```
  DoAlpha true
  NRoots 4
  DTol 1e-6
  DoCore true
  DoCVS  true
  CoreOrb[0]=0,1
  CoreOrb[1]=0,1
  end

  *xyz 0 3
    O      0.0 0.0 0.0
    O      0.0 0.0 1.207
  *
step_end

new_step
  !UHF IP-EOM-CCSD cc-pVDZ ExtremeSCF KDIIS nofrozencore

  %mdci
  DoBeta true
  NRoots 4
  DTol 1e-6
  DoCore true
  DoCVS  true
  CoreOrb[0]=0,1
  CoreOrb[1]=0,1
  end

  *xyz 0 3
    O      0.0 0.0 0.0
    O      0.0 0.0 1.207
  *
step_end

end
```

The output for 'DoAlpha' looks like

```
-------------------------------
UHF IP-EOM-CCSD RESULTS (RHS)
-------------------------------


IROOT=  1: 20.137719 au    547.975 eV 4419718.6 cm**-1
  Amplitude    Excitation
   0.894649     0a -> x
   0.115737     0a -> x     5b ->  12b
   0.115737     0a -> x     6b ->  13b
  -0.123325     1a -> x     5b ->   7b
  -0.120347     1a -> x     5b ->   8b
  -0.120347     1a -> x     6b ->   7b
   0.123325     1a -> x     6b ->   8b
Percentage singles character=     80.04

IROOT=  2: 20.137008 au    547.956 eV 4419562.4 cm**-1
  Amplitude    Excitation
   0.894673     1a -> x
  -0.123144     0a -> x     5b ->   7b
  -0.120171     0a -> x     5b ->   8b
  -0.120171     0a -> x     6b ->   7b
   0.123144     0a -> x     6b ->   8b
   0.115678     1a -> x     5b ->  12b
```

```
    0.115678     1a -> x     6b ->  13b
Percentage singles character=     80.04

IROOT=  3:  1.418592 au     38.602 eV  311344.9 cm**-1
  Amplitude    Excitation
   0.531451     2a -> x
   0.266889     4a -> x     3b ->   7b
   0.431978     4a -> x     3b ->   8b
   0.116970     4a -> x     3b ->  14b
  -0.431978     5a -> x     3b ->   7b
   0.266889     5a -> x     3b ->   8b
  -0.116970     5a -> x     3b ->  15b
  -0.112676     7a -> x     2b ->   8b
   0.105473     7a -> x     4b ->   8b
  -0.112676     8a -> x     2b ->   7b
   0.105473     8a -> x     4b ->   7b
Percentage singles character=     29.23

IROOT=  4:  0.964260 au     26.239 eV  211630.5 cm**-1
  Amplitude    Excitation
   0.825207     3a -> x
   0.147947     6a -> x     5b ->   7b
   0.144375     6a -> x     5b ->   8b
   0.144375     6a -> x     6b ->   7b
  -0.147947     6a -> x     6b ->   8b
  -0.267515     7a -> x     3b ->   8b
  -0.267515     8a -> x     3b ->   7b
Percentage singles character=     68.10
```

and for 'DoBeta'

```
------------------------------
UHF IP-EOM-CCSD RESULTS (RHS)
------------------------------

IROOT=  1: 20.102122 au    547.007 eV 4411905.8 cm**-1
  Amplitude    Excitation
   0.904712     0b -> x
Percentage singles character=     81.85

IROOT=  2: 20.100495 au    546.962 eV 4411548.8 cm**-1
  Amplitude    Excitation
   0.904679     1b -> x
Percentage singles character=     81.84

IROOT=  3:  1.482975 au     40.354 eV  325475.4 cm**-1
  Amplitude    Excitation
   0.911468     2b -> x
  -0.437544     2b -> x     3b ->  10b
   0.117502     2b -> x     3b ->  17b
  -0.181512     2b -> x     3b ->  27b
  -0.150802     2b -> x     4b ->  16b
   0.155724     3b -> x     4b ->   9b
  -0.362017     3b -> x     4b ->  10b
   0.170790     3b -> x     4b ->  27b
   0.414703     2b -> x     5b ->  18b
  -0.477670     3b -> x     5b ->  15b
   0.121834     4b -> x     5b ->  13b
  -0.266578     4b -> x     5b ->  19b
  -0.414703     2b -> x     6b ->  19b
   0.477670     3b -> x     6b ->  14b
```

```
    0.121834      4b -> x      6b ->   12b
   -0.266578      4b -> x      6b ->   18b
   -0.132721      5b -> x      6b ->   20b
    0.918380      5b -> x      6b ->   21b
    0.170340      3b -> x      6a ->    9a
   -0.124771      5b -> x      7a ->    9a
   -0.124771      6b -> x      8a ->    9a
Percentage singles character=      83.16


IROOT=  4:  0.889071 au    24.193 eV  195128.5 cm**-1
  Amplitude    Excitation
    0.946265      3b -> x
    0.272057      4b -> x      5b ->    7b
   -0.223370      4b -> x      5b ->    8b
    0.223370      4b -> x      6b ->    7b
    0.272057      4b -> x      6b ->    8b
Percentage singles character=      89.54
```

5.15.3 Core-Excitation

The STEOM-CCSD approach provides an efficient and accurate way to do the K-edge core-excitation spectroscopy. A typical input file for the STEOM-CCSD will look like

```
!STEOM-CCSD ExtremeSCF cc-pCVTZ Bohrs NoFrozencore

%mdci
nroots 5
FollowCIS true
DoSimpleDens False # use exact STEOM transition moment
maxiter 500
DoCVS true
DoCore true
CoreOrb[0]=0,0
end

*xyz 0 1
O 0 0 0.913973
C 0 0 -1.218243
*
```

The output will be

```
-------------------------------
STEOM-CCSD RESULTS (SINGLETS)
-------------------------------

IROOT=  1: 19.685582 au    535.672 eV 4320485.8 cm**-1
  Amplitude    Excitation
 -0.932683      6 ->   8
  0.281517      6 ->  12
 -0.211943      6 ->  14
  Ground state amplitude:  0.000000


Percentage Active Character     99.41


  Amplitude    Excitation in Canonical Basis
 -0.846006      0 ->   7
 -0.428151      0 ->   8
  0.252869      0 ->  12
```

```
    0.151677     0 ->  15

IROOT=  2: 19.685582 au   535.672 eV 4320485.9 cm**-1
  Amplitude    Excitation
 -0.932691     6 ->   7
  0.281484     6 ->  11
  0.211959     6 ->  15
  Ground state amplitude:  0.000000

Percentage Active Character     99.41

  Amplitude    Excitation in Canonical Basis
 -0.428151     0 ->   7
  0.846006     0 ->   8
 -0.252868     0 ->  11
 -0.151677     0 ->  14

IROOT=  3: 19.964529 au   543.262 eV 4381707.6 cm**-1
  Amplitude    Excitation
  0.978863     6 ->   9
  0.157708     6 ->  10
 -0.101384     6 ->  16
  Ground state amplitude: -0.001155

Percentage Active Character     99.39

  Amplitude    Excitation in Canonical Basis
 -0.978751     0 ->   9
  0.125406     0 ->  10
 -0.112036     0 ->  18
  0.102538     0 ->  21

IROOT=  4: 20.091389 au   546.714 eV 4409550.1 cm**-1
  Amplitude    Excitation
  0.269952     6 ->   8
  0.958312     6 ->  12
  Ground state amplitude: -0.000000

Percentage Active Character     99.78

  Amplitude    Excitation in Canonical Basis
  0.218969     0 ->   7
  0.110818     0 ->   8
 -0.210211     0 ->  11
  0.940678     0 ->  12

IROOT=  5: 20.091389 au   546.714 eV 4409550.1 cm**-1
  Amplitude    Excitation
  0.269914     6 ->   7
  0.958327     6 ->  11
  Ground state amplitude: -0.000000

Percentage Active Character     99.78

  Amplitude    Excitation in Canonical Basis
  0.110818     0 ->   7
 -0.218969     0 ->   8
 -0.940678     0 ->  11
 -0.210211     0 ->  12
```

