



**Computational Chemistry Workshops**  
**West Ridge Research Building-UAF Campus**  
**9:00am-4:00pm, Room 009**

Electronic Structure - July 19-21, 2016  
Molecular Dynamics - July 26-28, 2016

**Computational Ultraviolet, Visible, Infrared,  
and Raman Spectroscopy**

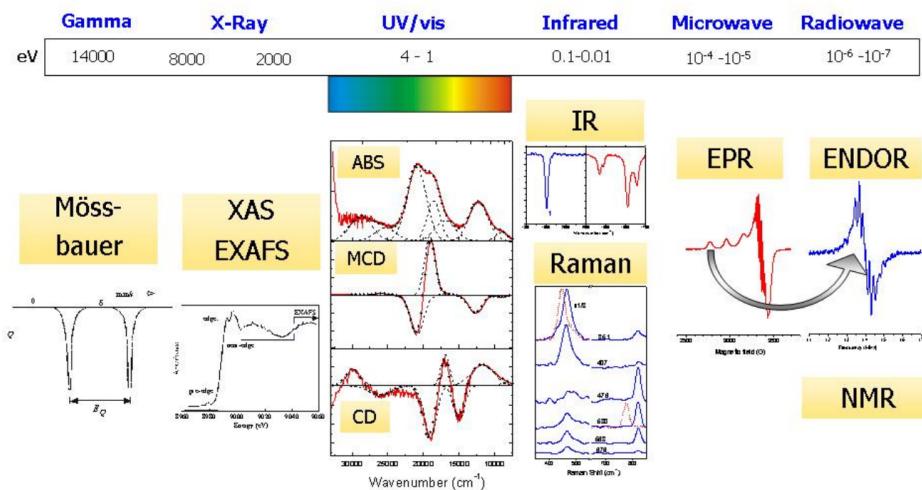
# UV/Visible Spectroscopy

In the first part of these exercises, the UV/Visible region of the spectrum are studied and the energy levels that are associated in electronic and vibrational transitions are calculated.

In interpreting the results of the computations, the language of molecular orbitals is used. It is, however, very important to understand that in experiments, one never observes molecular orbitals. Every experimental measurement reports only energies and properties of many electron states. It is crucial to properly distinguish between a one-electron molecular orbital (MO) and a many-electron state in any discussion of electronic structure, in order to avoid unnecessary mistakes and confusion! An electronic configuration is defined by specifying the integer occupation number for each MO in the system such that the sum of occupation numbers equals the total number of electrons, and each MO is occupied by either 0, 1 or 2 electrons.

UV/Visible spectroscopy is an experimental technique that is routinely used throughout all branches of chemistry, and the spectral bands correspond to the excitation of a molecule from the electronic ground state to an electronically excited state with simultaneous excitations of vibrational and rotational quanta. Thus, electronic transitions lead to quite large changes in the electronic structure of the investigated molecules. Since the nature of the bonds that are involved in the transitions change between the ground- and excited states, molecules in excited states generally assume a geometry that is different from the ground state equilibrium geometry. In fact, these large changes in bonding are the basis for the important field of photochemistry where the making and breaking of bonds in electronically excited states is of central interest.

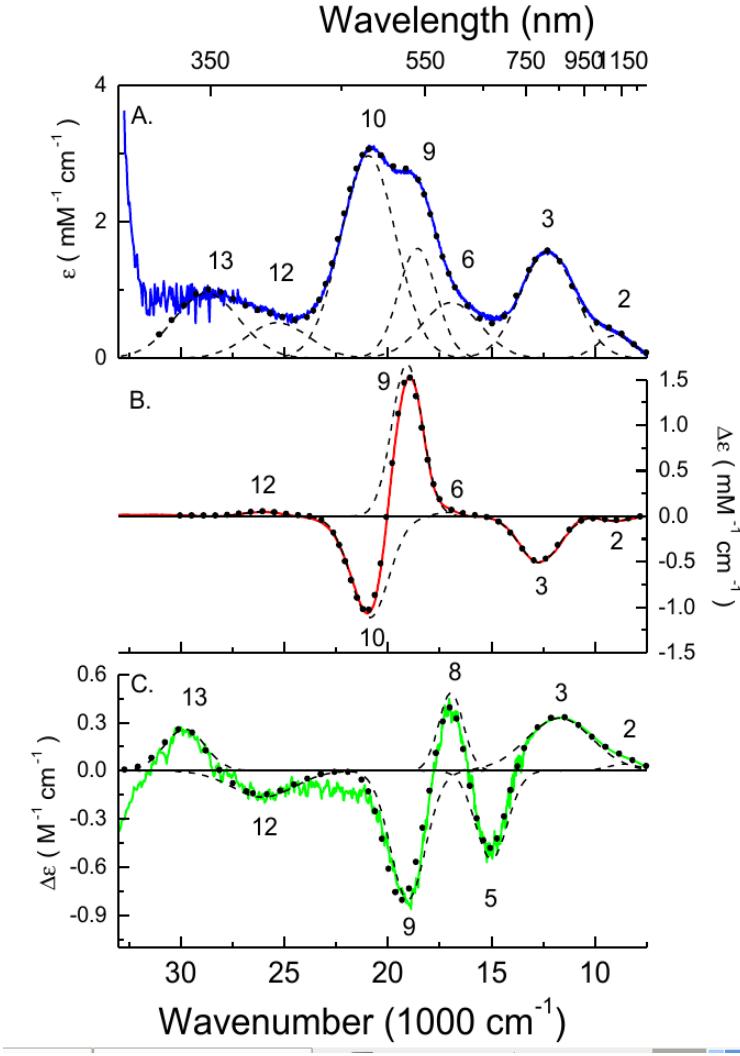
A graph of the energies for various spectroscopies is given in Figure 1, and it is important to note the wavelength region for UV/Visible spectroscopy.



**Figure 1:** Energy Scales for Various Spectroscopies

An absorption band corresponds to a transition of the ground-electronic state to an excited electronic state, but such transitions do not take the appearance of sharp absorption lines,

as in the spectra of atoms and ions, and are usually considerably broadened. In many cases there will be overlapping bands and one is faced with the problem of how to deconvolute the broad absorption envelope into contributions from individual transitions. In most cases, one assumes that the shape of each individual absorption band is that of a Gaussian, and then applies as many Gaussian functions as are necessary in order to accurately represent the absorption envelope. A typical example is shown in Figure 2.



**Figure 2:** Deconvolution of an absorption spectrum into contributions from individual electronic transitions by fitting them to Gaussian functions. The upper panel represents the absorption spectrum plotted on a wavenumber scale. The middle panel represents the Magnetic Circular Dichroism (MCD) spectrum, the bottom panel displays the Circular Dichroism (CD) spectrum of the same compound. The MCD and CD spectra help the deconvolution because they are both signed quantities.

This is an approximate procedure which is not without problems. The accurate band-shapes do not follow the shapes of Gaussian functions, the fits are often not well defined, and, unless one has additional information, for example, Circular Dichroism (CD) or Magnetic Circular

Dichroism (MCD) spectra, the fit should be viewed with caution. Additional Gaussians should not be used to improve a fit, unless there is a well-defined maximum, or a well-defined shoulder, in the absorption envelope.

Electronic circular dichroism (CD) involves the absorption of both left-handed and right-handed circularly polarized light that is propagated with different velocities which is absorbed to a different extent in the region of an electronic absorption band. The fact that each electronic band in the CD signal can have either a positive or negative sign allows an ability to resolve ambiguity in the spectral deconvolution. For example, two strongly overlapping bands in an absorption spectrum can have different signs in the corresponding CD spectrum, thus providing evidence for two electronic transitions in a given spectral range. Typically, CD spectra are analyzed together with corresponding absorption spectra, since they arise from the same set of electronic transitions. Each band in CD spectrum corresponding, to the transition from the ground state to the  $I^{\text{th}}$  electronically excited state is characterized by the rotatory strength,  $R_{0 \rightarrow I}$  which is calculate as the following:

$$R_{0 \rightarrow I} = 0.229 \times 10^{-38} \int_{\text{Band}} \Delta\epsilon^I(\tilde{\nu}) \frac{d\tilde{\nu}}{\tilde{\nu}}$$

