



A QUANTUM LEAP INTO THE FUTURE OF CHEMISTRY

Computing Franck-Condon factors

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Description: Students will calculate vibrational progressions (Franck-Condon factors) in spectra of polyatomic molecules. This assignment builds on the students' previous experience computing optimized molecular structures, vibrational frequencies, and excited or ionized states.

Suggested level: Graduate or advanced undergraduate.

Learning objectives: Understand how the vibrational states of a molecule influence the energetics and the probabilities of radiative transitions; understand vibrational profiles of electronic spectra.

Requirements:

- IQmol (<http://iqmol.org/downloads.html>)
- ezFCF (<http://iopenshell.usc.edu/downloads/>). Requires Unix-like operating system (for example, Linux or macOS). Instructions to download and install ezFCF are in section 2.2 of this handout. Note that ezFCF depends on LAPACK and BLAS libraries that may need to be installed for the executables to work.
- A working knowledge of terminal and Unix commands.

1. Theoretical Background

1.1 The Born-Oppenheimer and Condon approximations

Radiative transitions are changes in the electronic state of a molecule resulting from the absorption or emission of a photon. For such transitions to occur, the energy difference between the initial and final states of the molecule must match the frequency of the absorbed (emitted) photon. For an incident photon of appropriate energy, the probability P_{if} of exciting a molecule from an initial state of wave function ψ_i to a final state with wave function ψ_f is proportional to the square of the transition dipole moment:

$$P_{if} \propto \left(\int \psi_i(\mathbf{r}, \mathbf{R}) \hat{\mu} \psi_f(\mathbf{r}, \mathbf{R}) d\mathbf{r} d\mathbf{R} \right)^2 \quad (1)$$

where \mathbf{r} and \mathbf{R} are respectively the coordinates of all the electrons and all the nuclei in the molecule, and $\hat{\mu}$ is an operator that describes the influence of the incident electromagnetic radiation on the molecule.

Within the Born-Oppenheimer approximation, the state wavefunctions $\psi(\mathbf{r}, \mathbf{R})$ can be written as the product of a nuclear wavefunction $\chi(\mathbf{R})$ and an electronic wavefunction $\varphi(\mathbf{r}; \mathbf{R})$. The latter

depends only parametrically on the nuclear coordinates. With the further assumption that the electronic transition occurs much faster than the timescales of nuclear motion, then the transition probability can be evaluated at a given set of nuclear coordinates (e.g., at the equilibrium geometry \mathbf{R}_e) and it is possible to write:

$$P_{i'f''} \propto \left(\int \varphi_i(\mathbf{r}; \mathbf{R}_e) \hat{\mu} \varphi_f(\mathbf{r}; \mathbf{R}_e) d\mathbf{r} \right)^2 \left(\int \chi_{i'}(\mathbf{R}) \chi_{f''}(\mathbf{R}) d\mathbf{R} \right)^2 \quad (2)$$

The integral inside of the first parenthesis yields the electronic probability component. For electronic excitations, this quantity is related to the oscillator strength. The integral inside the second parenthesis is known as the Frank-Condon Factor (FCF). Note how in equation (2) the indices i' and f'' are used to denote specific (nuclear) vibrational states corresponding to electronic states i and f . This lab is focused on calculating FCFs.

1.2 Harmonic vibrational modes

For a given state, the geometry of a molecule consisting of N atoms is given by a set of $3N$ nuclear coordinates: $\mathbf{R} = (R_1, R_2, \dots, R_{3N})$. Those are, for example, x, y, z , for each nucleus. If there is no time-dependent external field acting on the molecule, then the potential energy V at the geometry \mathbf{R} , displaced by $\Delta\mathbf{R} = \mathbf{R} - \mathbf{R}_e$ from the equilibrium geometry, can be obtained through a Taylor expansion about \mathbf{R}_e as:

$$V(R_1, R_2, \dots, R_{3N}) = V(R_{e1}, R_{e2}, \dots, R_{e3N}) + \sum_{i=1}^{3N} \left(\frac{dV}{dR_i} \right)_{\mathbf{R}_e} \Delta R_i + \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} \left(\frac{d^2V}{dR_i dR_j} \right)_{\mathbf{R}_e} \Delta R_i \Delta R_j + \dots \quad (3)$$

Since potential energy is indefinite in an additive constant, we can set $V(R_{e1}, R_{e2}, \dots, R_{e3N}) = 0$ and the condition that determines the equilibrium geometry \mathbf{R}_e is precisely that $\left(\frac{dV}{dR_i} \right)_{\mathbf{R}_e} = 0$.

