

(continued from previous page)

```

Amplitude      Excitation
-0.142146      4 ->  8
-0.988793      7 ->  8
Ground state amplitude:  0.000000

Percentage Active Character      99.79

Amplitude      Excitation in Canonical Basis
-0.134936      4 ->  8
-0.955031      7 ->  8
 0.236743      7 -> 13

IROOT=  2:  0.308093 au      8.384 eV   67618.5 cm**-1
Amplitude      Excitation
 0.971471      7 ->  9
 0.214898      7 -> 10
Ground state amplitude: -0.000000

Percentage Active Character      99.67

Amplitude      Excitation in Canonical Basis
 0.956929      7 ->  9
-0.236568      7 -> 11
 0.102573      7 -> 16

IROOT=  3:  0.331790 au      9.028 eV   72819.4 cm**-1
Amplitude      Excitation
 0.993677      5 ->  8
Ground state amplitude: -0.000000

Percentage Active Character      98.87

Amplitude      Excitation in Canonical Basis
 0.957221      5 ->  8
-0.250140      5 -> 13
-0.105951      5 -> 18

IROOT=  4:  0.346876 au      9.439 eV   76130.4 cm**-1
Amplitude      Excitation
-0.104901      4 -> 10
 0.198176      7 ->  9
-0.972572      7 -> 10
Ground state amplitude: -0.000000

Percentage Active Character      99.65

Amplitude      Excitation in Canonical Basis
 0.100880      4 -> 11
 0.218873      7 ->  9
 0.956923      7 -> 11
-0.113897      7 -> 19

IROOT=  5:  0.347460 au      9.455 eV   76258.7 cm**-1
Amplitude      Excitation
 0.139551      4 -> 11
 0.106649      4 -> 12
-0.801186      6 ->  8
 0.455613      7 -> 11
 0.302458      7 -> 12
Ground state amplitude:  0.027275

```

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```

Percentage Active Character      87.08

Warning:: the state may have not converged with respect to active space
----- Handle with Care -----

Amplitude      Excitation in Canonical Basis
  0.163791      4 -> 10
 -0.785701      6 ->  8
  0.159149      6 -> 13
  0.527833      7 -> 10
 -0.133085      7 -> 17

IROOT=  6:  0.379059 au      10.315 eV      83193.9 cm**-1
Amplitude      Excitation
 -0.983700      4 ->  8
  0.155239      7 ->  8
Ground state amplitude:  0.000000

Percentage Active Character      99.48

Amplitude      Excitation in Canonical Basis
 -0.951092      4 ->  8
  0.235046      4 -> 13
  0.157714      7 ->  8

```

The IP and EA versions can be called by using the keywords IP-EOM-DLPNO-CCSD and EA-EOM-DLPNO-CCSD, respectively. As in canonical STEOM-CCSD, the first set of excitation amplitudes, printed for each root, are calculated in the CIS NTO (Natural Transition Orbitals) basis, while the second set is evaluated in the RHF canonical basis.

5.5 Excited State Dynamics

ORCA can now also be used to compute dynamic properties involving excited states such as absorption spectra, fluorescence and phosphorescence rates and spectra, as well as resonant Raman spectra using the new ORCA_ESD module. We do this by analytically solving the Fermi's Golden Rule-like equation from Quantum Electrodynamics (see the section [Excited State Dynamics](#)), using a path integral approach to the dynamics, as described in our recent papers [600, 601]. The computation of these rates relies on the harmonic approximation for the nuclear normal modes. Provided this approximation holds, the results closely match experimental data.

The theory can do most of what ORCA_ASA can and more, such as including vibronic coupling in forbidden transitions (the so-called Herzberg-Teller effect, HT), considering Duschinsky rotations between modes of different states, solving the equations using different coordinate systems, etc. There are also seven new approaches to obtain the excited state geometry and Hessian without necessarily optimizing its geometry. Many keywords and options are available, but most of the defaults already give good results. Let's get into specific examples, starting with the absorption spectrum. Please refer to section [Excited State Dynamics](#) for a complete keyword list and details.

5.5.1 Absorption Spectrum

The ideal model, Adiabatic Hessian (AH)

To predict absorption or emission rates, including all vibronic transitions, ideally, one requires both the ground state (GS) and excited state (ES) geometries and Hessians. For instance, when predicting the absorption spectrum for benzene, which exhibits one band above 220 nm corresponding to a symmetry-forbidden excitation to the S1 state, the process is straightforward. Ground state information can be obtained from (Sec. [Geometry Optimizations](#)):

```
!B3LYP DEF2-SVP OPT FREQ
* XYZFILE 0 1 BEN.xyz
```

and the S1 ES from (Sec. *Excited State Geometry Optimization*):

```
!B3LYP DEF2-SVP OPT FREQ
%TDDFT
  NROOTS    5
  IROOT     1
END
* XYZFILE 0 1 BEN_S1.xyz
```

Assuming DFT/TD-DFT here, but other methods can also be used (see *Tips, Tricks and Troubleshooting*). With both Hessians available, the ESD module can be accessed from:

```
!B3LYP DEF2-SVP TIGHTSCF ESD (ABS)
%TDDFT
  NROOTS    5
  IROOT     1
END
%ESD
  GSHESSIAN "BEN.hess"
  ESHESSIAN "BEN_S1.hess"
  DOHT      TRUE
END
* XYZFILE 0 1 BEN.xyz
```

Important

The geometry must match that in the GS Hessian when calling the ESD module. You can obtain it from the .xyz file after geometry optimization or directly copy it from the .hess file (remember to use BOHRS on the input to correct the units, if obtained from the .hess).

You must provide both names for the Hessians and set DOHT to TRUE here because the first transition of benzene is symmetry forbidden, with an oscillator strength of $2e-6$. Therefore, all intensity arises from vibronic coupling (HT effect) [600]. In molecules with strongly allowed transitions, this parameter can typically remain FALSE (the default). Some calculation details are printed, including the computation of transition dipole derivatives for the HT component, and the spectrum is saved as BASENAME.spectrum.

Energy	TotalSpectrum	IntensityFC	IntensityHT
10807.078728	2.545915e-02	2.067393e-07	2.545894e-
↪ 02			
10828.022679	2.550974e-02	2.071508e-07	2.550954e-
↪ 02			
10848.966630	2.556034e-02	2.075624e-07	2.556013e-
↪ 02			
...			

The first column has the total spectrum, but the contributions from the Franck-Condon part and the Herzberg-Teller part are also discriminated. As you can see, the FC intensity is less than 1% of the HT intensity here, highlighting the importance of including the HT effect. It is important to note that, in theory, the absorbance intensity values correspond to the experimental ϵ (in L mol cm^{-1}), and they depend on the spectral lineshape. The TotalSpectrum column can be plotted using any software to obtain the spectrum named Full AH spectrum (shown in blue), in Fig. 5.4 below.

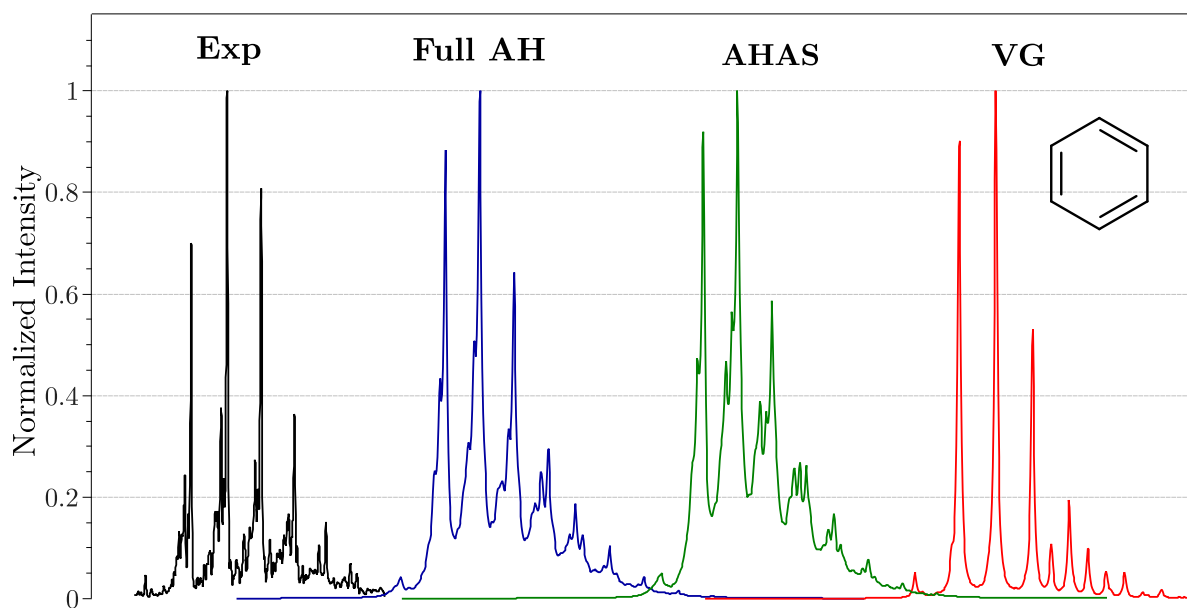


Fig. 5.4: Here is the experimental absorption spectrum for benzene (shown in black on the left), alongside predictions made using ORCA_ESD at various PES approximations.

The spectrum obtained is very close to the experimental results at 298K, even when simply using all the defaults, and it could be further improved by adjusting parameters such as lineshape, as discussed in detail in Sec. *Fluorescence Rates and Spectrum* and Sec. *Excited State Dynamics*.

Note

- The path integral approach in ORCA_ESD is much faster than the more traditional approach of calculating all vibronic transitions with non-negligible intensities, one by one [602]. This is especially true for large systems, where the number of bright vibronic transitions may potentially scale exponentially, but our approach's scaling remains polynomial (in fact near linear scaling in favorable cases [600]). The price to pay is that one can no longer read off the compositions of the vibronic states from the spectrum, in other words, one cannot assign the peaks without doing further calculations. However, one can know whether a given vibrational mode contributes to a given peak, by repeating the ESD calculation with a few modes removed, and see if the peak is still present. This can be conveniently done using the MODELIST or SINGLEMODE keywords. More information can be found in Sec. *Excited State Dynamics*.
- The Huang-Rhys factors are important tools for qualitative and quantitative analysis of the contributions of each vibrational mode to the vibrationally resolved spectrum (and also to the transition rate constants, as will be discussed later). They can be requested by setting PRINTLEVEL in the %ESD module to 3 or above.

Of course, it is not always possible to obtain the excited state (ES) geometry due to root flipping, or it might be too costly for larger systems. Therefore, some approximations to the ES Potential Energy Surface (PES) have been developed.

The simplest model, Vertical Gradient (VG)

The minimal approximation, known as Vertical Gradient (VG), assumes that the excited state (ES) Hessian equals the ground state (GS) Hessian and extrapolates the ES geometry from the ES gradient and that Hessian using some step (Quasi-Newton or Augmented Hessian, which is the default here). Additionally, in this scenario, the simplest Displaced Oscillator (DO) model is employed, ensuring fast computation [600]. To use this level of approximation, simply provide an input like:

```
!B3LYP DEF2-SVP TIGHTSCF ESD (ABS)
%TDDFT
  NROOTS      5
  IROOT       1
END
%ESD
  GSHESSIAN   "BEN.hess"
  DOHT        TRUE
  HESSFLAG    VG      #DEFAULT
END
* XYZFILE 0 1 BEN.xyz
```

OBS: If no GSHESSIAN is given, it will automatically look for an BASENAME.hess file.

Choosing one of the methods in ORCA to compute excited state information is essential. Here, we utilize TD(A)-DFT with IROOT 1 to compute properties for the first excited state. TD(A)-DFT is currently the sole method offering analytic gradients for excited states; selecting any other method will automatically enforce NUMGRAD.

Important

Please note that certain methods, such as STEOM-DLPNO-CCSD, require significant time to compute numerical gradients. In such cases, we recommend using DFT/TD-DFT Hessians and employing the higher-level method solely for single points.

If everything is set correctly, after the regular single point calculation, the ESD module in ORCA will initiate. It proceeds to obtain the excited state (ES) geometry, compute derivatives, and predict the spectrum. The resulting normalized spectrum can be observed in Fig. 5.4, depicted in red. Due to such simple model, the spectrum is also simplified. While this simplicity is less critical for larger molecules, it highlights the potential benefit of employing an intermediate model.

A better model, Adiabatic Hessian After a Step (AHAS)

A reasonable compromise between a full geometry optimization and a simple step with the same Hessian is to perform a step and then recalculate the ES Hessian at that geometry. This approach is referred to here as Adiabatic Hessian After Step (AHAS). In our tests, it can be invoked with the following input:

```
!B3LYP DEF2-SVP TIGHTSCF ESD (ABS)
%TDDFT
  NROOTS      5
  IROOT       1
END
%ESD
  GSHESSIAN   "BEN.hess"
  DOHT        TRUE
  HESSFLAG    AHAS
END
* XYZFILE 0 1 BEN.xyz
```

The spectrum obtained corresponds to the green line in Fig. 5.4. As shown, it closely resembles the spectrum obtained using AH, where a full geometry optimization was performed. Although not set as the default, this method comes highly recommended based on our experience [600]. Another advantage of this approach is that the derivatives of the

transition dipole are computed simultaneously over Cartesian displacements on the ES structure using the numerical Hessian. Subsequently, these modes are straightforwardly converted.

OBS: The transition dipoles used in our formulation are always those of the FINAL state geometry. For absorption, this corresponds to the ES, so in AHAS, the derivatives are computed over this geometry. For fluorescence, the default behavior is to recompute the derivatives over the GS geometry. Alternatively, you can choose to save time and convert directly from ES to GS by setting CONVDER TRUE (though this is an approximation). For more details, refer to Sec. *Excited State Dynamics*.

Other PES options

There are also a few other options that can be set using HESSFLAG. For example, you can calculate the vertical ES Hessian over the GS geometry and perform a step, known as the **Vertical Hessian (HESSFLAG VH)** method. This method has the advantage that the geometry step is expected to be better because it does not assume the initial ES Hessian is equal to the GS Hessian. However, it is likely to encounter negative frequencies on that VH, since you are not at the ES minimum. By default, ORCA will turn negative frequencies into positive ones, issuing a warning if any were lower than -300 cm^{-1} . You can also choose to completely remove them (and the corresponding frequencies from the GS) by setting IFREQFLAG to REMOVE or leave them as negative with IFREQFLAG set to LEAVE under %ESD. Just be aware that an odd number of negative frequencies might disrupt the calculation of the correlation function, so be sure to check.

If your excited state is localized and you prefer not to recalculate the entire Hessian, you can opt for a **Hybrid Hessian (HH)** approach. This involves recomputing the ES Hessian only for specific atoms listed in HYBRID_HESS under %FREQ (*Vibrational Frequencies*). The HH method uses the GS Hessian as a base but adjusts it at the specified atoms. This computation can be performed either before or after the step, offering two variations: **Hybrid Hessian Before Step (HESSFLAG HHBS)** or **Hybrid Hessian After Step (HESSFLAG HHAS)**. When using either of these options, derivatives are recalculated across the modes as needed.

Another approach involves comparing the ES Hessian with the GS Hessian and selectively recomputing frequencies that differs. This method works by applying a displacement based on the GS Hessian and evaluating the resulting energy change. If the predicted mode matches the actual mode, the prediction should be accurate. However, if the difference exceeds a specified threshold, the gradient is computed, and the frequency for that mode is recalculated accordingly. The final ES Hessian is then derived from the **Updated Frequencies (UF)** and the original GS Hessian.

This approach offers the advantage of minimizing the computation of ES gradients typical in standard ES Hessians, thereby speeding up the process. By default, the system checks for frequency errors of approximately 20%. You can adjust this threshold using the UPDATEFREQERR flag; for instance, setting UPDATEFREQERR to 0.5 under %ESD allows for a larger error tolerance of 50%. Additionally, you can implement either the **Updated Frequencies Before Step (HESSFLAG UFBS)** or the **Updated Frequencies After Step (UFAS)** methods. Transition dipole derivatives are computed concurrently with the update process.

OBS: All these options apply to Fluorescence and resonant Raman as well.

Duschinsky rotations

The ES modes can sometimes be expressed as linear combinations of the GS modes (see Sec. *General Aspects of the Theory*), a phenomenon known in the literature as Duschinsky rotation [603]. In our formulation within ORCA_ESD, it is possible to account for this effect, which reflects a closer approximation to real-world scenarios, albeit at a higher computational cost.

You can enable this feature by setting USEJ TRUE; otherwise, the rotation matrix J defaults to unity. For instance, in the case of benzene, while the effect may not be pronounced, there is noticeable improvement in matching peak ratios with experimental data when incorporating rotations. Exploring this option may reveal more significant impacts in other cases.

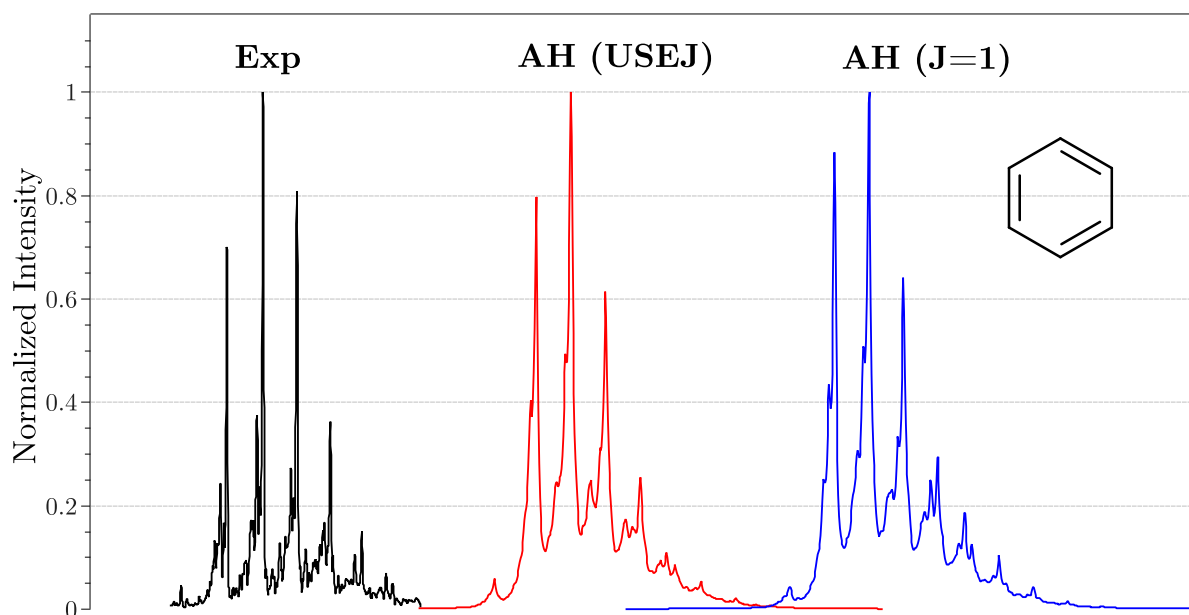


Fig. 5.5: Experimental absorption spectrum for benzene (black on the left) and the effect of Duschinsky rotation on the spectrum.

Temperature effects

In our model, the effects of the Boltzmann distribution due to temperature are exactly accounted for [600]. The default temperature is set to 298.15 K, but you can specify any other temperature by adjusting the TEMP parameter under %ESD. However, it is important to note that when approaching temperatures close to 0 K, numerical issues may arise. For instance, if you encounter difficulties modeling a spectrum at 5 K or wish to predict a jet-cooled spectrum, setting TEMP to 0 will activate a set of equations specifically tailored for T=0 K conditions.

As can be seen in Fig. 5.6, at 0 K there are no hot bands and fewer peaks, while at 600 K there are many more possible transitions due to the population distribution over the GS.

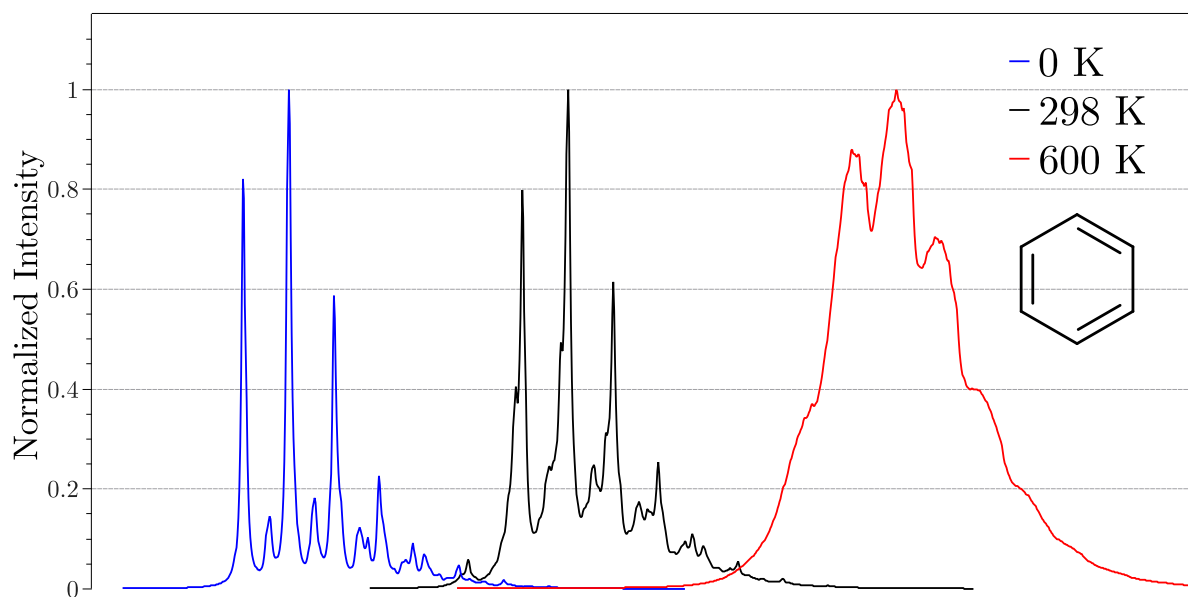


Fig. 5.6: Predicted absorption spectrum for benzene at different temperatures.

Multistate Spectrum

If you want to predict a spectrum that includes many different states, you should ignore the IROOT flag in all modules and instead use the STATES flag under %ESD. For example, to predict the absorption spectra of pyrene in the gas phase and consider the first twenty states, you would specify:

```
!B3LYP DEF2-TZVP (-F) TIGHTSCF ESD (ABS)
%TDDFT
  NROOTS      20
END
%ESD
  GSHESSIAN   "PYR.hess"
  ESHESSIAN   "PYR_S1.hess"
  DOHT        TRUE
  STATES       1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20
  UNIT        NM
END
* XYZFILE 0 1 PYR.xyz
```

This input would result in the spectra shown in Fig. 5.7. In this case, each individual spectrum for every state will be saved as BASENAME.spectrum.root1, BASENAME.spectrum.root2, etc., while the combined spectrum, which is the sum of all individual spectra, will be saved as BASENAME.spectrum.

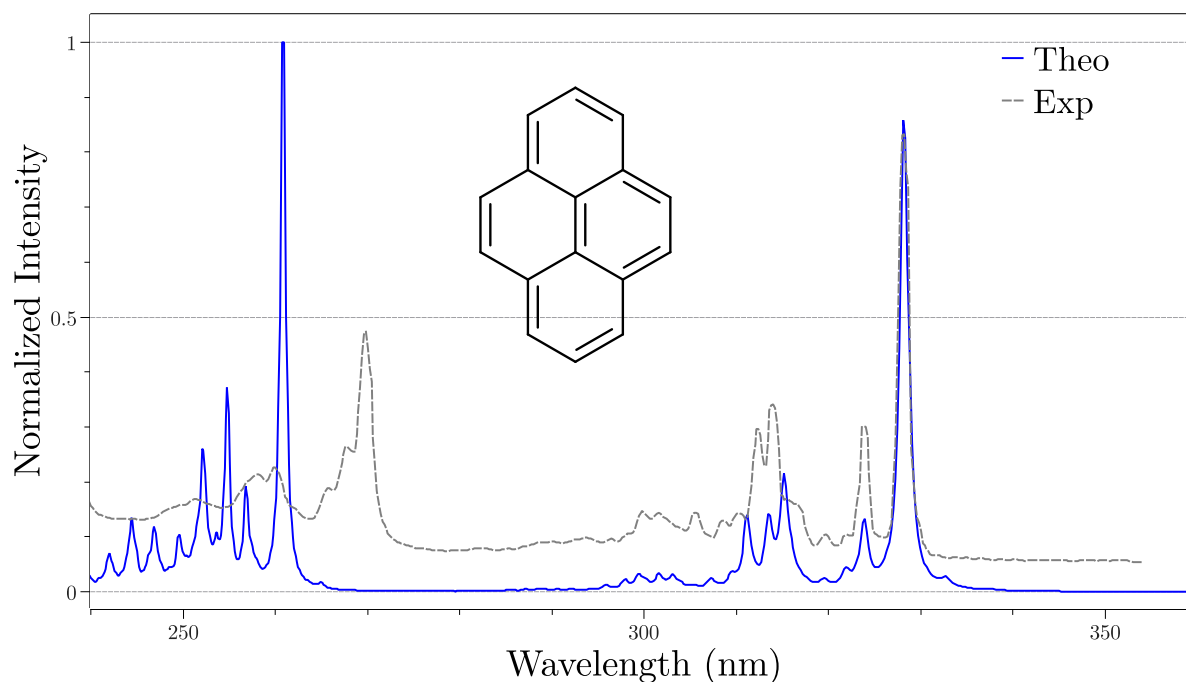


Fig. 5.7: Predicted absorption spectrum for pyrene in gas phase (solid blue) in comparison to the experiment (dashed grey) at 298 K.

OBS: The flag UNIT can be used to control the output unit of the X axis. Its values can be CM-1, NM or EV and it only affects the OUTPUT, the INPUT should always be in cm^{-1}

5.5.2 Fluorescence Rates and Spectrum

General Aspects

The prediction of fluorescence rates and spectra can be performed in a manner analogous to absorption, as described above, by using ESD(FLUOR) on the main input line. You can select any of the methods described earlier to obtain the Potential Energy Surface (PES) by setting the appropriate HESSFLAG. The primary distinction is that the transition dipoles must correspond to the geometry of the ground state (GS), while all other aspects remain largely unchanged.

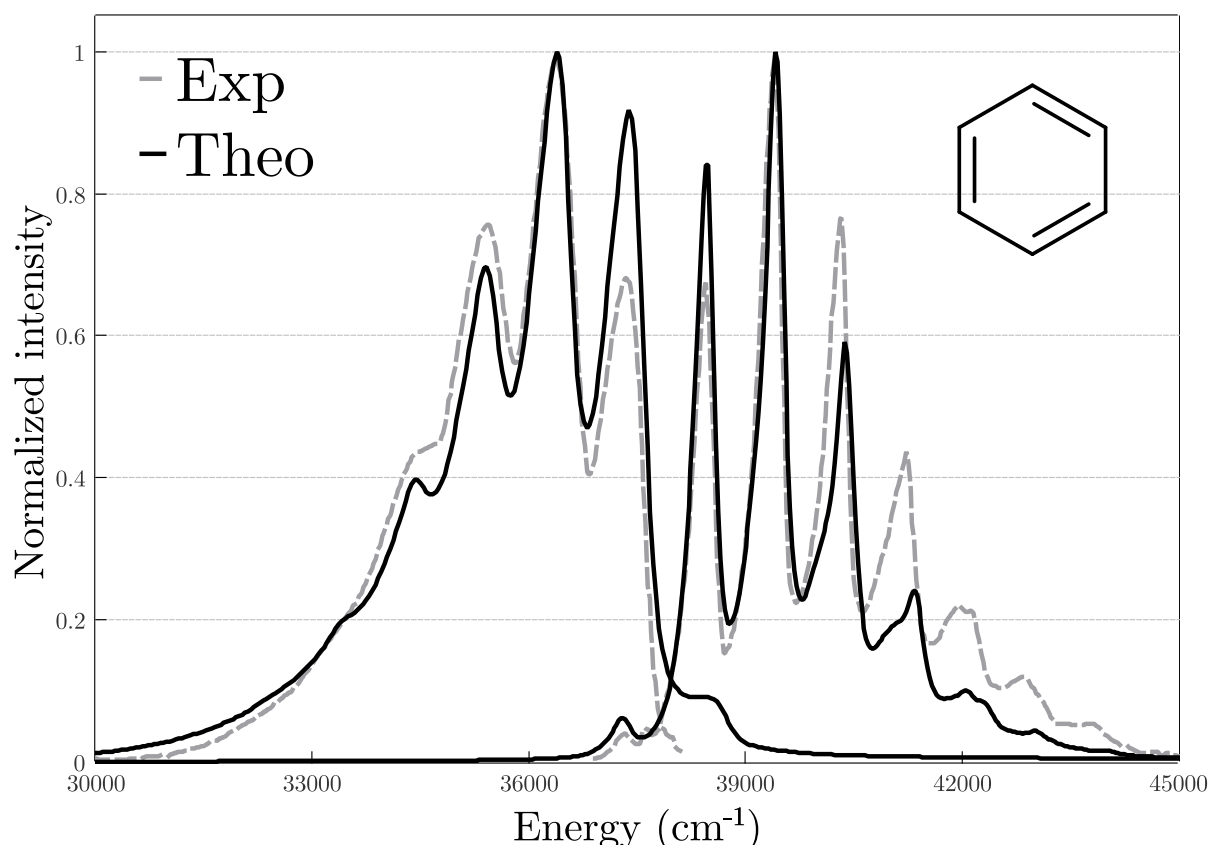


Fig. 5.8: Predicted absorption (right) and emission (left) spectrum for benzene in hexane at 298.15 K.

As depicted in Fig. 5.8, the fluorescence spectrum also closely matches the experimental data [600]. The difference observed in the absorption spectrum in Fig. 5.8, compared to previous spectra, arises because the experiment was conducted in a solvent environment. Therefore, we adjusted the linewidth to align with the experimental data.

OBS: It is common for the experimental lineshape to vary depending on the setup, and this can be adjusted using the LINEW flag (in cm^{-1}). There are four options for the lineshape function controlled by the LINES flag: DELTA (for a Dirac delta function), LORENTZ (default), GAUSS (for a Gaussian function), and VOIGT (a Voigt profile, which is a product of Gaussian and Lorentzian functions).

OBS2: The DELE and TDIP keywords can be used to input adiabatic (not vertical!) excitation energy and transition dipole moment computed at a higher level of theory. This enables calculating the computationally intensive Hessians (especially the excited state Hessian) at a low level of theory without compromising the accuracy. For more details, see Sec. *Mixing methods*.

If you need to control the lineshapes separately for Gaussian (GAUSS) and Lorentzian (LORENTZ), you can set LINEW for Lorentzian and INLINEW for Gaussian (where “I” stands for Inhomogeneous Line Width).

```
!B3LYP DEF2-SVP TIGHTSCF ESD(FLUOR)
%TDDFT
```

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```

NROOTS      5
IROOT       1
END
%ESD
GSHESSIAN   "BEN.hess"
ESHESSIAN   "BEN_S1.hess"
DOHT        TRUE
LINES       VOIGT
LINEW       75
INLINEW     200
END
* XYZFILE 0 1 BEN.xyz

```

OBS: The LINEW and INLINEW are NOT the full width half maximum ($FWHM$) of these curves. However, they are related to them by: $FWHM_{lorentz} = 2 \times LINEW$; $FWHM_{gauss} = 2.355 \times INLINEW$.

For the VOIGT curve, it is a little more complicated but in terms of the other FWHMs, it can be approximated as: $FWHM_{voigt} = 0.5346 \times FWHM_{lorentz} + \sqrt{(0.2166 \times FWHM_{lorentz}^2 + FWHM_{gauss}^2)}$.

Rates and Examples

When you select ESD(FLUOR) on the main input, the fluorescence rate will be printed at the end of the output, with contributions from Franck-Condon (FC) and Herzberg-Teller (HT) mechanisms discriminated. If you use CPCM, the rate will be multiplied by the square of the refractive index, following Strickler and Berg [604].

If you calculate a rate without CPCM but still want to account for the solvent effect, remember to multiply the final rate by this factor. Below is an excerpt from the output of a calculation with CPCM (hexane):

Warning

Whenever using ESD with CIS/TD-DFT and solvation, CPCMEQ will be set to TRUE by default, since the excited state should be under equilibrium conditions! More info in [Including solvation effects via LR-CPCM theory](#).

```

...
***Everything is set, now computing the correlation function***

Homogeneous linewidth is:          50.00 cm-1
Number of points:                  131072
Maximum time:                      1592.65 fs
Spectral resolution:                3.33 cm-1
Temperature used:                   298.15 K
Z value:                           5.099843e-42
Energy difference:                  41049.37 cm-1
Reference transition dipole (x,y,z): (0.00004 0.00000),
                                      (0.00002 0.00000),
                                      (-0.00058 0.00000)

Calculating correlation function:    ...done
Last element of the correlation function: 0.000000,-0.000000
Computing the Fourier Transform:    ...done

The calculated fluorescence rate constant is      1.688355e+06 s-1*
with 0.00% from FC and 100.00% from HT

*The rate is multiplied by the square of the refractive index

The fluorescence spectrum was saved in          BASENAME.spectrum

```

In one of our theory papers, we investigated the calculation of fluorescence rates for the set of molecules presented in Fig. 5.9. The results are summarized in Fig. 5.10 for some of the methods used to obtain the Potential Energy Surface (PES) mentioned.