MultiCore excitations are also available by setting 'CoreOrb[0]=0,1'. In following example, we directly access the oxygen 1S and carbon 1S core excitations

```
!STEOM-CCSD ExtremeSCF cc-pCVTZ Bohrs NoFrozencore

%mdci
nroots 5
FollowCIS true
DoSimpleDens False # use exact STEOM transition moment
maxiter 500
DoCVS true
DoCore true
CoreOrb[0]=0,1
end

*xyz 0 1
O 0 0 0.913973
C 0 0 -1.218243
*
```

It will give the oxygen and carbon K-edge spectrum as follows

```
------------------------------
STEOM-CCSD RESULTS (SINGLETS)
------------------------------

IROOT=  1: 10.577651 au   287.833 eV 2321526.1 cm**-1
  Amplitude    Excitation
  -0.508570     6 ->   7
   0.849534     6 ->   8
   0.127575     6 ->  10
  Ground state amplitude: -0.000000


Percentage Active Character    99.67


  Amplitude    Excitation in Canonical Basis
   0.803788     1 ->   7
   0.418299     1 ->   8
  -0.381488     1 ->  12
  -0.116973     1 ->  15


IROOT=  2: 10.577651 au   287.833 eV 2321526.1 cm**-1
  Amplitude    Excitation
   0.849534     6 ->   7
   0.508570     6 ->   8
   0.127575     6 ->  11
  Ground state amplitude:  0.000000


Percentage Active Character    99.67


  Amplitude    Excitation in Canonical Basis
   0.418299     1 ->   7
  -0.803788     1 ->   8
   0.381488     1 ->  11
   0.116973     1 ->  14


IROOT=  3: 10.900722 au   296.624 eV 2392431.9 cm**-1
  Amplitude    Excitation
  -0.893589     6 ->   9
   0.426665     6 ->  12
  Ground state amplitude:  0.000202


Percentage Active Character    79.85

Warning:: the state may have not converged with respect to active space
```

(continues on next page)

```
------------------- Handle with Care -------------------

  Amplitude    Excitation in Canonical Basis
 -0.972609     1 ->   9
  0.135434     1 ->  10
 -0.157896     1 ->  18

IROOT=  4: 19.690061 au   535.794 eV 4321468.9 cm**-1
  Amplitude    Excitation
  0.677274     5 ->   7
 -0.726090     5 ->   8
  Ground state amplitude: -0.000000

Percentage Active Character    98.89

  Amplitude    Excitation in Canonical Basis
 -0.733267     0 ->   7
 -0.606483     0 ->   8
  0.247689     0 ->  12
  0.137742     0 ->  15

IROOT=  5: 19.690061 au   535.794 eV 4321468.9 cm**-1
  Amplitude    Excitation
 -0.726090     5 ->   7
 -0.677274     5 ->   8
  Ground state amplitude:  0.000000

Percentage Active Character    98.89

  Amplitude    Excitation in Canonical Basis
 -0.606483     0 ->   7
  0.733267     0 ->   8
 -0.247689     0 ->  11
 -0.137742     0 ->  14
```

The core-valence separation should be used similar to that in the core-ionization. The only difference is that the natural orbital based active space selection scheme in STEOM-CCSD always rotate the particular core orbital to the HOMO. Now ORCA will automatically set the core orbitals to be the HOMO in STEOM-CCSD irrespective of the core-hole. One should use the exact STEOM-CCSD transition moment by using DoSimpleDens False. Fig. 5.32 presents the STEOM-CCSD oxygen K-edge spectra in thymine.
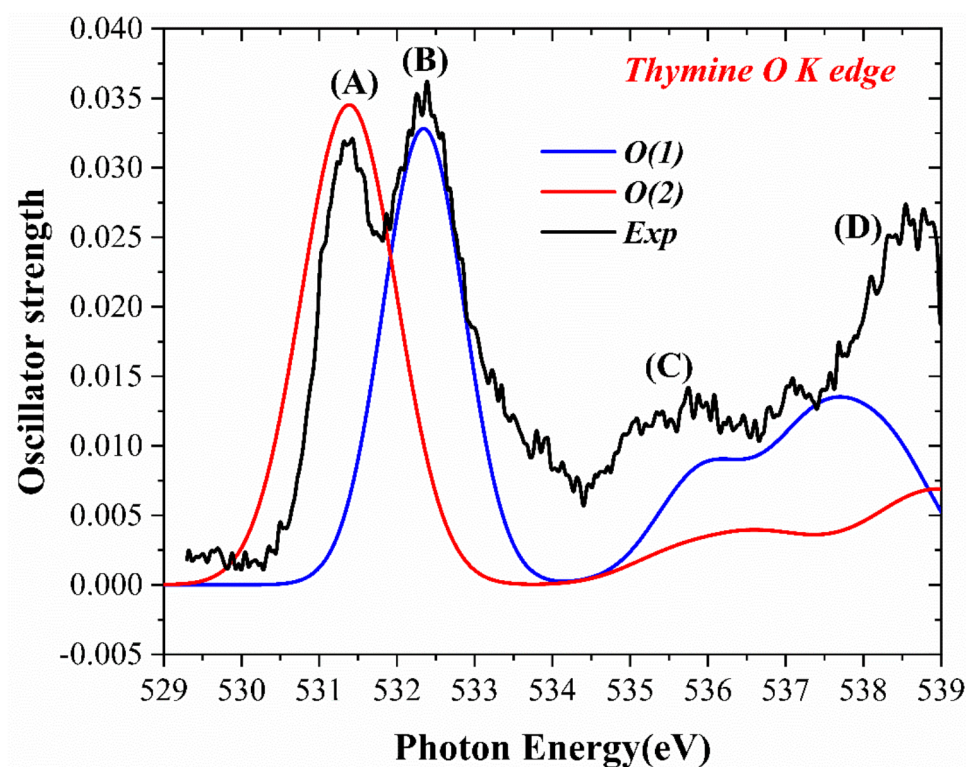
Fig. 5.31: Comparison of theoretical and experimental X-ray absorption spectra of oxygen K-edge in thymine. The simulated spectrum is shifted by -3.7 eV to align with the experimental spectrum.