## Electronic Transitions

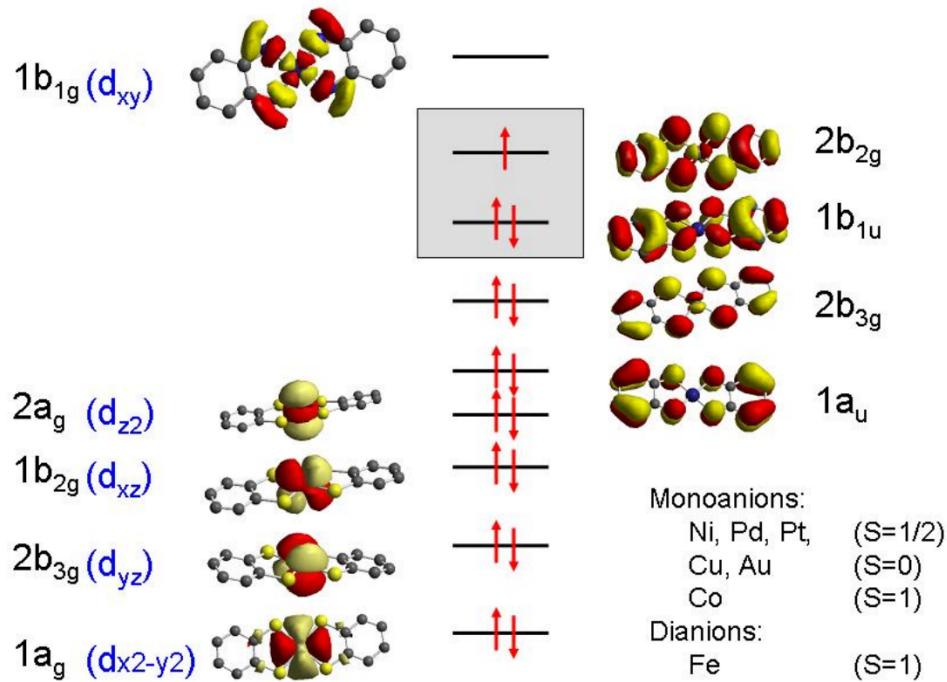
On a most elementary level, electronic transitions correspond to the transitions from one electronic configuration to another. An example is shown in Figure 3. What is shown there is the ground state electronic configuration of a square-planar transition metal-dithiolene complex. It consists of a series of molecular orbitals that are drawn according to increasing energy. According to the Aufbau principle, all MOs are filled by two electrons, and, in the present case, one unpaired electron remains and occupies a singly-occupied MO (SOMO). The MOs transform under the irreducible representation of the molecular point group and the symmetry labels are given for each MO.

The many electron states found from distributing the electrons among the available orbitals also have a symmetry that is designated by a term symbol  $\Gamma$  and spin multiplicity  $2S + 1$ . Here,  $2S + 1$  is the multiplicity of the electronic state,  $S$  is the total spin, and  $^{2S+1}\Gamma$  is the symmetry. The symmetry is found by taking the direct product of all partially occupied MOs.

Note, that lowercase symbols are used to represent one-electron functions and uppercase symbols are used to represent many-electron states.

In general, this leads to a reducible representation of the molecular point group. However, for non-degenerate point groups ( $D_{2h}$  and subgroups), the direct product directly yields the symmetry of the electronic state. In the example above, a single  $b_{2g}$  MO is singly occupied which leads to a  $^2B_{2g}$  ground state. Excited states are formed by promoting electrons from lower-lying orbitals into partially occupied or empty MOs. For example, the transition  $1b_{1u} \rightarrow 2b_{2g}$  leads to  $(1b_{1u})^1(2b_{2g})^2$ , which corresponds to a  $^2B_{1u}$  excited state. Transition from  $1a_u$  to  $1b_{1g}$  yields  $(1a_u)^1(2b_{2g})^1(1b_{1g})^1$ , which corresponds to the electron state,  $a_u \otimes b_{2g} \otimes b_{1g} = ^2B_{3u}$ . However, this configuration has three unpaired electrons and,

consequently, also gives rise to a  ${}^4B_{3u}$  excited state. In order to distinguish different states of the same symmetry one typically uses X for the ground state, the letters A,B,C for excited states of the same multiplicity, and a,b,c for excited states of different multiplicity. Thus, in the present case, the transitions,  $X - {}^2B_{2g} \rightarrow A - {}^2B_{1u}$ , and  $X - {}^2B_{2g} \rightarrow B - {}^2B_{3u}$ , and  $X - {}^2B_{2g} \rightarrow a - {}^4B_{3u}$  have been identified.



**Figure 3:** An example of electronic states and transitions, showing the ground-state configuration with orbitals in order of decreasing energy. Excited states are formed by promoting electrons from lower-lying MOs into higher lying partially occupied or empty MOs.

## Electronic Selection Rules

In order to perform an assignment of the electronic spectrum, it is necessary to determine the symmetries of the excited states involved and identify the donor and acceptor MO pairs involved in the transitions. A typical example is shown in Figure 4. In order to find out whether an electronic transition is allowed or not, the following rules apply:

- Transitions between states of different multiplicity are forbidden. This is a fairly strong selection rule and such transitions typically have  $\epsilon$  values  $< 1 \text{ M}^{-1} \text{ cm}^{-1}$ .

This selection rule is lifted by spin-orbit coupling. For heavier elements, formally spin-forbidden transitions become increasingly allowed.

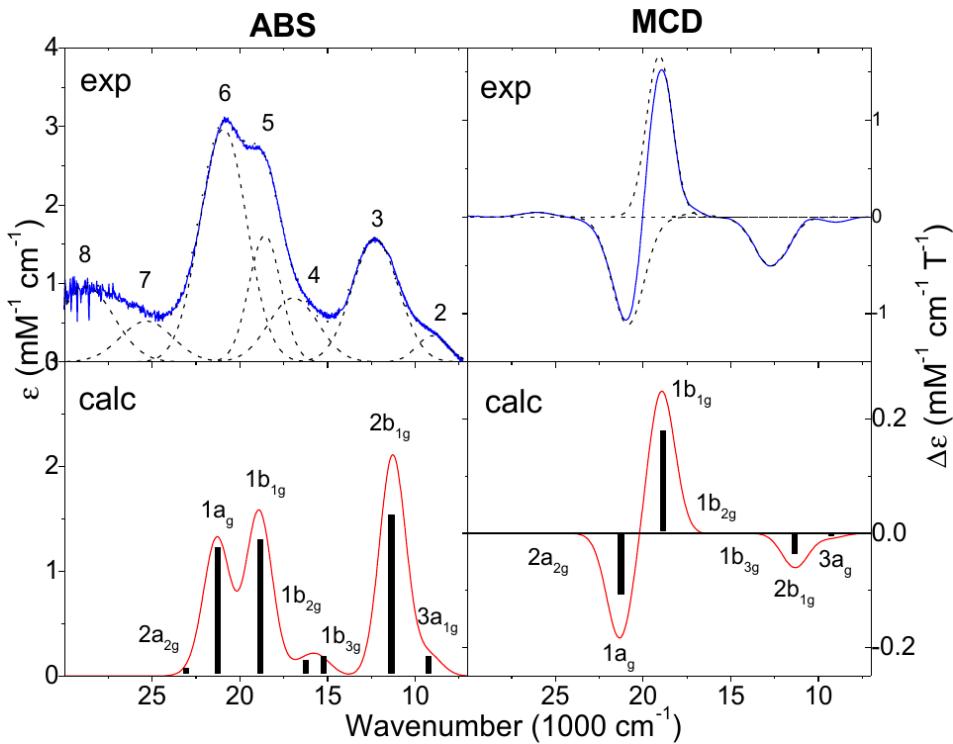
- The direct product of the irreducible representations for the initial and final states involved in the transition, and the irreducible representations spanned by the electric

dipole operator must, contain the totally symmetric representation. Otherwise, the transition is forbidden by symmetry.

The electric-dipole operator transforms like the molecular translations which can be found with the labels  $x$ ,  $y$ , and  $z$  in usual group theoretical tables.

3. If the point group contains a center of inversion, only  $g \rightarrow u$  or  $u \rightarrow g$  transitions are allowed. Other transitions are said to be *parity forbidden*.

The selection rules are a good guide to identifying strongly and weakly allowed transitions in a spectrum. However, don't be surprised to find a formally forbidden transition in your spectrum. In the real world there are almost always additional perturbations that break the symmetry of the system and make formally forbidden transitions weakly allowed. A typical example are the parity forbidden d-d transitions.



**Figure 4:** An example of an assigned absorption spectrum. The experimental absorption and MCD spectra are given in the top panel, and calculated spectra are shown in the bottom panel. The acceptor MO is always a  $b_{3u}$  orbital in this case, and the lowercase symbols on the calculated transitions merely represent the symmetry of the donor MO. The calculations yield only the black bars in the lower panels, which have been empirically convoluted by Gaussian functions, in order to produce an envelope than can be compared with experimental measurements.