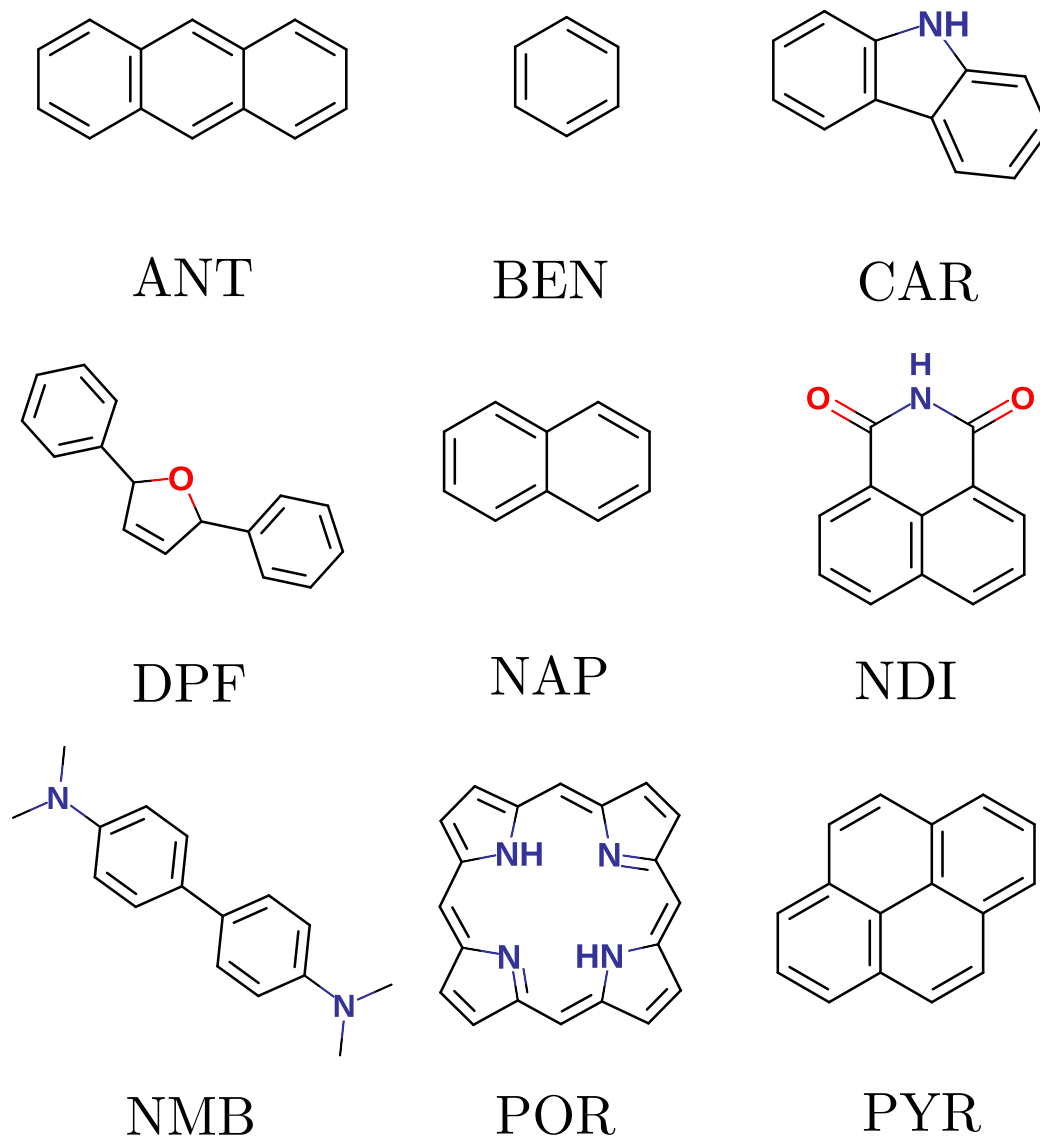


Fig. 5.9: The set of molecules studied, with rates on Fig. 5.10.

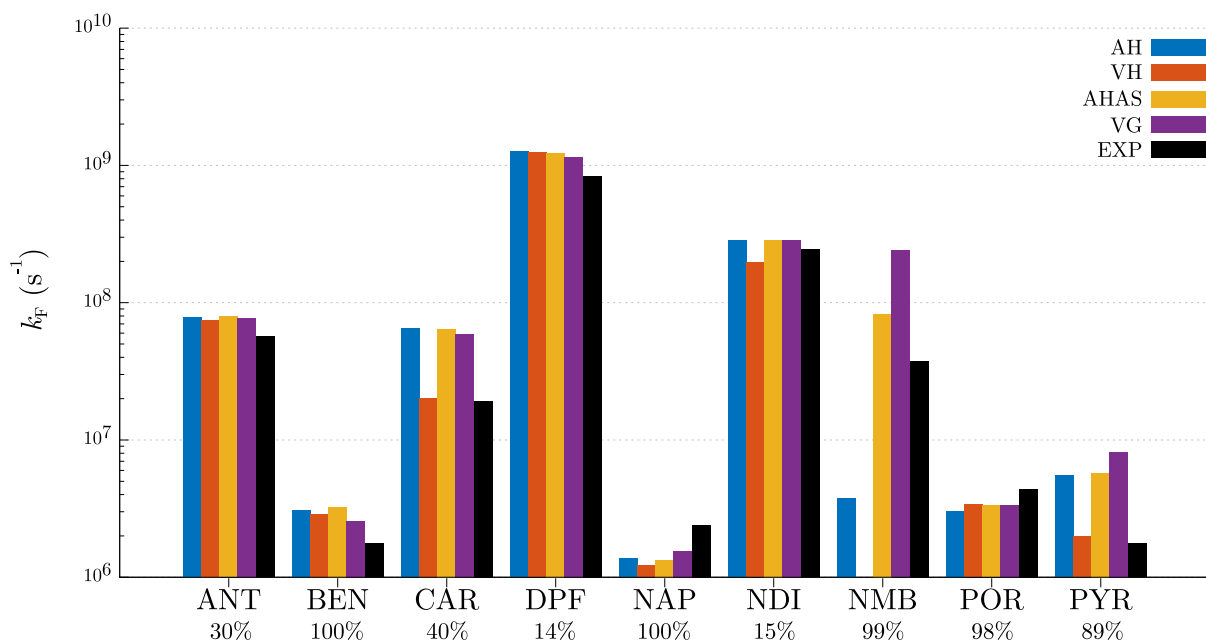


Fig. 5.10: Predicted emission rates for various molecules in hexane at 298.15 K. The numbers below the labels are the HT contribution to the rates.

5.5.3 Phosphorescence Rates and Spectrum

General Aspects

As with fluorescence, phosphorescence rates and spectra can be calculated if spin-orbit coupling is included in the excited state module (please refer to the relevant publication [601]). To enable this, ESD(PHOSP) must be selected in the main input, and both a GSHESSIAN and a TSHESSIAN must be provided. The triplet Hessian can be computed analytically from the spin-adapted triplets.

```
!B3LYP DEF2-TZVP (-F) CPCM(ETHANOL) OPT FREQ
%TDDFT
  NROOTS 5
  IROOTMULT TRIPLET
END
* XYZ 0 1
C      -0.82240      -0.05739      0.00515
C       0.42295       0.77803      0.02146
H      -0.85252      -0.69527      0.89195
H      -0.85090      -0.66429     -0.90325
H      -1.69889       0.59680      0.01431
C       1.74379       0.02561     -0.01818
C       2.98907       0.86121     -0.00686
H       3.01366       1.50199     -0.89176
H       3.86561       0.20724     -0.02398
H       3.02300       1.46514      0.90332
O       0.42398       2.00161      0.06749
O       1.74282      -1.19814     -0.05965
*
```

or, in this case, by computing the ground state triplet by simply setting the multiplicity to three:

```
!B3LYP DEF2-TZVP (-F) CPCM(ETHANOL) OPT FREQ
* XYZFILE 0 3 BIA.xyz
```

Alternatively, one can use methods like VG, AHAS, etc., to approximate the triplet geometry and Hessian. However, this approach requires preparing the Hessian in a separate ESD run (Sec. *Approximations to the excited state PES*).

Additionally, you must input the adiabatic energy difference between the ground singlet and ground triplet states at their respective geometries (without any zero-point energy correction) using the DELE flag under %ESD. In this case, the spin-adapted triplet computed previously serves as our reference triplet state. An example input for the rate calculation using TDDFT is as follows:

```
!B3LYP DEF2-TZVP (-F) TIGHTSCF CPCM(ETHANOL) ESD (PHOSP) RI-SOMF (1X)
%TDDFT
  NROOTS 20
  DOSOC TRUE
  TDA FALSE
  IROOT 1
END
%ESD
  GSHESSIAN "BIA.hess"
  TSHESSIAN "BIA_T1.hess"
  DOHT TRUE
  DELE 17260
END
* XYZFILE 0 1 BIA.xyz

$NEW_JOB

!B3LYP DEF2-TZVP (-F) TIGHTSCF CPCM(ETHANOL) ESD (PHOSP) RI-SOMF (1X)
%TDDFT
  NROOTS 20
  DOSOC TRUE
  TDA FALSE
  IROOT 2
END
%ESD
  GSHESSIAN "BIA.hess"
  TSHESSIAN "BIA_T1.hess"
  DOHT TRUE
  DELE 17260
END
* XYZFILE 0 1 BIA.xyz

$NEW_JOB

!B3LYP DEF2-TZVP (-F) TIGHTSCF CPCM(ETHANOL) ESD (PHOSP) RI-SOMF (1X)
%TDDFT
  NROOTS 20
  DOSOC TRUE
  TDA FALSE
  IROOT 3
END
%ESD
  GSHESSIAN "BIA.hess"
  TSHESSIAN "BIA_T1.hess"
  DOHT TRUE
  DELE 17260
END
* XYZFILE 0 1 BIA.xyz
```

Phosphorescence rate calculation are always accompanied by the generation of the vibrationally resolved phosphorescence spectrum, which can be visualized in the same way as fluorescence spectra.