Neglecting higher order terms, we can take:

$$V(R_1, R_2, \dots, R_{3N}) = \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} \left(\frac{\partial^2 V}{\partial R_i \partial R_j} \right)_{\mathbf{R}_e} \Delta R_i \Delta R_j \quad (4)$$

This is known as the harmonic approximation.

The Hessian matrix formed by the $\frac{\partial^2 V}{\partial R_i \partial R_j}$ derivatives was already presented in another lab [[IR & NMR Spectra](#)]. From the Hessian, one can obtain the molecule's normal modes of vibration and the corresponding normal frequencies. One way of doing so is to diagonalize the matrix formed by the terms: $A_{ij} = \frac{\partial^2 V}{\partial R_i \partial R_j} \cdot m_i^{-1/2} \cdot m_j^{-1/2}$, where m_i is the mass of the atom to which coordinate i is linked. The resulting $3N$ pairs of eigenvalues and eigenvectors can be separated into those corresponding to translational motion (three of them), those corresponding to rotational motion of the molecule (three except for linear molecules that only have two) and the remaining that correspond to vibrational degrees of freedom. It is those $3N-6$ eigenvalues and eigenvectors (or $3N-5$ in the case of linear molecules) that determine the frequencies and normal modes of vibration of the molecule, respectively.

The normal frequencies are all different and therefore the normal modes ($3N$ -dimensional vectors that specify the amplitude of oscillation of each atom in 3D space) are linearly independent and form a basis for the molecule's internal coordinates. If we consider only the $3N-6$ space of the molecule's internal coordinates, it is possible to further simplify equation (4) with a transformation of coordinates. Transforming the \mathbf{R} set of coordinates into the "normal

coordinates" \mathbf{Q} (obtained from the vibrational eigenvectors), the terms $\left(\frac{\partial^2 V}{\partial Q_i \partial Q_j}\right)_{R_e}$ become 0 when the index $j \neq i$. That is, the Hessian is diagonal when the internal coordinates' space is expanded in the basis formed by the vibrational normal modes. It is then possible to write:

$$V(Q_1, Q_2, \dots, Q_{3N-6}) = \frac{1}{2} \sum_{i=1}^{3N-6} \left(\frac{\partial^2 V}{\partial Q_i^2}\right)_{R_e} Q_i^2 \quad (5)$$

Back to the nuclear wavefunctions, since the individual harmonic potentials along each Q_i are independent, it is possible to express the nuclear wavefunctions as a product of unidimensional harmonic wavefunctions along the normal modes:

$$\chi(\mathbf{Q}) = \prod_{i=1}^{3N-6} \chi_{i,v_i}(Q_i) \quad (6)$$

where $\chi_{i,v_i}(Q_i)$ is the harmonic wavefunction corresponding to a linear harmonic oscillator of vibrational quantum number v_i along Q_i . The fundamental frequency of vibration ν_i of a mode is determined from $\frac{\partial^2 V}{\partial Q_i^2}$. Every mode contributes an energy $E_i = h\nu_i \left(v_i + \frac{1}{2}\right)$ to the vibrational energy of the molecule, where v_i is the number of quanta in that vibrational mode. The total vibrational energy of the system is:

$$E = \sum_{i=1}^{3N-6} E_i.$$

1.3 Evaluating the FCFs

The overlap integral can now be evaluated using equation (6) for both the initial and the target state. If the normal vibrational modes are equal for both the initial i and final f states (that is, if for a given mode each atom vibrates in the same direction in states i and f) then the overlap of the harmonics can be calculated independently over the corresponding coordinates:

$$P_{i'f''} \propto \left(\int \chi_{i'}(\mathbf{Q}) \chi_{f''}(\mathbf{Q}) d\mathbf{Q} \right)^2 = \left(\prod_{j=1}^{3N-6} \int \chi_{i',j}(Q_j) \chi_{f'',j}(Q_j) dQ_j \right)^2 \quad (7)$$

Where $\chi_{i',j}(Q_j)$ is the harmonic wavefunction for the initial state i' along the normal mode Q_j , and $\chi_{f'',j}(Q_j)$ is the harmonic wavefunction of the final state along the same mode. Directly evaluating equation (7) is known as the parallel-mode approximation. When the difference between the modes prevents the use of this approximation, it is possible to transform the normal coordinates of one mode into the other's. Duschinsky rotations can be used for such transformations.