Since the rotational strength of a transition is proportional to the scalar product of the electric and magnetic dipole transition moments, the selection rules are different for CD absorption, than those for the case of electron dipole absorption. The  $g \rightarrow g$  and  $u \rightarrow u$

transitions are formally electric-dipole forbidden, while  $g \rightarrow u$  and  $u \rightarrow g$  are magnetic-dipole forbidden, it becomes immediately apparent that centrosymmetric molecules are not optically active.

More generally, it can be shown that a molecule must not contain an  $S_n$  axis, including  $S_1 = \sigma$  and  $S_2 = i$ , to be optically active, that is to only those molecules with non-superimposable mirror images. Such molecules are called chiral. Enantiomers, which are stereoisomers that are nonsuperimposable complete mirror images of each other, show CD absorptions of equal amplitudes but different signs. Only molecules belonging to the point groups  $C_n, D_n, O, T$ , or,  $I$  are optically active, and discrete transitions must be both electric- and magnetic-dipole allowed to exhibit CD.

## The Born-Oppenheimer (BO) Approximation

In the BO approximation, the total wavefunction,  $\Theta_I(r, R)$ , describes the combined electronic, vibrational and rotational state of the system. As mentioned above, an electronic absorption band also contains vibrational and rotational structure. Although for small molecules in the gas phase, the rotational-vibrational structure may be resolved and analyzed, the UV/Visible absorption spectra of larger molecules are usually measured in solution. Since the rotational quanta are small, and the rotation is hindered by the solvent molecules, no rotational structure is seen in solution, even with high-resolution spectrometers. Thus, any remaining structure on the absorption band may be attributed to vibrations. Upon the neglect of rotations the total wavefunction,  $\Theta_I(r, R)$ , may be written as the product of the electronic and vibronic wavefunctions of the form:

$$\Theta_{In}(r, R) = \Psi_I(r, R) \times \chi_n^I(R)$$

where  $\chi_n^I(R)$  is the nuclear vibrational wavefunction, and  $I$  and  $n$  are the indices of the electronic and vibrational states, respectively. In other words, the Born-Oppenheimer Approximation allows for the separation of electronic and nuclear motion.s Even within the limitations of the BO approach, there are a number of approximations that are usually made in order to make the analysis and calculations of the absorption spectra of molecules feasible:

1. Molecules are assumed to be excited from the ground vibrational state of the electronic ground state, and is called the zero-temperature approximation. Typically, an account of thermal population of the excited vibrational levels leads to some broadening of the absorption band.
2. The electronic transition dipole moment defined as

$$\mathbf{d}_{0I}(\mathbf{R}) = \int \Psi_0(r, R) \mathbf{d} \Psi_I(r, R) dr$$

does not depend upon nuclear coordinates, and equal to the value corresponding to the ground-state equilibrium geometry,  $R_0$ :

$$\mathbf{d}_{0I}(\mathbf{R}) \approx d_{0I}(R_0) = const.$$

This statement constitutes the essence of the so-called Franck-Condon approximation.

- The vibronic nature of the molecular states the excitation of the  $0 \rightarrow k$  electronic transition implies a co-excitation of vibrational quanta from the ground vibrational state of the electronic ground state into the ground- and excited vibrational states on the  $k^{\text{th}}$  electronic state. For a given electronic transition,  $0 \rightarrow k$ , the excitation of the vibrational quanta in a given normal mode constitute a vibrational progression.

## Franck-Condon Approximation

In the general case, the intensity distribution within such a vibrational progression corresponding to transitions of the form,  $\Psi_0(r, R) \chi_0^0(R) \rightarrow \Psi_I(r, R) \chi_n^I(R)$  is determined by the square of the vibrational-overlap integrals  $| \langle \chi_0^0 | \chi_n^I \rangle |^2$  (Franck-Condon factors).

Their precise calculation for larger molecules and a realistic PES is a quite complicated problem and calls for further simplifications. The Franck-Condon (FC) principle states that the electronic ground-state vibrational wavefunction,  $\chi_0^0(R)$ , has large overlap with the excited-state wavefunctions,  $\chi_n^I(R)$ , only if the energy levels are close to the vertical transition. The vertical transition occurs when the molecule is promoted from the electronic ground state to the electronically excited state at the ground state equilibrium geometry as shown in Figure 5.

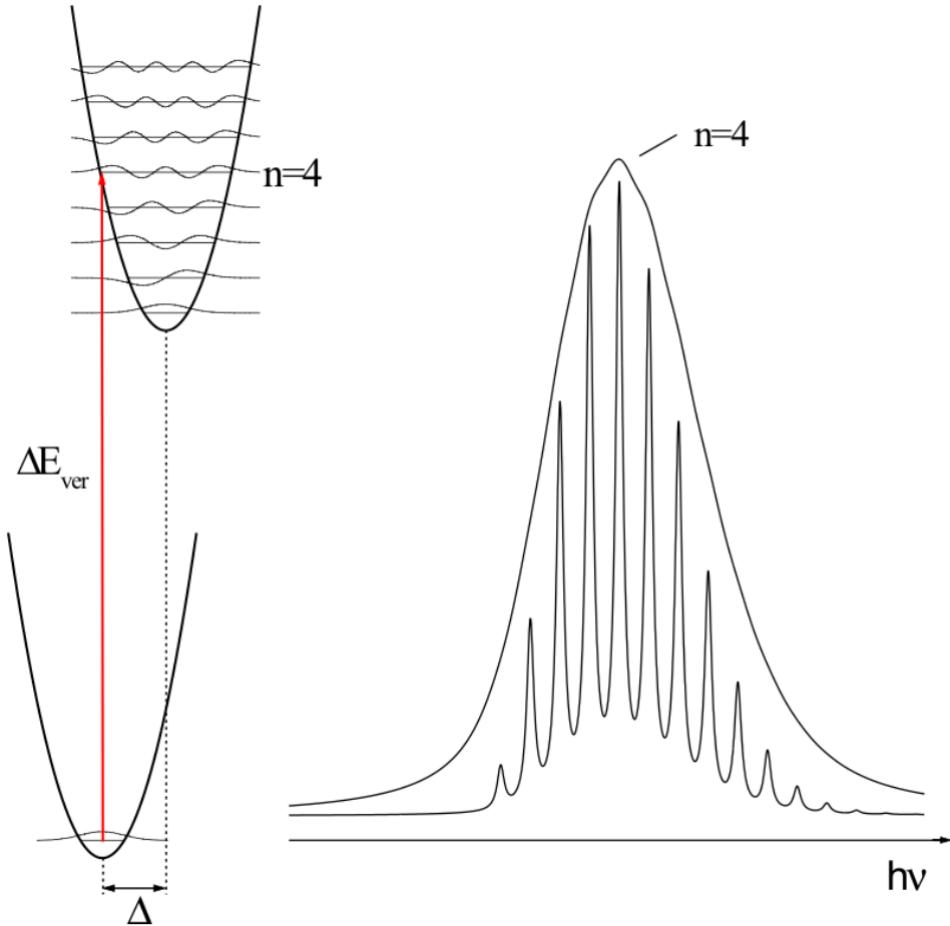
## Vibrational Fine Structure

Although the absorption spectra of various chemical species are characterized by vibrational structure, the latter is frequently obscured due to intermolecular collisions, solvent effects and spectral crowding. In such a case, an absorption band may be viewed as the envelope of different vibronic transitions, as shown in Figure 5.

The intensity (area under the absorption band) is given by the oscillator strength. The simultaneous neglect of vibrational and rotation fine structure together with the zero-temperature and Franck-Condon approximation on harmonic potential energy surfaces present the most simplified level of theoretical description. It requires only a knowledge of the energies and electronic wavefunctions of the ground and excited states which are all evaluated at the ground-state equilibrium geometry. Despite the many simplifying assumptions, this represents a very useful level of theory.

The FC principle can be rigorously derived only for a diatomic harmonic PES, and, for many-atom molecules and more complicated shapes of the PES, it should be used with caution.

The prediction of the vibrational structure of the absorption spectra is based on the calculations of vibrational-overlap integrals,  $| \langle \chi_0^0 | \chi_n^I \rangle |^2$ , which, in general, depend in a complicated way, on the shape of the PES. However, under the simplifying assumption of harmonic potentials, the problem can be solved exactly. In this case the distribution of intensity between various vibronic bands depends on



**Figure 5:** Illustration of the Franck-Condon principle. The excitation into electronic band involves the coexcitation of vibrational levels which results in the vibrational progression of the absorption. The vibronic peak of maximum intensity corresponds to the excited-state vibrational level which is most close to the intersection of the vertical transition (red line) with the excited-state PES. As a result the maximum of the broadened absorption spectrum occurs close to the vertical transition energy. For the IMDHO model the number of intense peaks in the absorption progression correlates with the value of  $\Delta$ .