One can interpret the results in terms of NTOs caculated from STEOM-CC eigen vectors
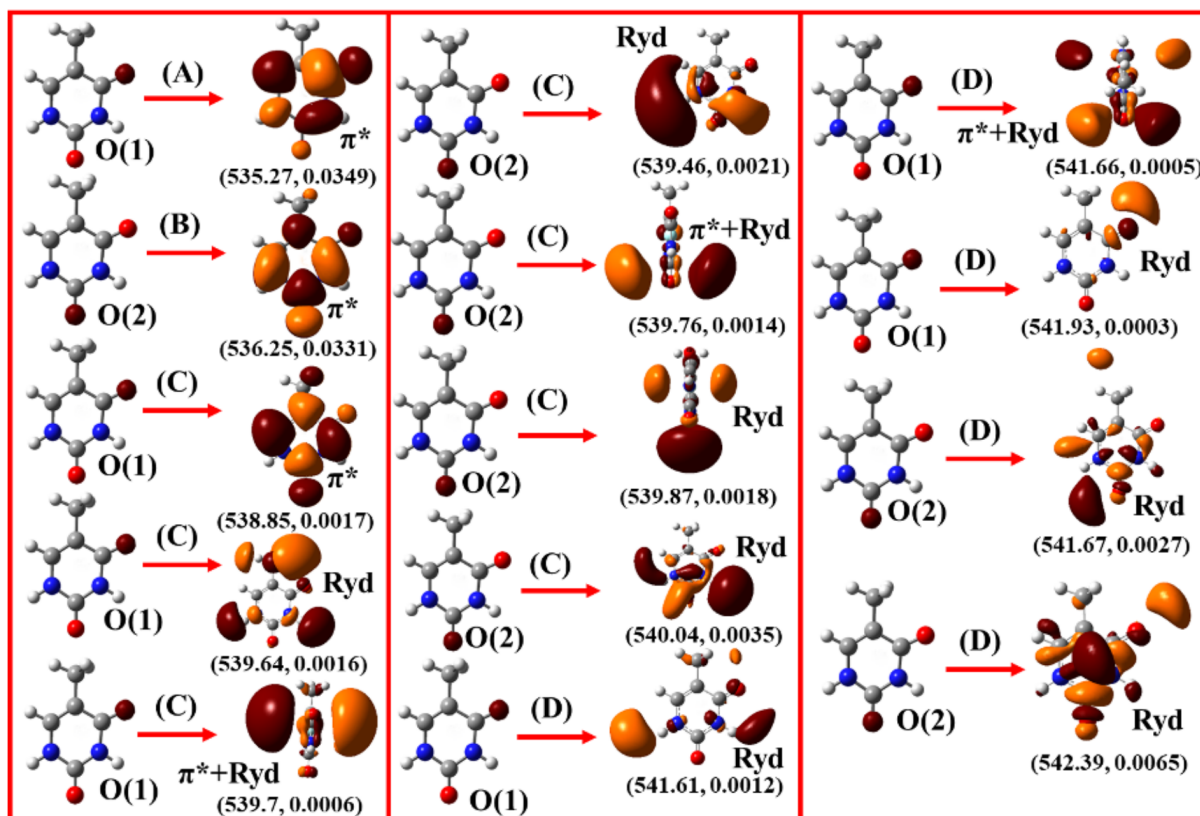
Fig. 5.32: Natural transition orbitals (ntos) for the oxygen K edge spectrum of thymine. All the core EE values mentioned are in eV and provided in the format (EE,Oscillator Strength).

5.15.4 Core-Excitation (UHF)

ORCA is now able to also perform core-excitations using the open-shell STEOM-CCSD method in a similar way to that of closed-shell.[671] By setting 'CoreOrb' for each spin channel we can perform a single core or a multicore calculation. In the following example, we determine the nitrogen and oxygen K-Shell excitations in the NO radical.

```
!UHF STEOM-CCSD ExtremeSCF nofrozencore usesym
!cc-pCVDZ

%mdci
nroots 10
DoCVS true
DoCore true
CoreOrb[0]=0,1       #N and O core orbitals (spin up)
CoreOrb[1]=0,1  #N and O core orbitals (spin down)
end

*xyz 0 2
  N          0.00000000000000      0.00000000000000      0.00490803701002
  O          0.00000000000000      0.00000000000000      1.14109196298998
*
```

and its corresponding output

```
---------------------
UHF STEOM-CCSD RESULTS
---------------------

IROOT=  1: 14.743862 au   401.201 eV 3235903.7 cm**-1 <S**2>= 0.877361  Sym: A2
```

```
  Amplitude    Excitation
   0.637991    7a ->   8a
   0.750732    6b ->   7b
   0.136839    6b ->  10b

Percentage Active Character    99.93

  Amplitude    Excitation in Canonical Basis
  -0.613647    1a ->   8a
  -0.186064    1a ->  11a
  -0.722892    1b ->   7b
  -0.225768    1b ->  10b

IROOT=  2: 14.786433 au   402.359 eV 3245247.0 cm**-1 <S**2>= 0.849392  Sym: A1
  Amplitude    Excitation
   0.985414    6b ->   8b
   0.154505    6b ->  11b

Percentage Active Character    99.49

  Amplitude    Excitation in Canonical Basis
  -0.954188    1b ->   8b
   0.267334    1b ->  12b
  -0.121297    1b ->  16b

IROOT=  3: 14.794166 au   402.570 eV 3246944.1 cm**-1 <S**2>= 2.669487  Sym: A2
  Amplitude    Excitation
  -0.772273    7a ->   8a
   0.623458    6b ->   7b

Percentage Active Character    99.47

  Amplitude    Excitation in Canonical Basis
   0.754282    1a ->   8a
   0.166288    1a ->  11a
  -0.611046    1b ->   7b
  -0.132336    1b ->  10b

IROOT=  4: 15.243078 au   414.785 eV 3345469.0 cm**-1 <S**2>= 1.387083  Sym: B1
  Amplitude    Excitation
  -0.682643    7a ->   9a
  -0.101529    7a ->  11a
  -0.697873    6b ->   9b
  -0.133350    6b ->  12b

Percentage Active Character    98.11

  Amplitude    Excitation in Canonical Basis
   0.573243    1a ->   9a
   0.237647    1a ->  12a
  -0.265168    1a ->  13a
  -0.165128    1a ->  14a
   0.583678    1b ->   9b
   0.348965    1b ->  11b
   0.201568    1b ->  14b

IROOT=  5: 15.285144 au   415.930 eV 3354701.4 cm**-1 <S**2>= 2.434830  Sym: B1
  Amplitude    Excitation
  -0.690438    7a ->   9a
  -0.146046    7a ->  13a
   0.676597    6b ->   9b
```

```
   0.173127     6b ->  13b


Percentage Active Character    93.48



----------------------- Handle with Care --------------------------

Warning:: State   5 may have not converged with respect to active space
-------------------------------------------------------------------
  Amplitude    Excitation in Canonical Basis
   0.645706     1a ->   9a
   0.148300     1a ->  12a
  -0.211256     1a ->  13a
  -0.147915     1a ->  14a
  -0.643471     1b ->   9b
  -0.207585     1b ->  11b
  -0.158649     1b ->  14b

IROOT=  6: 19.682450 au   535.587 eV 4319798.5 cm**-1 <S**2>= 2.233840  Sym: A2
  Amplitude     Excitation
  -0.952369     6a ->   8a
  -0.128170     6a ->  10a
  -0.262026     5b ->   7b

Percentage Active Character    99.52

  Amplitude     Excitation in Canonical Basis
  -0.940546     0a ->   8a
   0.202713     0a ->  16a
  -0.254077     0b ->   7b

IROOT=  7: 19.714860 au   536.469 eV 4326911.7 cm**-1 <S**2>= 1.012274  Sym: A2
  Amplitude     Excitation
  -0.427285     6a ->   8a
   0.895703     5b ->   7b

Percentage Active Character    99.27

  Amplitude     Excitation in Canonical Basis
  -0.425513     0a ->   8a
   0.883394     0b ->   7b
  -0.176873     0b ->  15b

IROOT=  8: 19.746849 au   537.339 eV 4333932.5 cm**-1 <S**2>= 0.787890  Sym: A1
  Amplitude     Excitation
   0.992767     5b ->   8b

Percentage Active Character    99.45

  Amplitude     Excitation in Canonical Basis
   0.973851     0b ->   8b
   0.215849     0b ->  16b

IROOT=  9: 20.119392 au   547.476 eV 4415696.1 cm**-1 <S**2>= 2.441183  Sym: B1
  Amplitude     Excitation
   0.771305     6a ->   9a
  -0.127276     6a ->  11a
   0.122051     6a ->  13a
   0.592132     5b ->   9b

Percentage Active Character    96.84
```