Figure 1 illustrates the way vibrational progression shape the absorption spectral profile of a molecule. The ground state (red), and two target states (blue and green) are represented. The target states could be electronically excited states or ionized states. The one-dimensional harmonic potentials and wavefunctions along a normal mode are depicted in the corresponding color.

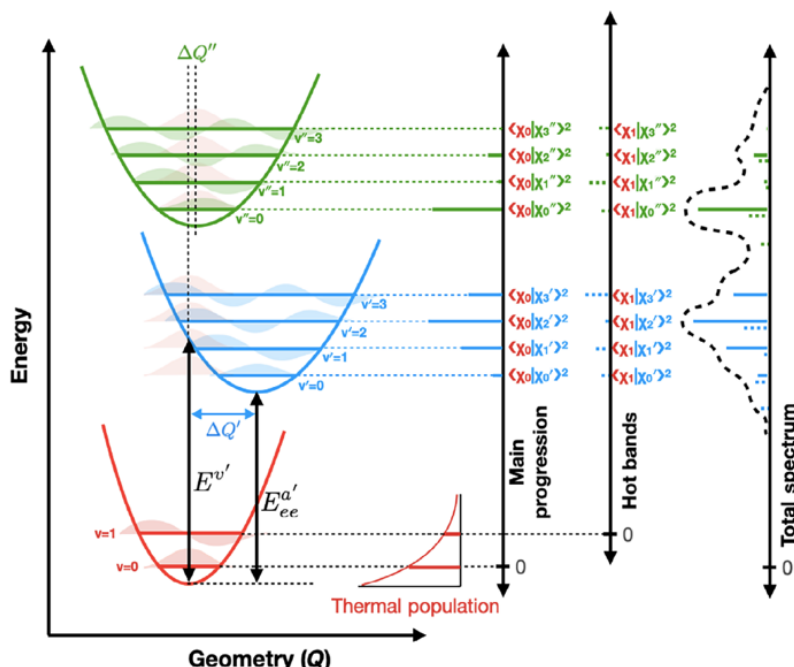


Fig. 1. Influence of vibrational modes and thermal population in the electronic excitation spectrum of a molecule. Here, we drop the subscript i that specifies the represented mode and use Q and ν instead of Q_i and ν_i used in equations 5-7. Adapted from: [WIREs Comp. Mol. Sci. 12, e1546 \(2022\)](#).

For the ground state, the two lowest vibrational states are shown. Molecules populate these vibrational states thermally, according to the Boltzmann distribution. Therefore, transitions from the lowest vibrational state ($\nu = 0$) will have the largest contribution to the spectra and the intensity of the main progression is determined by the overlap of the ground state's $\nu = 0$ wavefunction and each of the target state vibrational wavefunctions ($\nu' = 0, 1, 2, \dots$ and $\nu'' = 0, 1, 2, \dots$). Transitions from higher vibrational states ($\nu = 1, 2, \dots$) gain importance at high temperatures and lead to the appearance of “hot bands.” In other words, hot bands arise from the overlap of the $\nu = 1, 2, \dots$ wavefunction with the target state vibrational wavefunctions.

The total spectrum includes both the main progression and hot bands. Solvation effects result in a broadened experimental spectrum like the one shown with black dashed lines on the right.

Figure 1 also shows the electronic vertical ($E^{v'}$) and adiabatic ($E_{ee}^{a'}$) excitation energies for the first target state. The vertical excitation energy is the electronic energy difference between the two (initial and final) states at the equilibrium geometry of the initial state. The adiabatic electronic excitation energy is the energy difference between the two states at their respective equilibrium geometries. These quantities are easily determined by quantum chemistry programs and are therefore widely used. Accounting for the zero-point vibrational energies (i.e., all $\nu_i = \nu_i' = 0$) can give the 0-0 adiabatic excitation energy ($E_{00}^{a'}$). From $E_{00}^{a'}$ it is possible to determine the energy of a vibronic transition by accounting for the vibrational energies of the initial and final states.

2. Procedure

To illustrate the theory presented thus far, students will compute the photoelectron spectrum of the phenolate anion and will compare it to [the experimental spectrum](#). It has been established that the ω B97X-D/cc-pVTZ level of theory and the parallel approximation are sufficient to describe [the photoelectron stick spectrum of this molecule](#). Note that diffuse basis functions are necessary for accurate detachment energies, but we will use experimentally determined detachment energies.