- the **equilibrium shift**, which is the displacement of the excited-state origin relative to the ground state along a one-dimensional normal coordinate,
- the **frequency alteration**, which is the change of vibrational frequencies in the excited state due to the change of bonding,
- and **normal mode rotation** in the excited state, which is a fairly complicated effect, known as a Duschinsky rotation.

This arises from the fact that the force field of the molecule is different for each electronic state. Thus, the shapes of normal modes also change from state to state which leads to additional complexity in the calculation of FC factors.

The entire absorption bandshape can be written in the closed form as a function of several parameters. Of these factors, only the first one, the equilibrium shift,  $\Delta$ , is of major importance. The neglect of the normal mode rotations leads to the Independent Mode Displaced Harmonic Oscillator (IMDHO) model. In this simplified framework, the vibrational progression is determined solely by the equilibrium shift and vibrational frequency alteration between the ground- and excited-state PES.

Thus, in a given electronic absorption band, one can observe a manifold of vibrational transitions at energies:

$$E_n = E_0 + \sum_{\alpha}^{3N-6} n_{\alpha} \hbar \omega_{\alpha}$$

corresponding to different sets of vibrational wavefunctions  $|\chi_{n_{\alpha}}\rangle$ , which have relative intensities  $|<\chi_0^0|\chi_n^I>|^2$  and energy separation,  $E_0$  between the ground- and excited-state PES minima. The vertical transition energy,  $E_V$  can then be recast to utilize the displacements,  $\Delta_{\alpha}$ , of the IMDHO model, in the following way:

$$E_V = E_0 + \sum_{\alpha}^{3N-6} n_{\alpha} \hbar \omega_{\alpha} \frac{\Delta_{\alpha}^2}{2}$$

## Electronic Absorption Spectroscopy

The calculation of electronically excited states of molecules presents a number of additional challenges to quantum chemistry that can not be discussed in depth in the framework of these exercises. A rather simple picture of the excitation process as involving the promotion of an electron from an occupied molecular orbital in the ground-state into an unoccupied orbital (one-electron picture) is pursued. Within this approximation, the assignment of an absorption spectrum consists in the determination of which donor and acceptor MOs give the dominant contribution to the observed absorption bands, as exemplified above. In general, this picture is oversimplified since the excited state is usually not well represented in terms of a single Slater determinant and secondly, the orbitals of the ground state will not be appropriate for the electronically excited state. Nevertheless, the simplest reasonable

approximation is to write the ground state as a single determinant (for example, the Hartree-Fock determinant):

$$\Psi_0 = | \psi_1 \cdots \psi_i \cdots \psi_N |$$

And the excited states may be assumed to be represented as a superposition of singly-excited determinants:

$$\Psi_I = \sum_{i,a} t_i^a \Psi_i^a$$

Where the excited determinants,  $\Psi_i^a$ , have an occupied MO ( $\psi_i$ ) replaced by a virtual MO ( $\psi_a$ ), and the quantities,  $t_i^a$ , are the amplitudes of the excitation. The quantity,  $(t_i^a)^2$ , is the weight of the excited determinant,  $\Psi_i^a$ , in the excited state,  $\Psi_I$ . The amplitudes are determined from solving the so-called configuration-interaction with single excitations (CIS) eigenvalue problem. The eigenvalues of this matrix correspond to the vertical excitation energies at this level of approximation, and the eigenvectors are the excitation amplitudes. Note that there is a different set of excitation amplitudes for each excited state.

Calculations in the CIS framework do not lead to very accurate results but are suitable to provide an initial orientation prior to more accurate calculations and is also feasible for larger molecules. In the framework of density functional theory (DFT), one employs the so-called time dependent density functional theory (TD-DFT) in-order to predict vertical transition energies. TD-DFT is based on a different philosophy than CIS but leads to equations that are fairly similar, and that can be solved with comparable computational effort. The accuracy of TD-DFT is usually superior to that provided by CIS.

For an HF reference wavefunction (RHF or UHF), the program automatically chooses CIS calculations, and for the DFT model (RKS or UKS) TD-DFT is chosen.

## Calculation of Electronic Transitions

A key part of the ORCA output from a TD-DFT or CIS calculation is shown below:

```
-----
TD-DFT/TDA EXCITED STATES (SINGLETS)
-----
the weight of the individual excitations are printed if larger than 0.01

STATE 1: E= 0.095176 au      2.590 eV      20888.6 cm**-1
        78a -> 80a : 0.988777 (c= 0.99437248)

STATE 2: E= 0.108238 au      2.945 eV      23755.5 cm**-1
        79a -> 80a : 0.945608 (c= -0.97242400)
        79a -> 83a : 0.010346 (c= 0.10171342)
```

In this part of the output, the results for each state are summarized, including the excitation energy (in atomic units, eV, and  $\text{cm}^{-1}$ ), and the largest amplitudes (squared) in the CI expansion. For example, the 1st excited state is mainly presented by one leading configuration (with the weight of 0.988777) in which the spin-up orbital 78 (the donor MO) in the reference determinant is replaced with the virtual orbital 80 (the acceptor MO). The symbol a in the output, next to the orbital number, means that this is a spin-up orbital. Alternatively, b corresponds to spin-down orbitals.

Transition energies and oscillator strengths for the calculated excited states are given in the following part of the output:

```
-----
ABSORPTION SPECTRUM
-----
State   Energy   Wavelength   fosc          T2          TX          TY          TZ
       (cm-1)     (nm)           (au**2)       (au)         (au)         (au)         (au)
-----
1      20888.6    478.7    0.094387411  1.48758    0.08858  -1.21644  -0.00006
2      23755.5    421.0    0.167847587  2.32609  -0.00002  -0.00013  -1.52515
3      32083.8    311.7    0.295677742  3.03395  0.13992   1.73619  0.00009
```

The column fosc shows calculated oscillator strengths. TX, TY, TZ are the components of electronic transition dipole moment, T2 is the square of transition moment.

The output of rotatory strengths for the calculated excited states has similar structure:

```
-----
CD SPECTRUM
-----
State   Energy   Wavelength   R          MX          MY          MZ
       (cm-1)     (nm)     (1e40*cgs)  (au)        (au)        (au)
-----
1      20888.6    478.7    3.659617854  0.32713  0.01744  -0.00002
2      23755.5    421.0   -166.793655155  0.96929  -0.50766  0.23200
3      32083.8    311.7   329.282848783  0.42056  0.36840  -0.12245
```

The column R shows calculated rotatory strengths. MX, MY, MZ are the components of magnetic transition dipole moment.

To obtain a plot of the absorption spectrum, the abs parameter, as input to the orca\_mapspc program is given:

```
orca_mapspc outputfile [abs] -x015000 -x135000 -w200 -n2000
```

will produce **outputfile.abs.dat** file containing absorption spectrum that can be plotted with standard graphics programs. Thus, in the above example, the absorption spectrum will be produced for 2000 equidistant points in the range  $15000\text{--}35000\text{ cm}^{-1}$  using full-width at half-maximum height equal to  $200\text{ cm}^{-1}$  for each transition.

A CD plot can be obtained by calling orca\_mapspc with cd parameter option:

```
orca_mapspc outputfile [cd] -x015000 -x135000 -w200 -n2000
```

which produces the file, **outputfile.cd.dat** containing CD spectrum.

## Infrared and Raman Spectroscopy

### Normal Modes and Vibrational Frequencies

Infrared (IR) and Raman spectroscopies are mutually complementary components of molecular vibrational spectroscopy. Their molecular physics is essentially the same since both are concerned with the observation of the excitation of molecular vibrational energy states associated with the electronic ground-state PES. In IR spectroscopy, vibrational excitations occur upon the absorption of electromagnetic radiation. In Raman measurements the excitation is a consequence of inelastic light scattering by molecule. Upon the assumption that the PES is quadratic in atomic displacements (harmonic model), the vibrational states of an N-atom molecule are described as a superposition of  $3N - 6$  ( $3N - 5$  for linear molecules) independent harmonic oscillators which describe the collective harmonic vibrational motion of the nuclei about their equilibrium configuration.

The shapes of different vibrations are characterized by different patterns of the joint nuclear displacements and are called normal modes (coordinates), which transform under the irreducible representations of the molecular symmetry group and may therefore be classified by their symmetry. The textbook example of the  $\text{H}_2\text{O}$  molecule is shown in Figure 6.