5.16 Simulation and Fit of Vibronic Structure in Electronic Spectra, Resonance Raman Excitation Profiles and Spectra with the orca_asa Program

> ℹ **Deprecated since ORCA 6.0.0**
>
> - The `orca_asa` program is no longer supported. It is still included in the 6.0.0 release and the documentation is preserved below. However, it may not function correctly and will be removed in a future ORCA version!
>
> - The `!NMScan` and `!NMGrad` keywords are still available but these calculations may fail or not generate valid input for `orca_asa`. Please use the *ESD module* instead, if applicable.

In this section various aspects of the simulation and fit of optical spectra, including absorption, fluorescence, and resonance Raman are considered. This part of the ORCA is fairly autonomous and can also be used in a data analysis context, not only in a "quantum chemistry" mode. The program is called `orca_asa`, where ASA stands for "Advanced Spectral Analysis". The program was entirely designed by Dr. Taras Petrenko.

The general philosophy is as follows: An ORCA run produces the necessary data to be fed into the `orca_asa` program and writes an initial input file. This input file may be used to directly run `orca_asa` in order to predict an absorption, fluorescence or resonance Raman spectrum. Alternatively, the input file may be edited to change the parameters used in the simulations. Last – but certainly not least – the `orca_asa` program can be used to perform a fit of the model parameters relative to experimental data.
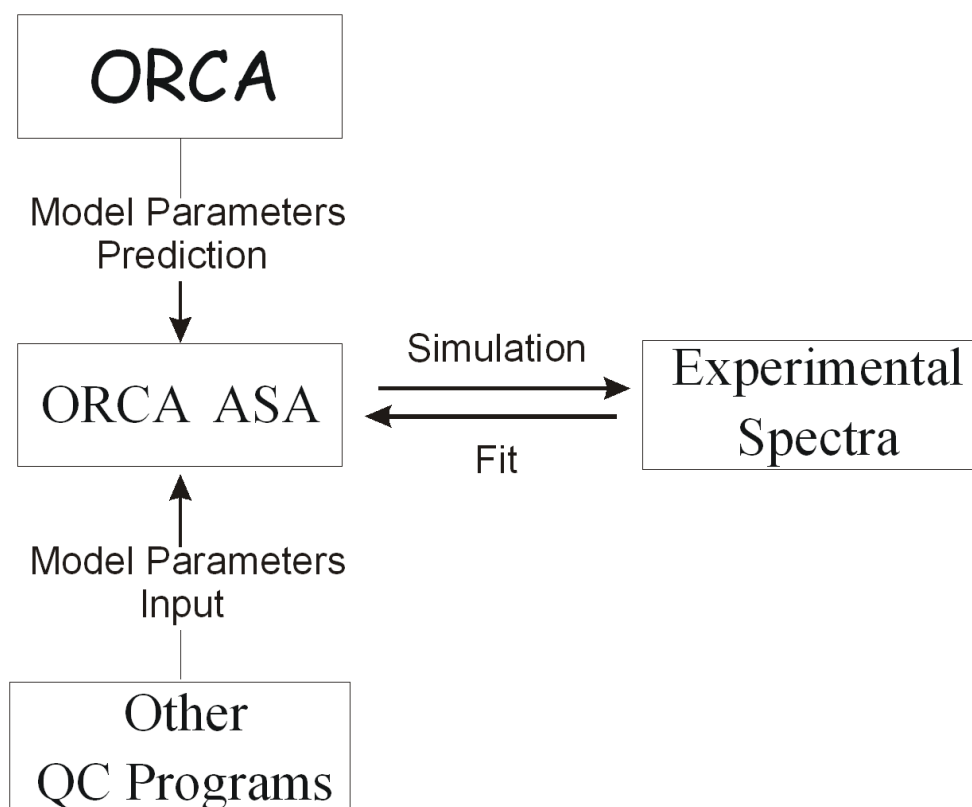
All examples below are taken from [672], which must be cited if you perform any work with the `orca_asa` program!

5.16.1 General Description of the Program

The program input comprises the following information: (1) model and specification of the model parameters characterizing the electronic structure of a molecule, as well as lineshape factors; (2) spectral ranges and resolution for simulations; (3) specification of vibrational transitions for rR excitation profile and spectra generation; (4) certain algorithm-selecting options depending on the model; (5) fitting options.

All optional parameters (1)-(3) are given in the `%sim` block, and fitting options are in the `%fit` block. The model parameters are specified within various blocks that will be described below. The program `orca_asa` is interfaced to ORCA and inherits its input style. The input for `orca_asa` run can be also generated upon ORCA run.

The current implementation features so called "simple", "independent mode, displaced harmonic oscillator" (IMDHO), and "independent mode, displaced harmonic oscillator with frequency alteration" (IMDHOFA) models.