2.1 Geometry optimization and frequency calculations in IQmol

In this section students will obtain the normal modes of vibration of the phenolate anion and of the molecule resulting after photoelectron detachment.

Note: Instructors may choose to skip this section and provide students with the normal modes of vibration, since the geometry optimization and frequency calculations can be time-consuming and require access to local computing resources.

Steps:

- I. Using IQmol, build a model of the phenolate molecule
- II. Optimize the geometry and carry out frequency calculations for the ground state at the wB97XD/cc-pVTZ level of theory (see lab [Lab1-IQmol-Intro for instructions if needed](#))
Note that charge = -1, multiplicity = 1.
- III. Optimize the geometry and obtain the vibrational normal modes for the electron-detached state at the same level of theory.
Mind that charge = 0, multiplicity = 2.
- IV. Verify that, for both the initial and target states, the frequencies of all modes are positive (real).

2.2 Computing vibrational progressions using ezFCF

For this section students will need:

1. The normal vibrational modes of the molecule in its initial and final state. (Refer to section 2.1, if not provided)
2. Access to ezFCF (iopencshell.usc.edu/downloads/)
3. A working knowledge of terminal and basic Unix commands.

Steps:

- I. Download ezFCF from <https://iopencshell.usc.edu/downloads/> and untar the file. If using terminal, you can untar using 'tar -xvzf ezFCF_v1.2.tar.gz'.
- II. Create a working directory in your computer and copy into it the file "atomicMasses.xml" — it can be found directly inside the downloaded folder.
- III. Familiarize yourself with the location of the two executables below since you will be using them. They are both found inside the downloaded ezFCF_v1.2/bin folder. You can also copy those two files into your working directory to access them more easily
 - a. "make_xml.py"
 - b. Either "ezFCF_linux.exe" or "ezFCF_mac.exe", depending on your operating system.

- IV. To run ezFCF it is necessary to create an XML file (a file ended in ".xml") that summarizes the information required for the calculations. Here are the steps to create it:
- Copy both output files containing the normal modes of vibration to your working directory (the ones obtained in section 2.1). The one corresponding to the initial state can be renamed to "initial.out" and the one corresponding to the detached state "target.out".
 - Open the terminal in your working directory and run the command:
`python3 /path/to/make_xml.py filename.xml initial.out target.out`
Instead of "/path/to/make_xml.py", use the actual path to the make_xml.py executable. Also, you may use any name instead of "filename" as long as you use the same file name consistently in the next steps.

- V. The steps above generate a new file "filename.xml". You can now open it and adjust the calculation parameters. You can do this on the terminal using (for example) vim or any software capable of reading and editing a text file. Initially, let's just change the parameter "excitation energy" from the default value of 1 to the adiabatic 0-0 detachment energy of the phenolate anion, which is 2.25 (eV). To do this, search for the tag `<excitation_energy units="eV">` inside the tag `<target_state>` and change the numerical value from 1 to 2.25.

All other parameters can be kept at their default values for now. Save the file and exit.

- VI. To run ezFCF, on the terminal run the command:

```
/path/to/ezFCF_mac.exe filename.xml > outputname.txt
```

Or:

```
/path/to/ezFCF_linux.exe filename.xml > outputname.txt
```

- VII. Check the results of the calculations by opening the newly created "outputname.txt". It will start by reproducing the input provided in filename.xml and readding it. Look for the line

`==== Reading the parallel approximation job parameters ===` followed by

`===== Overlap matrix of the target state #1 with the initial state =====`

Is there a warning stating that `"The normal modes overlap matrix with the initial state is non-diagonal!"`?

This happens because Q-Chem arranges the vibrational modes for each state in order of increasing frequency. However, for the parallel approximation the ground and excited state normal modes should be strongly overlapping. This may be fixed by reordering the modes of the target state so that the normal mode overlap matrix becomes diagonal, as discussed next.