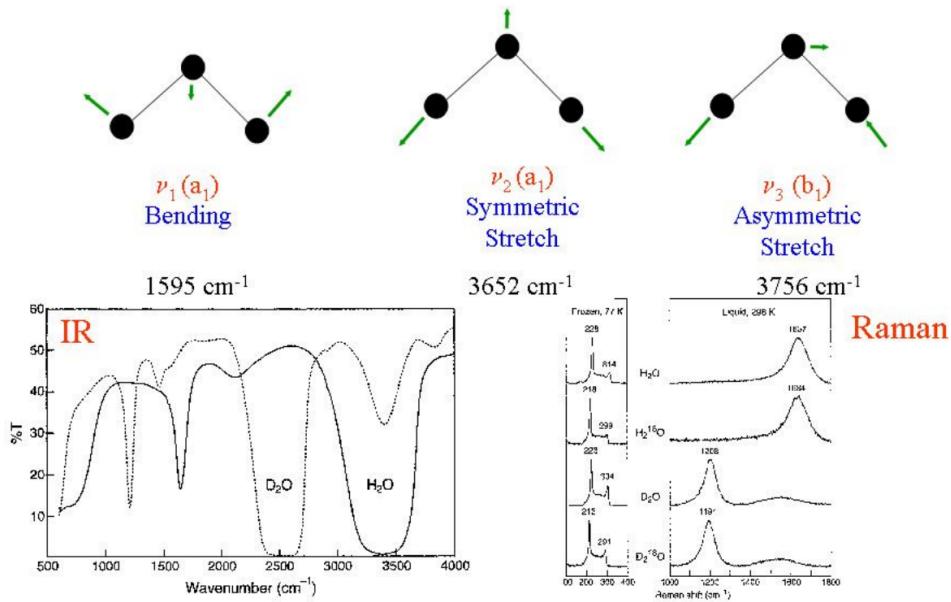
A quantum mechanical treatment provides the exact vibrational energies for the harmonic oscillator model:

$$E = \hbar\omega_1(n_1 + 1) + \hbar\omega_2(n_2 + 1) + \hbar\omega_3(n_3 + 1) + \dots$$

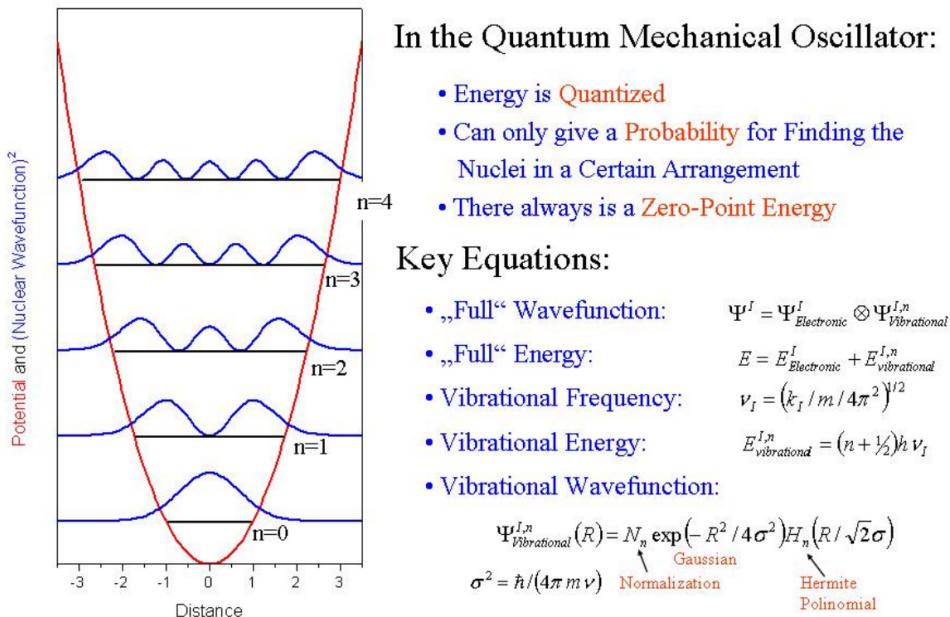
where  $n_i = 0, 1, 2, 3 \dots$  are the vibrational quantum numbers, and  $\omega_i$  are harmonic vibrational frequencies corresponding to the  $i$ -th normal mode.

For a purely harmonic oscillator the solution of the wavefunctions is shown in Figure 7, where  $\omega = \frac{\nu}{2\pi}$ .

The vibrational frequencies of the normal modes reflect the force-field for the molecule. It is a measure of the shape of the PES of the electronic state under investigation (usually the



**Figure 6:** The normal coordinates of the  $\text{H}_2\text{O}$  molecule together with its IR and Raman spectra on natural abundance, as well as isotopically labeled forms of  $\text{H}_2\text{O}$ .



**Figure 7:** Eigenfunctions and Eigenenergies of the Harmonic Oscillator.

electronic ground state) which, in turn, depends on the strengths of the bonds between the different nuclei. For a diatomic molecule, the force constant  $k$  is simply the second derivative of the electronic energy at the equilibrium distance:

$$k = \left. \frac{\partial^2 E^I}{\partial R^2} \right|_{R=\bar{R}}$$

From which the vibrational frequency is readily calculated as:

$$\omega = \frac{1}{2\pi c} \sqrt{\frac{k}{m}}$$

where the reduced mass  $m$  is defined in Figure 8 below.

**Newton's law:**

$$F = -\frac{\partial V(R)}{\partial R} = m \frac{\partial^2 R(t)}{\partial t^2}$$

**Molecule:**

$$V(R) = V_0 + \underbrace{\frac{\partial V}{\partial R} \Big|_{R=\bar{R}}}_{0} (R - \bar{R}) + \underbrace{\frac{1}{2} \frac{\partial^2 V}{\partial R^2} \Big|_{R=\bar{R}}}_{k} (R - \bar{R})^2 + \dots$$

**Thus:**

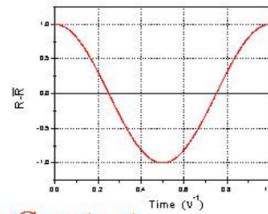
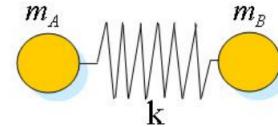
$$\frac{\partial^2 R(t)}{\partial t^2} = -\frac{k}{m} (R - \bar{R})$$

**Solution:**

$$R(t) = \bar{R} + c_1 \sin\left(\sqrt{\frac{k}{m}}t\right) + c_2 \cos\left(\sqrt{\frac{k}{m}}t\right)$$

**Characteristic Quantities:**

$$\text{Vibrational Frequency } \nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad \text{Force Constant} \quad \text{Reduced Mass } m = \frac{m_A m_B}{m_A + m_B}$$



**Figure 8:** Vibrations of a Diatomic Molecule.

For a general polyatomic molecule, the definition of the force constant must be generalized, and is replaced by the Hessian matrix, with the definition:

$$H_{AB} \frac{\partial^2 E^I}{\partial X_A \partial X_B} \Big|_{X_A=X_B=\dots=\bar{X}}$$

where  $X_A, X_B, \dots$  are Cartesian coordinates of atoms  $A, B, \dots$ . The diagonalization of the mass-weighted Hessian matrix,  $H'_{AB} = \frac{H_{AB}}{\sqrt{(m_A m_B)}}$ , yields the normal modes and harmonic vibrational frequencies of the system.

## Selection Rules for Infrared and Raman Spectroscopy

The important difference between IR and Raman spectroscopies is that for non-zero IR intensity, there must be a change of dipole moment along a given normal mode. For diatomic molecules, this means that they must have a permanent dipole moment in order to be IR active. For nonzero Raman intensities there must be a change in the polarizability during the vibration.

Taking into account only linear terms in variations of dipole moment (for IR) and polarizability (for Raman) during the vibration, leads to the vibrational selection rule for the harmonic case. It states that excitations with  $\Delta n = \pm 1$ , in only one single mode, are allowed upon the vibrational transition. For such a case, IR and Raman spectra consist only of fundamental transitions at the frequencies which coincide with the vibrational harmonic frequencies of the molecule. The use of group theory and symmetry arguments can be of great assistance in determining which vibrations are IR or Raman active and which are not.