5.16.2 Spectral Simulation Procedures: Input Structure and Model Parameters

Example: Simple Mode

This model represents the simplest approach which is conventionally used in analysis of absorption spectra. It neglects vibrational structure of electronic transitions and approximates each individual electronic band by a standard lineshape, typically a Gaussian, Lorentzian or mixed (Voigt) function. This model can only make sense if vibrational progressions are not resolved in electronic spectra. Upon this approximation the intensity of absorption spectrum depends on the energy of the incident photon (E_L), the electronic transition energy (E_T), the transition electric dipole moment (M, evaluated at the ground-state equilibrium geometry). Lineshape factors are specified by homogeneous linewidth Γ and standard deviation parameter σ corresponding to Gaussian distribution of transition energies. The following example illustrates a simple input for simulation of absorption bandshapes using various intensity and lineshape parameters.

```
# example001.inp
#
# Input file to generate absorption spectrum consisting
# of 3 bands   with different lineshape factors:
#
# 1. Lorentzian centered at 18000cm**-1 (damping factor Gamma= 100 cm**-1)
# 2. Gaussian   centered at 20000cm**-1
#    (standard deviation Sigma= 100 cm**-1)
# 3. Mixed Gaussian-Lorentzian band representing Voigt profile
#    centered at 21000 cm**-1

%sim
        Model Simple

        # Spectral range for absorption simulation:
        AbsRange     17000.0,   23000.0

        # Number of points to simulate absorption spectrum:
        NAbsPoints  2000

end


#-------------------------------------------------------------------------
#  Transition       Gamma    Sigma  Transition Dipole Moment (atomic unit)
#  Energy (cm**-1)  (cm**-1) (cm**-1)     Mx           My          Mz
#-------------------------------------------------------------------------

$el_states
3     # number of electronic states
   1  18000.0         100.00        0.0         1.0         0.0         0.0
```

```
   2  20000.0              0.00    100.0         1.0         0.0         0.0
   3  22000.0             50.00     50.0         1.0         0.0         0.0
```

The parameters of of the final electronic states reached by the respective transitions are specified in the `$el_states` block. The spectral range and resolution used in the calculation are defined by the `AbsRange` and `NAbsPoints` keywords in `%sim` block. The calculation of the absorption spectrum is automatically invoked if `NAbsPoints>1`. After the `orca_asa` run you will find in your directory file `example001.abs.dat` containing absorption spectrum in simple two-column ASCII format suitable to be plotted with any spreadsheet program. Absorption spectra corresponding to individual electronic transitions are stored in file `example001.abs.as.dat` (the suffix "as" stands for "All States").
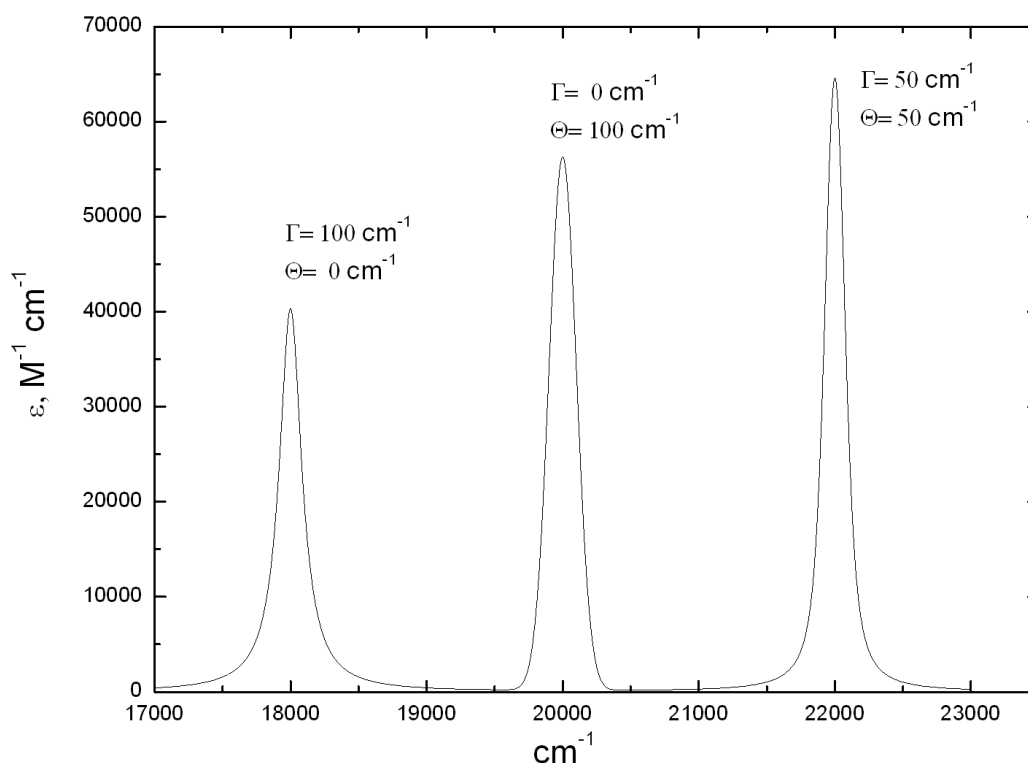

Fig. 5.33: Absorption spectrum generated after orca_asa run on file `example001.inp.` Three bands have different lineshape parararameters. Note that although all transitions are characterized by the same transition electric dipole moment their intensities are scaled proportionally to the transition energies.

The output of the program run also contains information about oscillator strengths and full-width-half-maximum (FWHM) parameters corresponding to each electronic band:

```
-----------------------------------------------
  State        EV         fosc    Stokes shift
           (cm**-1)                 (cm**-1)
-----------------------------------------------
    1:      18000.00    0.054676      0.00
    2:      20000.00    0.060751      0.00
    3:      22000.00    0.066826      0.00
```

```
----------------------------------------
  BROADENING PARAMETETRS (cm**-1)
----------------------------------------
  State     Gamma     Sigma     FWHM
----------------------------------------
    1:      100.00      0.00    200.00
    2:        0.00    100.00    235.48
    3:       50.00     50.00    180.07
```

Note that although all three types of lineshape functions are symmetric this is not true for the overall shapes of individual absorption bands since the extinction coefficient (absorption cross-section) is also proportional to the incident photon energy. Therefore, if the linewidth is larger than 10% of the peak energy the asymmetry of the electronic band can be quite noticeable.

Example: Modelling of Absorption and Fluorescence Spectra within the IMDHO Model

The IMDHO model is the simplest approach that successfully allows for the prediction of vibrational structure in electronic spectra as well as rR intensities for a large variety of real systems. This model assumes:

1. harmonic ground- and excited-state potential energy surfaces;

2. origin shift of the excited-state potential energy surface relative to the ground-state one;

3. no vibrational frequency alteration or normal mode rotation occurs in the excited state;

4. no coordinate dependence of the electronic transition dipole moment.

In addition to the parameters that enter the "Simple model" defined above it requires some information about the vibrational degrees of freedom. The required information consists of the ground-state vibrational frequencies $\{\omega_{gm}\}$ and (dimensionless) origin shifts $\{\Delta_{mi}\}$, where i and m refer to electronic states and normal modes respectively. Δ is expressed in terms of dimensionless normal coordinates. Accordingly, for the IMDHO model one has to specify the following blocks

- The $el_states block contains the parameters $E_T, \Gamma, \sigma, \mathbf{M}$ for each electronic state. By default E_T is assumed to be adiabatic minima separation energy. Alternatively, it can be redefined to denote for the vertical transition energy. This is achieved by specifying the keyword EnInput=EV in the %sim block.

- A $vib_freq_gs block specifies ground-state vibrational frequencies.

- A $sdnc block contains parameters $\{\Delta_{mi}\}$ in matrix form such that the i-th column represents the dimensionless displacements along all normal modes for the i-th excited-state PES.