OBS.: When computing phosphorescence rates, each rate from individual spin sub-levels must be requested separately. You may use the \$NEW_JOB option, just changing the IROOT, to write everything in a single input. After SOC, the three triplet states (T_1 with $M_S = -1, 0$ and $+1$) will split into IROOTs 1, 2 and 3, and all of them must be included when computing the final phosphorescence rate. In this case, it is reasonable to assume that the geometries and Hessians of these spin sub-levels are the same, and we will use the same .hess file for all three.

OBS2.: The ground state geometry should be used in the input file, similar to the case of fluorescence (vide supra).

OBS3.: Apart from DELE, one can also use the TDIP keyword to input a high-level transition dipole moment, similar to the fluorescence case. This enables e.g. the calculation of phosphorescence rates/spectra using e.g. NEVPT2 or

DLPNO-STEOM-CCSD transition dipole moments, with (TD)DFT geometries and Hessians. Note however that the transition dipole moment in phosphorescence processes is complex, so 6 instead of 3 components are required.

Here, we are computing the rate and spectrum for biacetyl in ethanol at 298 K. The geometries and Hessians were obtained as previously described, with the ground triplet computed from a simple open-shell calculation. To compute the rate, the flag DOSOC must be set to TRUE under %TDDFT (Sec *Spin-orbit coupling*), or the respective module, and it is advisable to set a large number of roots to ensure a good mixing of states.

Please note that we have chosen the RI-SOMF(1X) option for the spin-orbit coupling integrals, but any of the available methods can be used (Sec. *The Spin-Orbit Coupling Operator*).

Calculation of rates

As you can see, the predicted spectra for biacetyl (Fig. 5.11) are quite close to the experimental results [601, 605]. The calculation of the phosphorescence rate is more complex because there are three triplet states that contribute. Therefore, the observed rate must be taken as an average of these three states.

$$k_{av}^{phosp} = \frac{k_1 + k_2 + k_3}{3}$$

To be even more strict and account for the Boltzmann population distribution at a given temperature T caused by the Zero Field Splitting (ZFS), one should use [606]:

$$k_{av}^{phosp} = \frac{k_1 + k_2 e^{-(\Delta E_{1,2}/k_B T)} + k_3 e^{-(\Delta E_{1,3}/k_B T)}}{1 + e^{-(\Delta E_{1,2}/k_B T)} + e^{-(\Delta E_{1,3}/k_B T)}} \quad (5.28)$$

where $\Delta E_{1,2}$ is the energy difference between the first and second states, and so on.

After completion of each calculation, the rates for the three triplets were 8.91 s^{-1} , 0.55 s^{-1} , and 284 s^{-1} . Using (5.28), the final calculated rate is about 98 s^{-1} , while the best experimental value is 102 s^{-1} (at 77K) [607], with about 40% deriving from the HT effect.

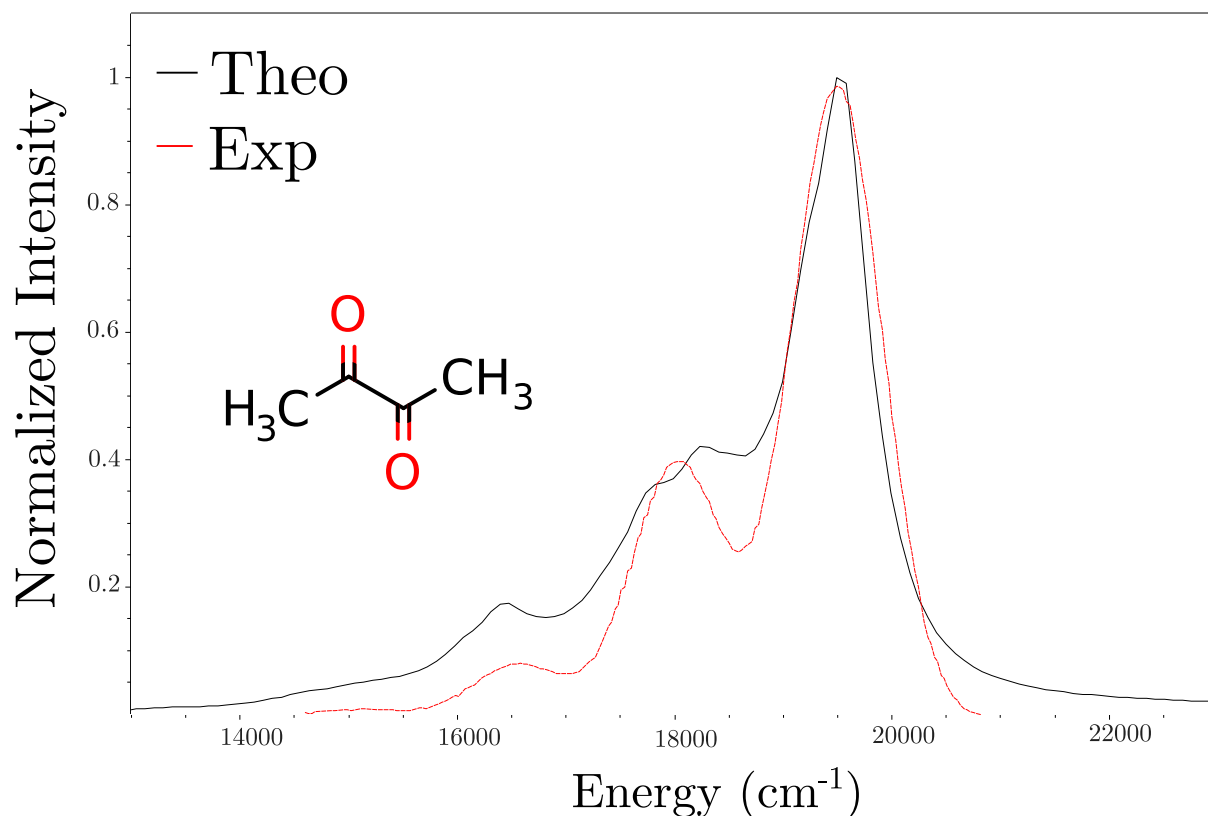


Fig. 5.11: The experimental (dashed red) and theoretical (solid black, displaced by about 2800 cm^{-1}) phosphorescence spectra for biacetyl, in ethanol at 298 K.

OBS: A subtlety arises when the final state is not a singlet state, for example in radical phosphorescence (doublet ground state) or singlet oxygen phosphorescence (triplet ground state). In this case the most rigorous treatment would be to sum over the final states but average over the initial states. For example, with quartet-to-doublet phosphorescence one gets

$$k_{av}^{phos} = \frac{k_{1 \rightarrow 1} + k_{2 \rightarrow 1} e^{-(\Delta E_{1,2}/k_B T)} + k_{3 \rightarrow 1} e^{-(\Delta E_{1,3}/k_B T)} + k_{4 \rightarrow 1} e^{-(\Delta E_{1,4}/k_B T)}}{1 + e^{-(\Delta E_{1,2}/k_B T)} + e^{-(\Delta E_{1,3}/k_B T)} + e^{-(\Delta E_{1,4}/k_B T)}} + \frac{k_{1 \rightarrow 2} + k_{2 \rightarrow 2} e^{-(\Delta E_{1,2}/k_B T)} + k_{3 \rightarrow 2} e^{-(\Delta E_{1,3}/k_B T)} + k_{4 \rightarrow 2} e^{-(\Delta E_{1,4}/k_B T)}}{1 + e^{-(\Delta E_{1,2}/k_B T)} + e^{-(\Delta E_{1,3}/k_B T)} + e^{-(\Delta E_{1,4}/k_B T)}}$$

where $k_{2 \rightarrow 1}$ is the phosphorescence rate constant from the second sublevel of the initial quartet to the first sublevel of the final doublet, etc. Note that the Boltzmann factors of the final state do not enter the expression. Unfortunately, since U-TDDFT is spin contaminated and unsuitable for calculating SOC-corrected transition dipole moments, the transition dipoles in this case have to be calculated by more advanced methods, such as DFT/ROCIS or multireference methods. The transition dipole should then be given in the input file using the TDIP keyword.

5.5.4 Intersystem Crossing Rates (unpublished)

General Aspects

Yet another application of the path integral approach is to compute intersystem crossing rates, or non-radiative transition rates between states of different multiplicities. This can be calculated if one has two geometries, two Hessians, and the relevant spin-orbit coupling matrix elements.