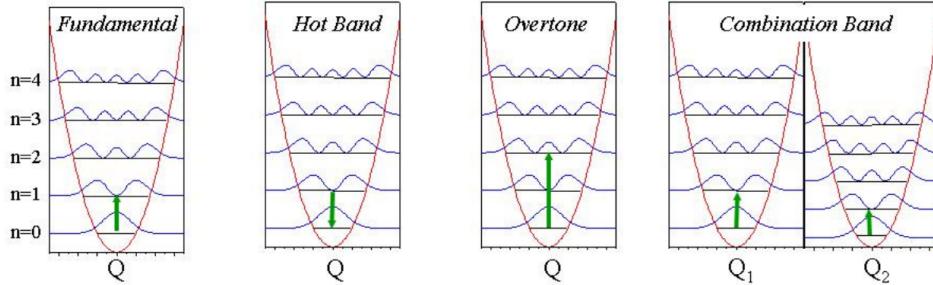
Character tables for the various symmetry groups can be used to predict how many of the  $3N - 6$  vibrations are IR active, and how many are Raman active. In particular, if the symmetry point group possesses a center of inversion, there is a mutual exclusion rule which states that vibrations allowed in the Raman spectrum are forbidden in IR, and vice versa. The symmetry of a molecule may also dictate that certain bands are forbidden in both the IR and Raman spectra, in which case even the combination of the two spectra will not provide the full information about the  $3N-6$  normal frequencies.

## Anharmonicities

A more detailed treatment of the vibrational spectra of molecules can be made if anharmonicity is included into consideration. In this case the quadratic model for PES function is extended by cubic and higher-power terms. The occurrence of anharmonicities has several important consequences for vibrational spectroscopy.

1. The energy levels are no longer equally spaced.
2. The first transition,  $n'' = 0 \rightarrow n' = 1$  (i.e. the fundamental transition), occurs at a slightly lower frequency than in the harmonic case.
3. The vibrational selection rule,  $\Delta n = \pm 1$ , breaks down and leads to the observation of overtone vibrations in the experimental spectra. Because the energy levels are no longer equidistant, the positions of the overtones are not given by integer multiples of the fundamental frequency,  $n'' = 0 \rightarrow n' = 1$ .
4. In addition to overtones, combination bands also become weakly allowed in which two different vibrational modes are simultaneously excited.

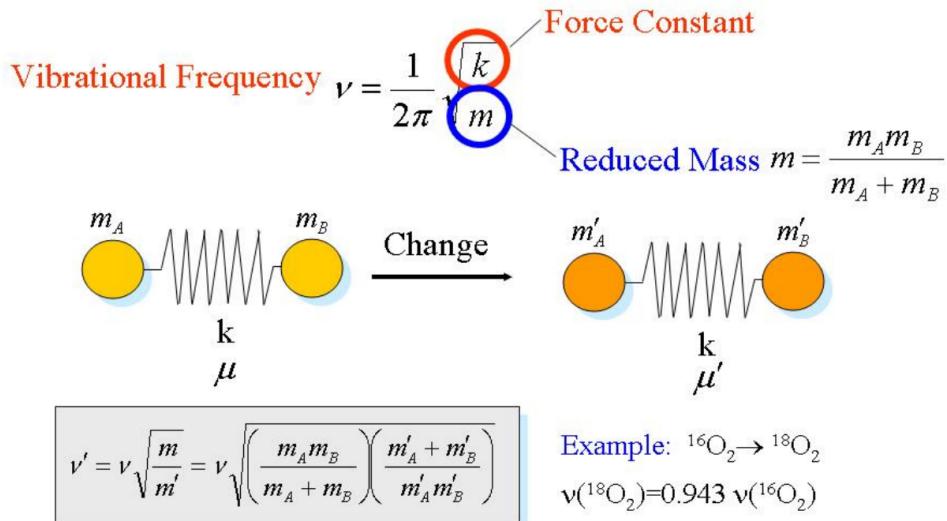
<b>Fundamentals</b>	: $n=0 \rightarrow n'=1$	$\Delta E = h\nu$
„Hot“ Bands	: $n=1 \rightarrow n'=n\pm 1$	$\Delta E = h\nu$
Overtones	: $n=0 \rightarrow n'=2,3,\dots$	$\Delta E = 2h\nu, 3h\nu,\dots$
Combination Bands	: $n_1=0, n_2=0 \rightarrow n_1'=1, n_2'=1$	$\Delta E = h\nu_1 + h\nu_2$



**Figure 9:** Description of Overtone, Combination, and Hot Bands in IR and Raman Spectra.

### Isotope Shifts

Since the vibrational energies depend on the masses of the vibrating atoms, it is possible to isotopically label the compounds of interest in order to arrive at an experimentally substantiated assignment of the experimental spectra, or in order to assist the fitting of the force fields of molecules. In the case of a diatomic molecule, the isotope shift is particularly transparent, since the form of the reduced mass is simply  $\frac{m_A m_B}{m_A + m_B}$ , where  $m_A$  and  $m_B$  are the masses of the two vibrating atoms as shown in Figure 10:



**Figure 10:** The reduced mass and isotope shifts in vibrational spectra of diatomic molecules.

### Calculation of IR and Raman Spectra

Within the harmonic approximation IR and Raman vibrational spectra are calculated in the course of frequency calculations. Since harmonic vibrational frequencies are determined by

the value of the Hessian matrix at the ground-state equilibrium geometry, it is necessary that frequencies are calculated for the geometrical structure optimized at the same level of theory as the frequency job.

IR spectral intensities are calculated automatically in frequency runs. Here is the part of the output of a frequency calculation containing information on IR intensities:

----- IR SPECTRUM -----						
Mode	freq (cm**-1)	T**2	TX	TY	TZ	
6:	1278.77	6.157280	( -2.481387	-0.000010	-0.000287)	
7:	1395.78	29.682711	( -0.000003	-5.448182	-0.004815)	
8:	1765.08	4.180497	( 0.000537	-0.022003	2.044508)	
9:	2100.53	8.550050	( 0.000080	0.011990	2.924022)	
10:	3498.72	1.843422	( 0.001027	-0.178764	-1.345907)	
11:	3646.23	19.778426	( 0.000035	4.446922	-0.057577)	

The Mode column indicates the number of the vibrational mode, followed by the value of vibrational frequency. The value T\*\*2 is the square of the change of the dipole moment along a given vibrational mode in km/mole, which is directly proportional to the intensity of a given fundamental in an IR spectrum. The command

**orca\_mapspc** **outputfile** **[ir]** **-w20**

is used to calculate the IR spectrum and produce the file **outputfile.ir.dat**. In order to predict the Raman spectrum of a compound one has to know the derivatives of the polarizability with respect to the normal modes. Thus, the Raman spectrum will be automatically calculated if a frequency run is combined with a polarizability calculation.

The output consists of the Raman activity ( $\text{\AA}^4/\text{amu}$ ) and the Raman depolarization ratios:

----- RAMAN SPECTRUM -----			
Mode	freq (cm**-1)	Activity	Depolarization
6:	1278.77	0.007349	0.749649
7:	1395.78	3.020010	0.749997
8:	1765.08	16.366586	0.708084
9:	2100.53	6.696490	0.075444
10:	3498.72	38.650431	0.186962
11:	3646.23	24.528483	0.748312

As with IR spectra, one can also obtain a plot of the Raman spectrum using:

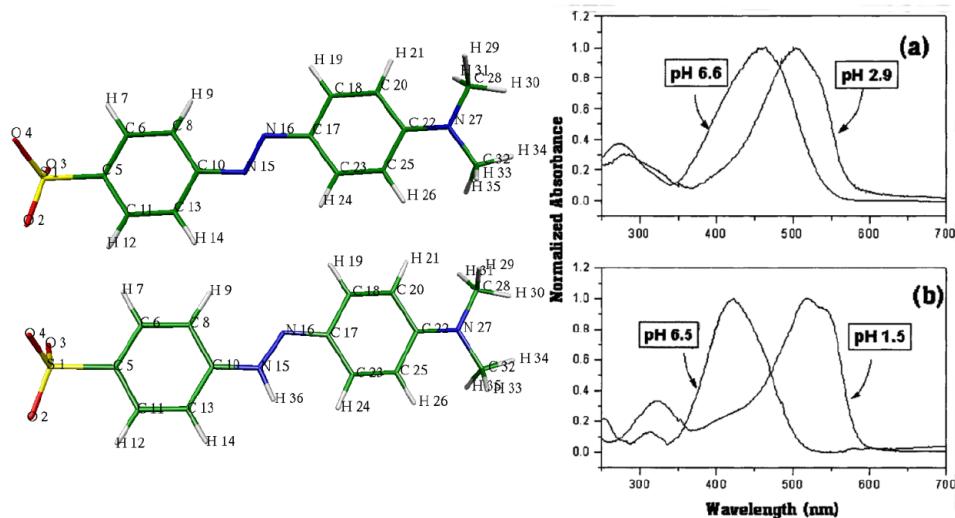
**orca\_mapspc** **outputfile** **[raman]** **-w20**

which produces the file, **outputfile.raman.dat**, containing the Raman spectrum.

