracene in cyclohexane upon the assumption of a single vibronically active mode. The black solid lines represent experimental spectra.

Both spectra show pronounced effective vibrational progressions that are dominated by 3 and 5 peaks, respectively.