The file example002.inp provides the input for simulation of absorption and fluorescence spectra of a system characterized by significant displacements of the excited-state origin along 5 normal coordinates.

```
# example002.inp
#
# Input file for simulation  of vibrational structure
# in absorption and fluorescence spectra assuming
# origin shift of excited PES along 5 normal coordinates.
# The simulated spectra closely reproduce the experimental
# optical bandshapes for the tetracene molecule.
#
%sim
    Model IMDHO

    # spectral range for absorption simulation (cm**-1)
    AbsRange    20000.0, 27000.0
    NAbsPoints  2000               # number of points in absorption spectrum

    # spectral range for simulation of fluorescence (cm**-1)
    FlRange     22000.0, 16000.0
```

```
     NFlPoints   2000      # number of points in fluorescence spectrum

     # the following options require the spectra to be normalized
     # so that their maxima are equal to 1.0
     AbsScaleMode Rel
     FlScaleMode  Rel  # default  for fluorescence

     # for absorption spectrum the default option is AbsScaleMode= Ext
     # which stands for extinction coefficient

end


#-------------------------------------------------------------------------
#  Transition        Gamma    Sigma  Transition Dipole Moment (atomic unit)
#  Energy (cm**-1)  (cm**-1) (cm**-1)     Mx           My           Mz
#-------------------------------------------------------------------------

$el_states
1
   1  21140.0          50.00    100.0         1.0          0.0          0.0


# Block specifying Stokes Shift parameter for each electronic state
# This information is optional
$ss
1   # number of excited states
   1   300.0       # the Stokes shift for the 1st electronic transition

# Block providing the values of VIBrational FREQuencies
# for 5 Ground-State normal modes.
# Obligatory for IMDHO and IMDHOFA models.
$vib_freq_gs
5
     1       310.0
     2      1193.0
     3      1386.0
     4      1500.0
     5      1530.0


# Block specifying origin Shift of the excite-state PES
# along each normal mode in terms of the ground-state
# Dimensionless Normal Coordinates
# Obligatory for IMDHO and IMDHOFA models.
$sdnc
5 1
               1
      1       0.698
      2      -0.574
      3       0.932
      4      -0.692
      5       0.561
```

The calculation of absorption and fluorescence spectra is automatically invoked if the parameters `NAbsPoints>1` and `NFlPoints> 1`. The input file also contains the optional block `$ss` which specifies the Stokes shift λ for each electronic transition. This parameter is equal to the energy separation between the 0-0 vibrational peaks in the absorption and fluorescence spectra as shown in Fig. 5.34 . In general λ accounts for solvent induced effects as well as unresolved vibrational structure corresponding to low-frequency modes that are not specified in the input. Note that we have specified parameters `AbsScaleMode=Rel` and `FlScaleMode=Rel` in `%sim` block in order to ensure that the simulated spectra are normalized to unity. The calculated absorption and fluorescence spectra are stored in `example002.abs.dat` and `example002.fl.dat` files, respectively.
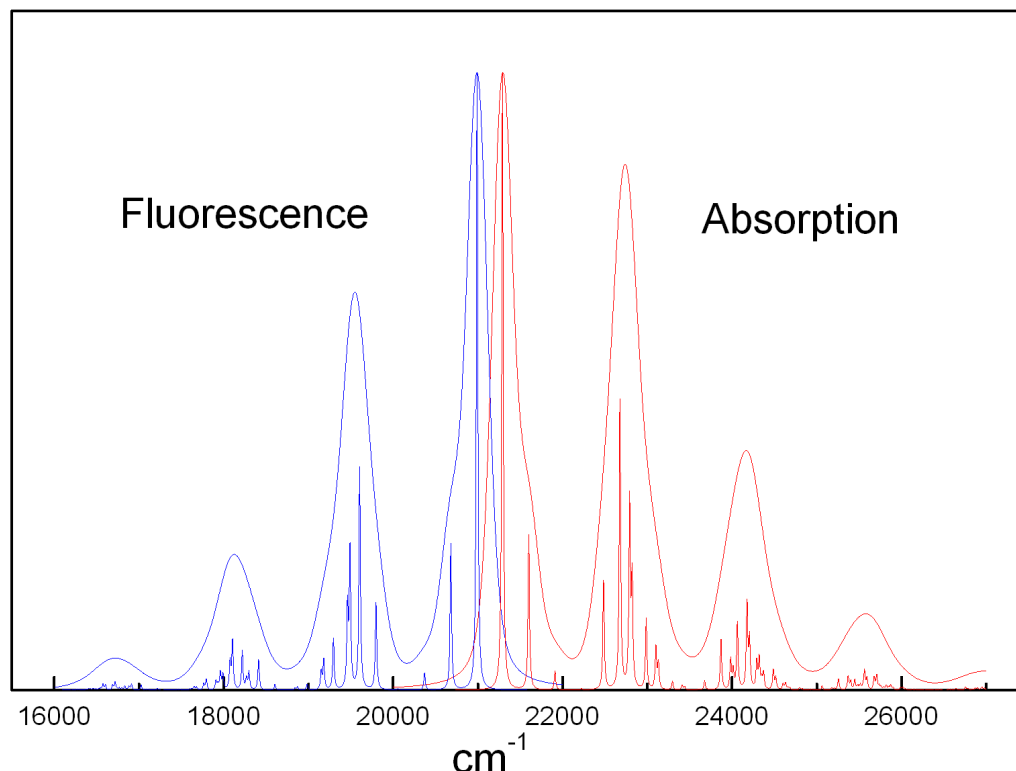
Fig. 5.34: Absorption and fluorescence spectra generated after `orca_asa` run on the file `example002.inp`. If the homogeneous broadening is set to be $\Gamma = 10\,\mathrm{cm}^{-1}$ one can resolve underlying vibrational structure and identify various fundamental and combination transitions.

Example: Modelling of Absorption and Fluorescence Spectra within the IMDHOFA Model