# Exercises for Electronic Absorption Spectroscopy

## Absorption Spectra of Acid and Basic Forms of Methyl Orange

Calculate the absorption spectra of the protonated and unprotonated forms of the dye methyl orange (Figure 11).



**Figure 11:** Cis isomers of the alkaline and monoprotonated azonium forms of methyl orange, optimized with BP/SV(P), which exist under alkaline and acid conditions, respectively. Experimental UV/visible spectra of (a) aqueous and (b) acetone solutions of methyl orange for different values of pH; Nero, J.D.; Araujo, R.E.; Gomes, A.S.L.; Melo, C.P.; (2005) J. Chem. Phys., 122, 104506.

Since the two forms show distinct absorption spectra, such dyes can be used as pH indicators. The protonated form ( $\text{pH} < 3.1$ ) is characterized by intense absorption in the blue-green spectral range (450-550 nm), while the absorption of the deprotonated form ( $\text{pH} > 4.4$ ) mainly occurs in the violet-blue range (400-470 nm). Consequently, upon a change of pH from 3.1 to 4.4, methyl orange changes its color from red to yellow. In this exercise, it is important to understand this change in pH from a spectroscopic perspective.

The focus of this calculation is the determination of the most intense electronic absorption band for both the protonated and the unprotonated form of methyl orange.

The SV(P)+ basis set will be used, although small, it includes diffuse functions since they are important for the quality of excited-state calculations.

1. From the output, determine the most intense transitions, their excitation energies, and oscillator strengths. Are the variations of transition energies consistent with experimentally observed spectral changes between two forms of methyl orange?
2. Analyze the electronic structure of the two monoprotonated azonium forms. Determine the nature of the most intense transitions by inspecting the shapes of donor and

acceptor MOs with a visualization program. How do these orbitals change upon going from unprotonated to protonated species?

3. Use the `orca_mapspc` program to plot absorption spectra in the visible spectral range and compare them with the experimental spectra.

## Vibrational Structure of Lowest Absorption Band in Hexatriene

In this exercise, the underlying vibrational and resonance Raman spectra spectra of the absorption band corresponding to the electronic transition of  $1^1A_g \rightarrow 1^1B_u$  of trans-1,3,5-hexatriene is calculated.

Assuming the IHMDO model, the calculation of vibronic structure in absorption spectra, as well as resonance Raman spectra, for dipole-allowed transitions involves four stages.

Resonance Raman (rR) calculations require several calculations to be performed.

1. First, a standard geometry optimization and frequency calculation must be performed to obtain the Hessian.
2. Next, a TD-DFT calculation, using the optimized geometry is performed to calculate the absorption spectrum.
3. Using the information obtained from the previous calculation another TD-DFT calculation with numerical gradient is performed.

The program employs the Hessian matrix obtained from the previous frequency calculation, since it provides frequencies and normal modes which are used in the transformation of the energy gradient from Cartesian to normal coordinates. Within the harmonic approximation, the origin displacements along different normal modes may be approximated by means of excited-state energy-gradient calculations.

The resulting output from this calculation will include information about the vibrations and excitations, as well as create an input file to be read by the `orca_asa` program, required for spectral simulations.

The file `hexatriene-uv.asa.inp` is created, which provides input information for spectral simulation.

4. Finally, the spectral simulations can be performed within the framework of Heller time-dependent theory, as implemented in the `orca_asa` stand-alone program, to produce the file `hexatriene-uv.abs.dat` containing the absorption spectrum along with the corresponding vibrational progression.

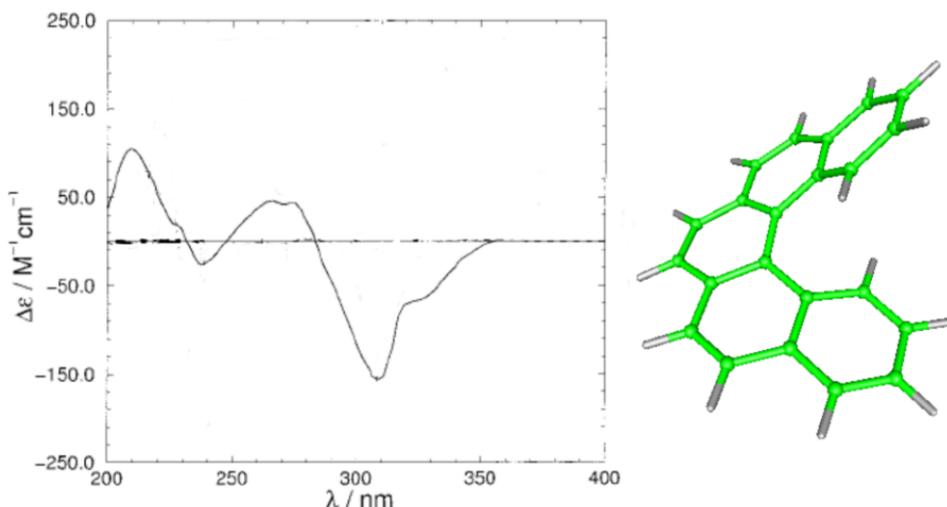
In the input file, `hexatriene-uv.asa.inp`, parameters, concerning various details of the simulation, such as spectral range and number of point for absorption, will need to be modified.

- Optimize the geometry of hexatriene, and perform a frequency calculation at the RHF/SV(P) level.

- Plot the spectrum using the data in the hexatriene-uv.abs.dat file.. Determine the position of the 0-0 vibronic peak in the absorption. Locate the vibronic peak with the maximum intensity and compare it with the calculated vertical transition energy. Explain the difference.
- Identify the most important overtone and combination transitions in the absorption band. How do their intensities correlate with the values of dimensionless normal coordinate displacements given in the input?

## CD Spectrum of (M)-Pentahelicene

Calculate CD spectrum of the (M)-pentahelicene, as shown in Figure 12.



**Figure 12:** Structure of (M)-pentahelicene and Experimental CD Spectrum; Brown, A.; Kemp, C.M.; Mason, S.F.; (1971) J. Chem. Soc. A, 751.

Experimental transition energies and intensities of the lowest energy transitions of (M)-pentahelicene are summarized in Table 3.

State	$\Delta E$ (nm)	$f$	$R(10^{-40}$ cgs)
1	392	0.002	0.1
2	328	0.115	-150
3	306	0.400	-400

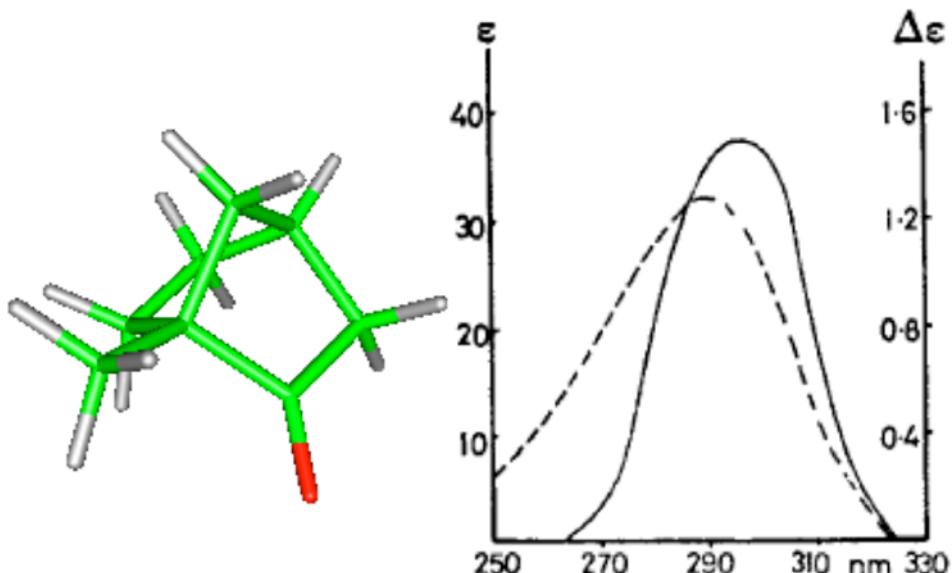
**Table 1:** Experimental results for the lowest excitations of (M)-pentahelicene in ethanol solution.

TD-DFT calculations for the 10 lowest excited states should be obtained. The COSMO approach is applied in order to model the solvent effect on the calculated transition energies and intensities.