The input is similar to those discussed above. Here ESD(ISC) should be used on the main input to indicate an InterSystem Crossing calculation, and the Hessians should be provided by ISCISHESSIAN and ISCFSSHESSIAN for the initial and final states, respectively. Please note that the geometry used in the input file should correspond to that of the FINAL state, specified through the ISCFSSHESSIAN flag. The relevant matrix elements can be computed using any method available in ORCA and inputted as SOCME Re,Im under %ESD where Re and Im represent its real and imaginary parts (**in atomic units!**).

As a simple example, one could compute the excited singlet and ground triplet geometries and Hessians for anthracene using TD-DFT. Then, compute the spin-orbit coupling (SOC) matrix elements for a specific triplet spin-sublevel using the same method (see the details below), potentially employing methods like CASSCF, MRCI, STEOM-CCSD, or another theoretical level. Finally, obtain the intersystem crossing (ISC) rates using an input such as:

```
!ESD(ISC) NOITER
%ESD
  ISCISHESSIAN  "ANT_S1.hess"
  ISCFSSHESSIAN "ANT_T1.hess"
  DELE         11548
  SOCME        0.0, 2.33e-5
END
* XYZFILE 0 1 ANT_T1.xyz
```

The SOCMEs between a singlet state and a triplet state consist of three complex numbers, not just one, because the triplet state has three sublevels. If the user uses the SOCME of one of the sublevels as input to the ISC rate calculation, this gives the ISC rate associated with that particular sublevel. However, experimentally one usually does not distinguish the three sublevels of a triplet state, and experimentally ISC rates are reported as if the three sublevels of a triplet state are the same species. Therefore, the rate of singlet-to-triplet ISC is the *sum* of the ISC rates from the singlet state to the three triplet sublevels. Fortunately, in case the Herzberg-Teller effect (vide infra) can be neglected, it is not necessary to perform three rate calculations and add up the rates, since the rate is proportional to the squared modulus of the SOCME. Thus, one can run a *single* ESD calculation where the SOCME is the square root of the summed squared moduli of the three SOCME components.

As an illustration, consider the S_1 to T_1 ISC rate of acetophenone. First, we optimize the S_0 geometry, and (after manually tweaking the geometry to break mirror symmetry) use it as an initial guess for the geometry optimization and frequency calculations of the S_1 and T_1 states. Then, we calculate the S_1 - T_1 SOCMEs at the T_1 geometry (note that, as usual, final state geometries should be used for ESD calculations; this may differ from some programs other

than ORCA). These calculations are conveniently done using a compound script, although the individual steps can of course also be done using separate input files.

```
%pal nprocs 16 end

* xyz 0 1
C      1.512698      7.783764     -0.013405
C      2.900029      7.735359     -0.016012
C      3.664170      8.950745      0.000408
C      2.952045     10.199539      0.007630
C      1.564497     10.214795      0.009890
C      0.827311      9.015246      0.000726
H      0.946857      6.847253     -0.027731
H      3.394565      6.763402     -0.041976
H      3.505090     11.140193      0.017889
H      1.039592     11.175094      0.019479
H     -0.265468      9.038211      0.000969
C      5.059695      8.958412      0.000442
O      5.733735     10.161120     -0.048672
C      5.927824      7.713913      0.020029
H      5.442615      6.938582      0.639989
H      6.073177      7.326421     -1.014490
H      6.923426      7.950459      0.447785
*

%compound

new_step # Compound 1: S1 opt
! B3LYP def2-SV(P) opt tightopt freq

%tddft
tda false
nroots 2
iroot 1
end

step_end

new_step # Compound 2: T1 opt
! B3LYP def2-SV(P) opt tightopt freq

* xyz 0 3
C      1.512698      7.783764     -0.013405
C      2.900029      7.735359     -0.016012
C      3.664170      8.950745      0.000408
C      2.952045     10.199539      0.007630
C      1.564497     10.214795      0.009890
C      0.827311      9.015246      0.000726
H      0.946857      6.847253     -0.027731
H      3.394565      6.763402     -0.041976
H      3.505090     11.140193      0.017889
H      1.039592     11.175094      0.019479
H     -0.265468      9.038211      0.000969
C      5.059695      8.958412      0.000442
O      5.733735     10.161120     -0.048672
C      5.927824      7.713913      0.020029
H      5.442615      6.938582      0.639989
H      6.073177      7.326421     -1.014490
H      6.923426      7.950459      0.447785
*

step_end
```

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```

new_step # Compound 3: SOC at T1 geometry
! B3LYP def2-SV(P)

%tddft
tda false
nroots 3
triplets true
dosoc true
end

# Here it is assumed that the input file is named "a.inp"
* xyzfile 0 1 a_Compound_2.xyz

step_end
end

```

After verifying that neither of the Hessians have imaginary frequencies (which is very important!), we can read the computed SOCMEs:

CALCULATED SOCME BETWEEN TRIPLETS AND SINGLETs						
Root		Z	<T HSO S>		(Re, Im) cm-1	Y
T	S		X			
1	0	(0.00 , -2.00)	(0.00 , 29.24)	(-0.00 , -		
41.11)	1	(0.00 , -0.59)	(0.00 , 1.79)	(-0.00 , -		
2.57)	1	(0.00 , 0.52)	(0.00 , -3.19)	(-0.00 , -		
3.21)	1	(0.00 , -2.39)	(0.00 , 14.57)	(-0.00 , -		
19.53)	2	(0.00 , -0.11)	(0.00 , 2.78)	(-0.00 , -		
2.72)	2	(0.00 , 2.25)	(0.00 , -20.07)	(-0.00 , -		
28.07)	2	(0.00 , 0.02)	(0.00 , -0.13)	(-0.00 , -		
0.29)	2	(0.00 , -0.17)	(0.00 , 0.59)	(-0.00 , -		
1.27)	3	(0.00 , -0.01)	(0.00 , 0.05)	(-0.00 , -		
0.06)	3	(0.00 , -0.01)	(0.00 , 0.19)	(-0.00 , -		
1.36)	3	(0.00 , -0.01)	(0.00 , -0.05)	(-0.00 , -		
0.14)	3	(0.00 , -0.00)	(0.00 , 0.14)	(-0.00 , -		
0.16)						

The “total” SOCME between S_1 and T_1 is then calculated, from the line that begins with “1 1”, as

$$\sqrt{0.00^2 + (-0.59)^2 + 0.00^2 + 1.79^2 + 0.00^2 + 2.57^2} \text{ cm}^{-1} = 3.19 \text{ cm}^{-1} = 1.45 \times 10^{-5} \text{ au}$$

One should therefore write `socme 1.45e-5` in the `%esd` block in the subsequent ISC rate calculation.

Importantly, the above approach is only applicable to singlet-to-triplet ISC, but not to triplet-to-singlet ISC (including, but not limited to, $T_1 \rightarrow S_0$ and $T_1 \rightarrow S_1$ processes). In the latter case, assuming that the triplet sublevels are

degenerate and in rapid equilibrium, we obtain that the observed rate constant is the *average*, not the sum, of the rate constants of the three triplet sublevels, because each triplet sublevel has a Boltzmann weight of 1/3. Therefore, the “effective” SOCME that should be plugged into the ESD module to get the observed rate constant is (here the squared modulus $|SOCME_x|^2$ should be calculated as $Re(SOCME_x)^2 + Im(SOCME_x)^2$, etc.)

$$SOCME_{av} = \sqrt{\frac{|SOCME_x|^2 + |SOCME_y|^2 + |SOCME_z|^2}{3}} \quad (5.29)$$

i.e. a factor of $\sqrt{3}$ smaller than the singlet-to-triplet case. However, both of the two assumptions (degenerate triplet sublevels, and rapid equilibrium between sublevels) may fail under certain circumstances, which may contribute to the error of the predicted rate. Nevertheless, in many cases the present, simple approach still provides a rate with at least the correct order of magnitude.

OBS.: The adiabatic energy difference is NOT computed automatically for ESD(ISC), so you must provide it in the input. This is the energy of the initial state minus the energy of the final state, each evaluated at its respective geometry.

OBS2.: All the other options concerning changes of coordinate system, Duschinsky rotation, etc., are also available here.

OBS3.: For many molecules, the $S_1 \rightarrow T_1$ ISC process is not the dominant ISC pathway. This is because the excited state compositions of S_1 and T_1 are often similar, and therefore ISC transitions between them frequently do not satisfy the El-Sayed rule. Even if the only experimentally observed excited states are S_1 and T_1 , it may still be that the initial ISC is dominated by $S_1 \rightarrow T_n (n > 1)$, followed by ultrafast $T_n \rightarrow T_1$ internal conversion.

OBS4.: Similarly, if the molecule starts at a high singlet state $S_n (n > 1)$, the dominant ISC pathway is not necessarily the direct ISC from S_n to one of the triplet states. Rather, it is possible (but not necessarily true) that S_n first decays to a lower singlet excited state before the ISC occurs.

OBS5.: If you calculate the DELE or SOCMEs at a higher level of theory and use it as an input for the ESD calculation, please make sure that you have chosen the same excited state (in terms of state composition, not energy ordering) in the Hessian and DELE/SOCME calculations. For example, suppose that you have obtained the geometry and Hessian of the T_2 state, but the T_2 state of the higher level of theory has a very different state composition than the T_2 state at the level of theory used in the Hessian calculation; rather, it is T_3 at the high level of theory that shares the same composition as the T_2 state at the lower level of theory. In this case, you should use the SOCME related to T_3 in the SOCME output file.

OBS6.: The ESD module does not require that the final state of the ISC process is energetically lower than the initial state. Therefore, reverse ISC (RISC) rates can be calculated in exactly the same way as ISC rates. Note however that (1) if you want to supply the adiabatic energy difference using the DELE keyword, the energy difference should be negative; and (2) whether one should sum or average the three components of the SOCMEs depend on whether the final state is a triplet state, not whether the lower state is a triplet state.

OBS7.: ISC transitions between states other than singlets and triplets (for example between a doublet state and a quartet state) can also be calculated, provided that the SOCMEs are calculated by a properly spin-adapted or multireference method, such as DFT/ROCIS or NEVPT2. The squared moduli of the sublevels’ SOCMEs should be summed over all final state spin sublevels but averaged over all initial state spin sublevels, similar to the phosphorescence case (*Calculation of rates*).

ISC, TD-DFT and the HT effect

In the anthracene example above, the result is an ISC rate (k_{ISC}) smaller than 1 s^{-1} , which is quite different from the experimental value of 10^8 s^{-1} at 77 K [607]. The reason for this discrepancy, in this particular case, is because the ISC occurs primarily due to the Herzberg-Teller effect, which must also be included. To achieve this, one needs to compute the derivatives of the SOCMEs over the normal modes, currently feasible only using CIS/TD-DFT.

When using the %CIS/TDDFT option, you can control the SROOT and TROOT flags to select the singlet and triplet states for which SOCMEs are computed, and the TROOTSSL flag to specify the triplet spin-sublevel (1, 0, or -1).

In practice, to obtain an ISC rate (k_{ISC}) close enough to experimental values, one would need to consider all possible transitions between the initial singlet and all available final states. For anthracene, these are predicted to be the ground triplet (T_1) and the first excited triplet (T_2), consistent with experimental observations [608], while the next triplet

(T_3) is energetically too high to be significant (Fig. 5.12 below). An example input used to calculate the k_{ISC} from S_1 to T_1 at 77 K is:

```
!B3LYP DEF2-TZVP (-F) TIGHTSCF ESD (ISC)
%TDDFT NROOTS 5
      SROOT 1
      TROOT 1
      TROOTSSL 0
      DOSOC TRUE
END
%ESD ISCISHES "ANT_S1.hess"
     ISCFSHES "ANT_T1.hess"
     USEJ TRUE
     DOHT TRUE
     TEMP 77
     DELE 11548
END
* XYZFILE 0 1 ANT_T1.xyz

$NEW_JOB

!B3LYP DEF2-TZVP (-F) TIGHTSCF ESD (ISC)
%TDDFT NROOTS 5
      SROOT 1
      TROOT 1
      TROOTSSL -1
      DOSOC TRUE
END
%ESD ISCISHES "ANT_S1.hess"
     ISCFSHES "ANT_T1.hess"
     USEJ TRUE
     DOHT TRUE
     TEMP 77
     DELE 11548
END
* XYZFILE 0 1 ANT_T1.xyz

...
```

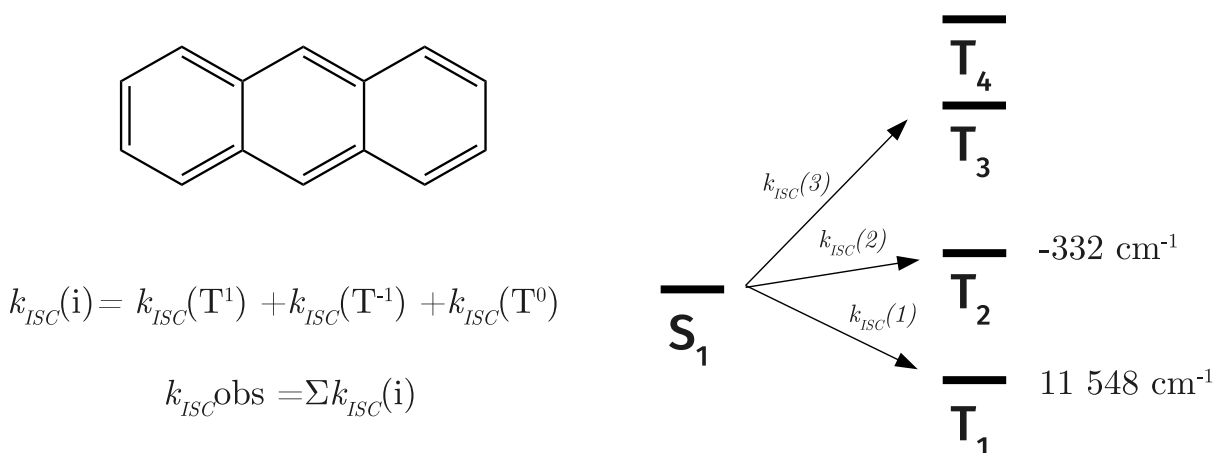


Fig. 5.12: Scheme for the calculation of the intersystem crossing in anthracene. The $k_{ISC}(i)$ between S_1 and each triplet is a sum of all transitions to the spin-sublevels and the actual observed k_{ISC}^{obs} , which consolidates these transitions. On the right, there is a diagram illustrating the distribution of excited states with $E(S_1) - E(T_n)$ depicted on the side. Since T_3 is energetically too high, intersystem crossing involving T_3 can be safely neglected.

Then, the derivatives of the SOCME are computed and the rates are printed at the end. By performing the same

calculations for the T_2 states and summing up these values, a predicted $k_{ISC}^{obs} = 1.17 \times 10^8 s^{-1}$ can be obtained, much closer to the experimental value, which is associated with a large error anyway.

OBS.: In cases where the SOCME are relatively large, e.g., $SOCME > 5 cm^{-1}$, the Herzberg-Teller effect might be negligible, and a simple Franck-Condon calculation should yield good results. This is typically applicable to molecules with heavy atoms, where vibronic coupling is less significant.

OBS2.: Always consider that there are actually THREE triplet spin-sublevels, and transitions from the singlet to all of them should be included.

OBS3.: ISC rates are extremely sensitive to energy differences. Exercise caution when calculating them. If a more accurate excited state method is available, it should be considered for prediction.

OBS4.: The Herzberg-Teller effect is not yet implemented for ISC transitions between states that are not singlets and triplets.

5.5.5 Internal Conversion Rates (unpublished)

The ESD module can also calculate internal conversion (IC) rates from an excited state to the ground state at the TDDFT and TDA levels. Apart from the ground state and excited state Hessians, the only additional quantity that needs to be calculated is the nonadiabatic coupling matrix elements (NACMEs).

The input file is simple:

```
# S1-S0 IC rate of azulene
! B3LYP D3 def2-SVP ESD(IC) CPCM(methanol)

%tddft
tda false # Full TDDFT is recommended over TDA
nroots 3
iroot 1 # Change to 2 for S2-S0 IC rate, etc.
nacme true # Calculate the NACME between the iroot-th root with the ground state
etf true # Use electron translation factor (recommended)
end

%esd
gshessian "azulene_S0.hess" # Ground state Hessian (B3LYP-D3/def2-SVP)
eshessian "azulene_S1.hess" # Excited state Hessian (TD-B3LYP-D3/def2-SVP)
usej true # Use Duschinsky rotation (recommended)
end

# Ground state geometry (B3LYP-D3/def2-SVP)
* xyzfile 0 1 azulene_S0.xyz
```

Here the S_0 geometry, as well as the S_0 and S_1 Hessian files, were obtained at the B3LYP-D3/def2-SVP level of theory. Note that the NACME calculation uses full TDDFT and also includes the electron-translation factor (ETF), which are the recommended practices in general. The “iroot 1” specifies that the initial state is S_1 ; the final state is always S_0 and this cannot be changed.

The computed IC rate constant is given near the end of the output file:

```
***Everything is set, now computing the correlation function***

Homogeneous linewidth is:      50.00 cm-1
Inhomogeneous linewidth is:    250.00 cm-1
Number of points:              32768
Maximum time:                  157.86 fs
Temperature used:               298.15 K
Z value:                        4.924300e-66
Cutoff for the correlation function: 1.00e-12
Adiabatic energy difference:     16699.89 cm-1
0-0 energy difference:          16382.09 cm-1
```

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