IMDHOFA (Independent Mode Displaced Harmonic Oscillators with Frequency Alteration) is based on the same assumptions as the IMDHO model except for vibrational frequency alteration in excited state can take place. The file `example003.inp` features almost the same input parameters as `example002.inp`. The IMDHOFA model is invoked by the keyword `Model=IMDHOFA` in the `%sim` block. Additionally, one has to provide the obligatory block `$vib_freq_es`. It contains the excited-state vibrational frequencies $\{\omega_{emi}\}$ in matrix form such that the i-th column represents the vibrational frequencies of all normal modes for the i-th excited-state PES.

```
# Block providing the values of VIBrational FREQuencies
# for 5 Excited-State normal modes.
# Obligatory for IMDHOFA model.

$vib_freq_es
5   1           # number of modes and number of excited states
            1
    1      410.0
    2     1293.0
    3     1400.0
    4     1600.0
    5     1730.0
```
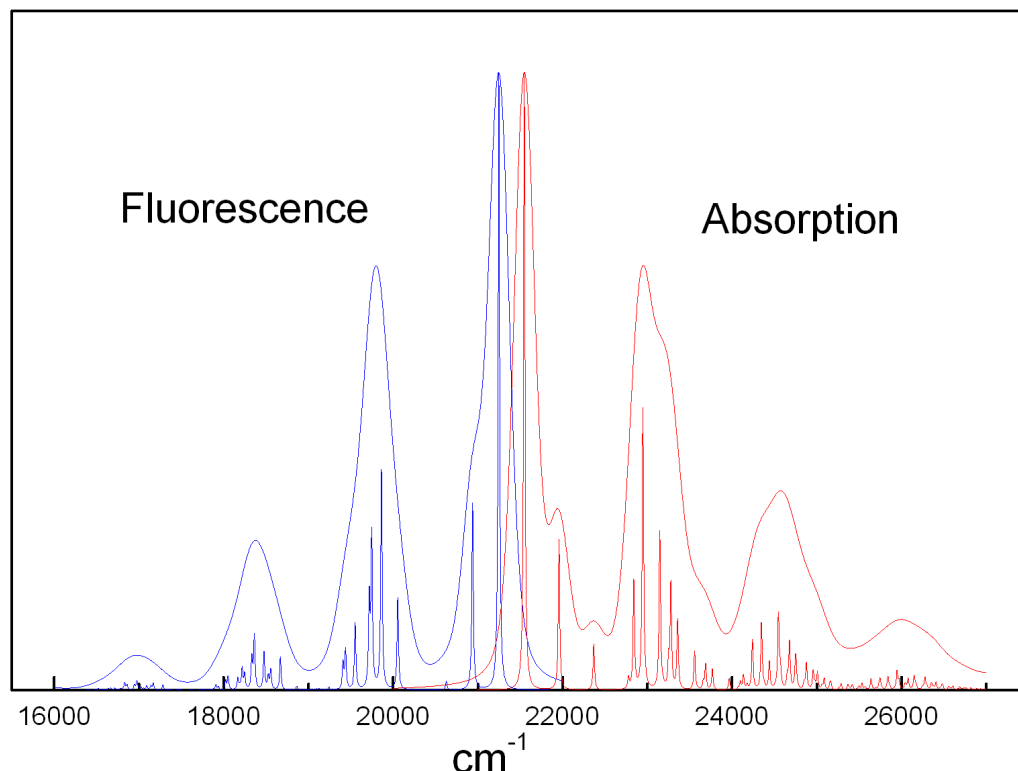
Fig. 5.35: Absorption and fluorescence spectra generated after `orca_asa` run on the file `example003.inp`. Also, the high-resolution spectra corresponding to homogeneous broadening $\Gamma = 10\,\text{cm}^{-1}$ are shown.

Example: Modelling of Effective Broadening, Effective Stokes Shift and Temperature Effects in Absorption and Fluorescence Spectra within the IMDHO Model

For the IMDHO model the `orca_asa` is capable to model absorption and emission spectra in the finite-temperature approximation. While the keyword `Model=IMDHO` assumes the zero-temperature approximation, the value of `Model=IMDHOT` invokes the calculation of the spectra for the finite temperature which is specified by the paramter `TK` in the block `%sim`:

```
# example004.inp
#
#
%sim
    Model IMDHOT
    TK 300 # temperature (in Kelvin)

    # spectral range for absorption simulation (cm**-1)
    AbsRange    18000.0, 35000.0
    NAbsPoints  5000            # number of points in absorption spectrum

    # spectral range for simulation of fluorescence (cm**-1)
    FlRange     22000.0, 10000.0
    NFlPoints   5000    # number of points in fluorescence spectrum

    # the following options require the spectra to be normalized
```

(continues on next page)

```
      # so that their maxima are equal to 1.0
      AbsScaleMode Rel
      FlScaleMode  Rel   # default  for fluorescence
end


#---------------------------------------------------------------------------
#   Transition       Gamma     Sigma   Transition Dipole Moment (atomic unit)
#   Energy (cm**-1)  (cm**-1)  (cm**-1)    Mx           My           Mz
#---------------------------------------------------------------------------

$el_states
1
   1  21140.0          50.00    100.0       1.0          0.0          0.0


# Block specifying Stokes Shift parameter for each electronic state
$ss
1   # number of excited states
  1   300.0       # the Stokes shift for the 1st electronic transition

# Block providing the values of VIBrational FREQuencies
# for 10 Ground-State normal modes.
$vib_freq_gs
10
    1        30.0
    2        80.0
    3       100.0
    4       120.0
    5       130.0
    6      140.0
    7      160.0
    8      200.0
    9      310.0
   10     1300.0

# Block specifying origin Shift of the excite-state PES
# along each normal mode in terms of the ground-state
# Dimensionless Normal Coordinates
$sdnc
 10  1
             1
     1       2.5
     2       2.0
     3       1.8
     4       1.9
     5       1.5
     6       1.9
     7       2.4
     8       1.9
     9       2.5
    10       0.9
```

This example illustrates a typical situation in large molecules which feature a number of low frequency modes with significant values of dimensionless displacements for a given excited-state PES. In the case of high density of vibrational states with frequencies below or comparable to the intrinsic value of FWHM (determined by Γ and σ) the vibrational progression is unresolved, whereby the spectra become very diffuse and show large separation between the maxima of absorption and emission spectra (Fig. 5.35). Besides, upon the condition $h\nu_i \leqslant kT$ the effective bandwidths and positions of maxima in the spectra can be strongly subject to temperature effects.
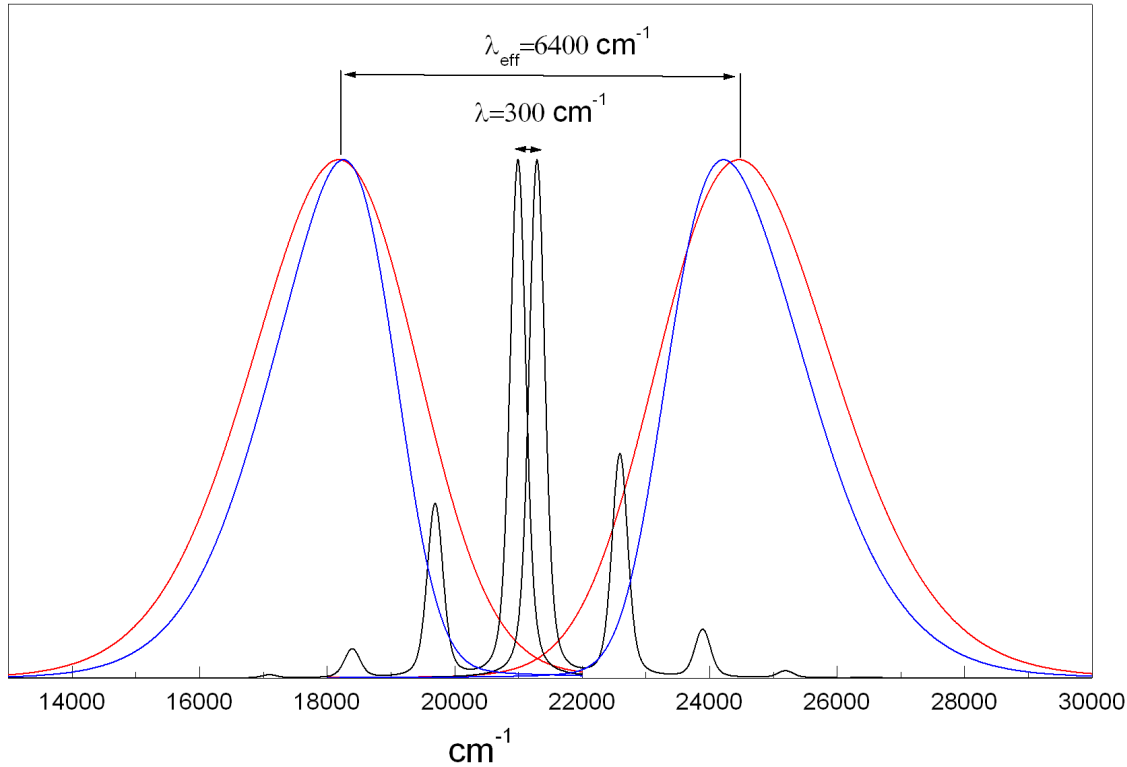
Fig. 5.36: Absorption and fluorescence spectra for T=0 K (blue) and T=300 K (red) generated after `orca_asa` run on the file `example004.inp`. Black lines show spectra corresponding to the case where all low-frequency modes were excluded from the calculation.