- From the output, determine the most intense transitions, their excitation energies, oscillator strengths, and rotatory strengths. Perform the assignment of the experimentally observed optical transitions.
- Determine the nature of the most intense transitions by inspecting the shapes of donor and acceptor MOs with a visualization program.
- Use the orca\_mapspc program to plot the CD spectrum in an appropriate spectral range, and compare it with the experimental spectrum.

## Absorption and CD Spectra of Camphor

The experimental absorption and CD spectra corresponding to the lowest energy transition in the 1,7,7-trimethyl-bicyclo[2.2.1]heptan-2-one (d-(+)-camphor), is shown in Figure 13. The



**Figure 13:** Structure of d-(+)-camphor and Experimental UV Absorption (dashed line) and CD (solid line) Spectra in Ethanol Solution, Corresponding to the Lowest Energy Electronic Band; Furche, F.; Ahlrichs, R.; Wachsmann, C.; Weber, E.; Sobanski, A.; Vgtle, F.; Grimme, S.; (2000) J. Am. Chem. Soc., 122, 1717. Gillard, R.D.; Mitchell, P.R.; (1969) Trans. Faraday Soc., 65, 2611.

main interest in this exercise involves the calculation of the low-energy electronic absorption and CD band of camphor.

The input file contains coordinates optimized at the BP86/SV(P). TD-DFT calculations for the 3 lowest excited states will be carried out, using the COSMO solvation model, in order to account for solvent effects on the calculated transition energies and intensities.

- From the output, examine the transitions, and determine which energy most closely matches the experimental one. Determine the nature of the transition by inspecting the shapes of donor and acceptor MOs with a visualization program.

2. Use the `orca_mapspc` program to plot absorption and CD spectra in the spectral range around 300 nm, including an appropriate value of the bandwidth which roughly matches the experimental one. Compare experimental and theoretical plots.
3. Does the rotatory strength have the proper sign for the given transitions? What parameter, that can be rather sensitive to the level of calculation, can result in observed disagreement? As a hint, consider the scalar product of the transition electric dipole and magnetic dipole moments in the form  $\mathbf{D}_{0 \rightarrow I} \cdot \mathbf{M}_{0 \rightarrow I} \cos\phi$ .

## Exercises for Infrared and Raman Spectroscopy

### Vibrational Frequencies and Intensities of Diatomic Molecules

Optimize the geometries, calculate vibrational frequencies, IR and Raman intensities of the following diatomic molecules using the BP86 functional and the TZVP basis set:

Molecule	$\omega_{\text{exp}}(\text{cm}^{-1})$
CO	2170
HF	4138
ClF	786
N <sub>2</sub>	2359
HCl	2991
Cl <sub>2</sub>	560

1. Analyze the origin of the trends in the calculated IR intensities using population analysis and chemical intuition .
2. Why do the stretching vibrations of the homonuclear diatomics not show any IR intensity? Provide a qualitative explanation on the origin of IR intensity for the heteronuclear species.
3. Compare the calculated harmonic frequencies with the values for the experimental harmonic frequencies. How reliable are the DFT results?

In general, the calculations always produce harmonic force constants and therefore also harmonic frequencies. The underlying assumption is that the potential energy surfaces behave exactly quadratically. In reality, however, the potential energy surfaces are anharmonic, and this leads to important modifications in the spacing of the vibrational levels. However, experimental harmonic frequencies are only known for very small molecules and anharmonic frequencies are difficult to calculate.

In practice, this limits the accuracy of the comparison between theory and experiment, and one usually compares calculated harmonic frequencies with observed fundamentals which contain anharmonic contributions.

## Vibrational Frequencies, IR and Raman Intensities of Benzene

Optimize the geometry, calculate vibrational frequencies, IR and Raman intensities of the benzene molecule using the BP86 functional and the TZVP basis set.

Experimental vibrational frequencies of the benzene are known from IR and Raman measurements:

IR ( $\text{cm}^{-1}$ )	Raman ( $\text{cm}^{-1}$ )
1485	605.0, 991.6, 1178.0, 1595.0

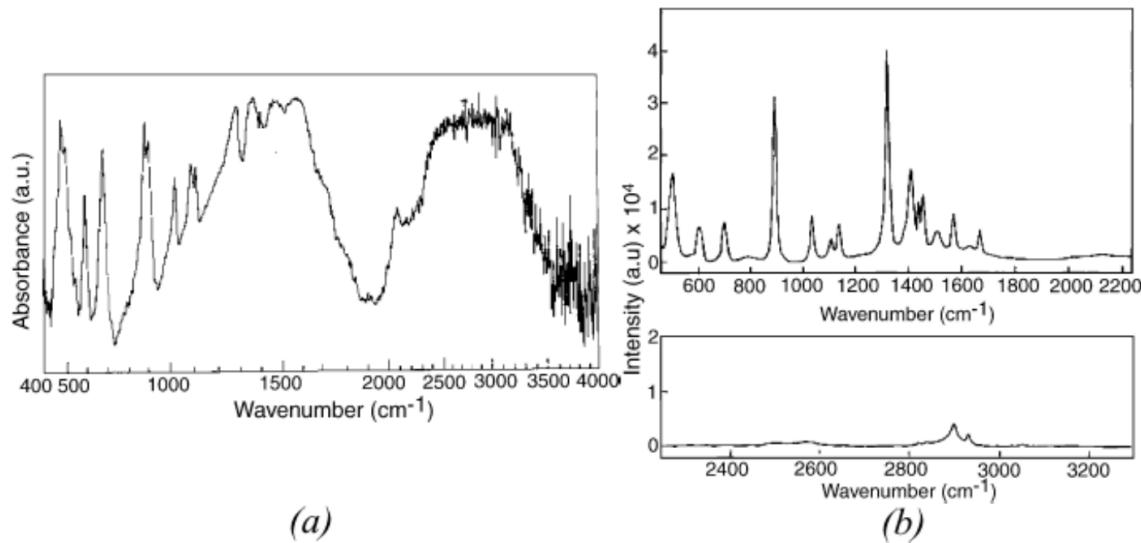
1. Assign experimental vibrational frequencies. Determine the character of IR and Raman active vibrations using a visualization program.
2. Plot the experimental versus the calculated frequencies.
3. Calculate the parameters of a linear regression analysis. How reliable are your predictions of vibrational frequencies? What is the mean deviation from experiment, and the maximum deviation?
4. The benzene molecule possesses a center of inversion. Show the complementary nature of Raman and IR spectra on the basis of the calculated IR intensities and Raman activities. Which symmetry species are active in IR and which in Raman? Which vibrations are forbidden in both IR and Raman spectra?

## Vibrational Frequencies of Hydrocarbon Molecules

Optimize the geometries and calculate vibrational frequencies of the following molecules using the BP86 functional and the TZVP basis set:



1. Discuss the trend in the variation of frequency of C-C stretching mode among the molecules. How do the frequencies depend on the bond order? Compare the results with the characteristic frequencies known for C–C, C=C, and C≡C bonds.
2. Use the orca\_vib program to obtain estimates of the C-C stretching force constants, and discuss how they vary with bond order?
3. Provide a qualitative explanation of the observed trend in the C-C bond stretching force constants on the basis of chemical intuition.



**Figure 14:** Experimental Infrared (a) and Raman (b) Powder Spectra of Glycine; Kumar, S.; Rai, A.K.; Singh, V.B.; Rai, S.B.; (2005) Spectrochim. Acta Part A, 61, 2741-2746.

## Vibrational Frequencies, IR and Raman Intensities of Glycine

The experimental IR and Raman powder spectra of glycine are given in Figure 14.

The experimental vibrational frequencies of glycine are provided below:

	$\text{cm}^{-1}$
IR:	504, 584, 607, 698, 893, 1034, 1334, 1410, 1504, 1610, 1703, 2128, 2920, 3084, 3414
Raman:	497, 602, 697, 893, 1033, 1323, 1410, 1508, 1667, 2123, 2930, 3050

1. Optimize the geometry, calculate vibrational frequencies, IR and Raman intensities of the glycine molecule ( $\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$ ) using the BP86 functional and the TZVP basis set.
2. Obtain the calculated IR and Raman spectra using the orca\_mapspc program, and then plot the results.
3. Assign experimental vibrational frequencies. Determine the character of IR and Raman active vibrations using a visualization program.
4. Find corresponding vibrations which are clearly identified in both IR and Raman spectra. Which normal modes have noticeable intensities only in IR or Raman?

Some of the vibrations may show slightly different frequencies in IR and Raman measurements which is due to slight variations in the wavelength calibration and the experimental conditions.

5. Plot the experimental versus the calculated frequencies.

6. Perform a linear regression analysis, and obtain the resulting parameters. How reliable are the predictions of vibrational frequencies? What is the mean deviation from experiment, and the maximum deviation?