The effective Stokes shift and linewidth parameters which are evaluated in the simple self-consistent procedure are given in the output of the `orca_asa` run:

```
------------------------------------------------------------------------------
State     E0            EV        fosc    Stokes shift  Effective Stokes shift
          (cm**-1)      (cm**-1)            (cm**-1)          (cm**-1)
------------------------------------------------------------------------------
  1:    21140.00    24535.85   0.074529    300.00           7091.70


------------------------------------------------------------------------------
↪------------
                          BROADENING PARAMETETRS (cm**-1)
------------------------------------------------------------------------------
↪------------
               Intrinsic                               Effective
 State    -------------------------   -------------------------------------------
↪----------
                                                    Sigma                     ↵
↪FWHM
       Gamma    Sigma    FWHM      ----------------------------   ------------------
↪----------
                                      0K      298.15K   300.00K     0K      298.
↪15K   300.00K
------------------------------------------------------------------------------
↪------------
  1:      50.00   100.00   293.50    1125.34   1411.13   1413.57   2703.84   3376.
↪75   3382.48
```

Note that the evaluation of the effective parameters is rather approximate and these values can noticeable deviate from those which can be directly deduced from the calculated spectra. However, such an information usually provides the proper order of magnitude of the effective vibronic broadening and Stokes shift. As indicated in the program output above, the effective bandshape has predominantly a Gaussian character which varies with the temperature so that $\sigma = 1125\,\mathrm{cm}^{-1}$ ($T = 0$ K) and $\sigma = 1414\,\mathrm{cm}^{-1}$ ($T = 300$ K). Indeed, as shown in Fig. 5.37 the absorption spectrum at $T = 300$ K can be well fitted using Gaussian lineshape with $\sigma = 1388\,\mathrm{cm}^{-1}$ (FWHM= $3270\,\mathrm{cm}^{-1}$). One can see that at higher temperatures the deviation between the spectrum and its Gauss fit becomes even smaller.

In molecules the normal distribution of the electronic transition energies in the ensemble would give rise to a Gaussian bandshape of the absorption band. However, the corresponding standard deviation is expected to be of the order of $100\,\mathrm{cm}^{-1}$, whereby a typical Gaussian bandwidth of the order of $1000\,\mathrm{cm}^{-1}$ appears to result from unresolved vibronic progression. In general, this statement is supported by quantum chemical calculation of the model parameters. In principle the effective bandwidth parameters can also be used for characterization and assignement of individual electronic bands.
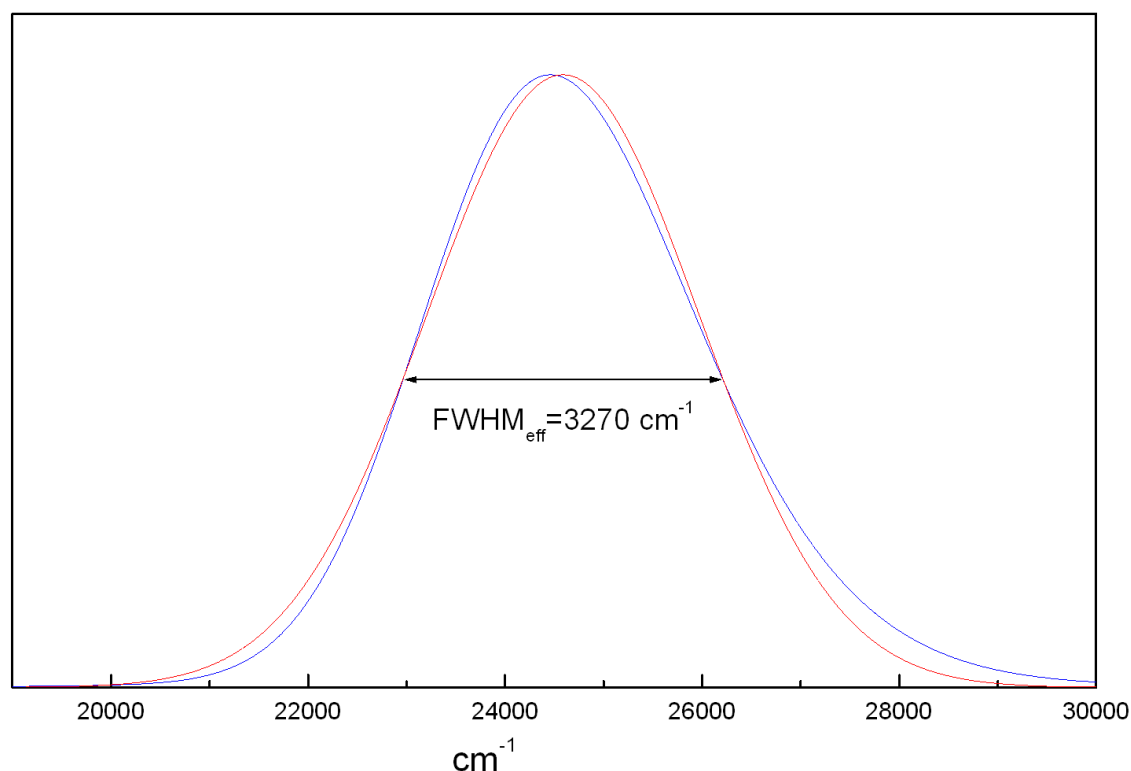

Fig. 5.37: Absorption spectrum (blue) for $T = 300$ K generated after `orca_asa` run on the file `example004.inp`. Red line represents the Gauss-fit of the calculated spectrum.

Example: Modelling of Absorption and Resonance Raman Spectra for the 1-^{1}A$_g$ → 1-^{1}B$_u$ Transition in *trans*-1,3,5-Hexatriene

The hexatriene molecule is characterized by 9 totally-symmetric normal modes which dominate vibrational structure in absorption and are active in rR spectra corresponding to the strongly dipole-allowed $1 - ^1 A_g \rightarrow 1 - ^1 B_u$ transition around $40000\,\mathrm{cm}^{-1}$. Except for some peculiarities related to the neglect of normal mode rotations in the excited state the optical spectra are quite satisfactorily described by the IMDHO model.

The following input exemplifies simulation of absorption spectrum and rR spectra for an arbitrary predefined number of excitation energies.

```
#
# example005.inp
```

(continues on next page)