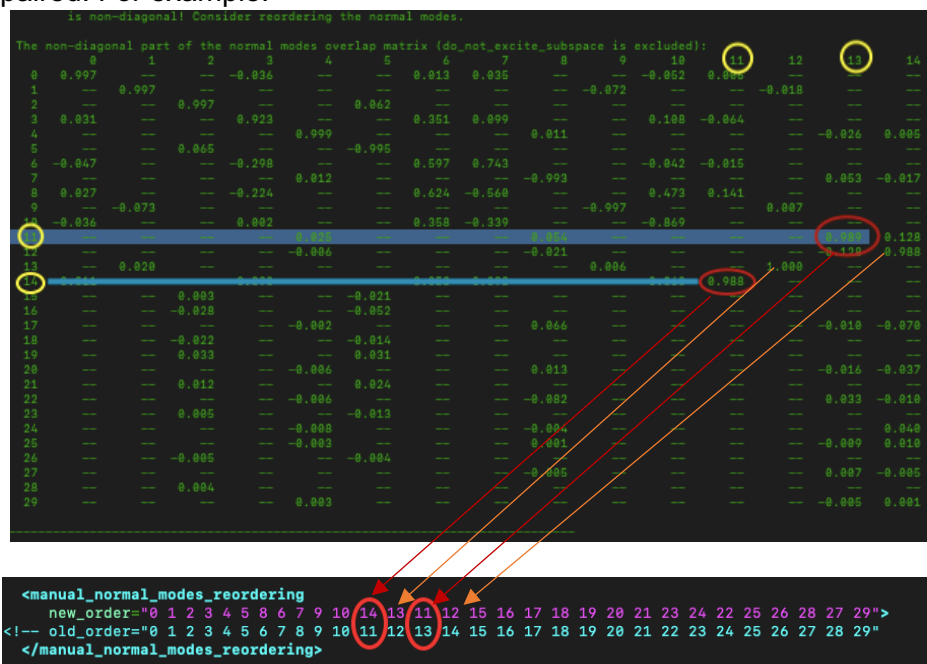
- VIII. Create another directory and copy into it the XML file you created previously and the file "atomicMasses.xml." In this new directory, open the XML file and reorder the normal modes:

- Look for the tag `<OPT_manual_normal_modes_reordering>` under the tag `<target_state>` it should be at the end of the file and look like this:

```
<OPT_manual_normal_modes_reordering
  new_order="0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29">
</OPT_manual_normal_modes_reordering>
```

- Delete "OPT_" from the start and the end of the tag to activate this keyword.
- On the line `new_order="0 1 2 ..."` rearrange the modes of the target state so that they are matched with a parallel mode on the initial state. To figure out the correct ordering, you will need to look back at the overlap matrix obtained in the

output file from subsection VII. Modes whose overlap is close to one should be paired. For example:



The line “<!-- old_order=“0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29” -->” is just a comment on the file to make the reordering easier for the user. It is not necessary, and it has no effect on how the program runs.

- IX. After saving the changes to the XML file you can now rerun ezFCF. If done correctly, the normal mode overlap matrix should now be diagonal.
- X. After running ezFCF you obtained a new file named “filename.xml. spectrum_parallel”. It contains the same stick photoelectron spectrum that appears in the output but is more convenient for plotting since it only contains the final spectrum. The first column presents the energy (in eV) of the vibronic transitions, and the second column the corresponding intensities. The last column identifies each vibronic transition. For example:
 - $0(0) \rightarrow 1(2v_0)$ means that the molecule is excited from the lowest vibrational state of the electronic ground state (given by the set of vibrational quantum numbers $\{v_i = 0 \mid i = 0, 1, 2, \dots, 3N - 7\}$) to a vibrational state described by the set $\{v_0' = 2, v_i' = 0 \mid i = 1, 2, \dots, 3N - 7\}$ that belongs to the first electronic target state. Notice that ezFCF numbers the vibrational modes starting with 0. The number outside the bracket indicates the electronic state (0 means ground state, 1 means first target state).
 - $0(1v_2) \rightarrow 1(1v_2, 1v_3)$ means that the molecule is excited from $\{v_0 = 0, v_1 = 0, v_2 = 1, v_i = 0 \mid i = 3, 4, \dots, 3N - 7\}$ in the ground state to $\{v_0' = 0, v_1' = 0, v_2' = 1, v_3' = 1, v_i' = 0 \mid i = 4, 5, \dots, 3N - 7\}$ of the target state. This is a so-called combination band
 - $0(1v_8) \rightarrow 1(0)$ means that the molecule is excited from the thermally occupied $\{v_0 = 0, \dots, v_7 = 0, v_8 = 1, v_i = 0 \mid i = 9, 10, \dots, 3N - 7\}$ in the ground state to the lowest vibrational level ($\{v_i' = 0 \mid i = 0, 1, 2, \dots, 3N - 7\}$) of the target state. Transitions like these final two give rise to “hot bands” in the experimental spectrum.

- XI. Using your favorite plotting software, compare the stick spectra you obtained with the experimental one below. The experimental data can be downloaded from Q-Chem's github collection of teaching resources.

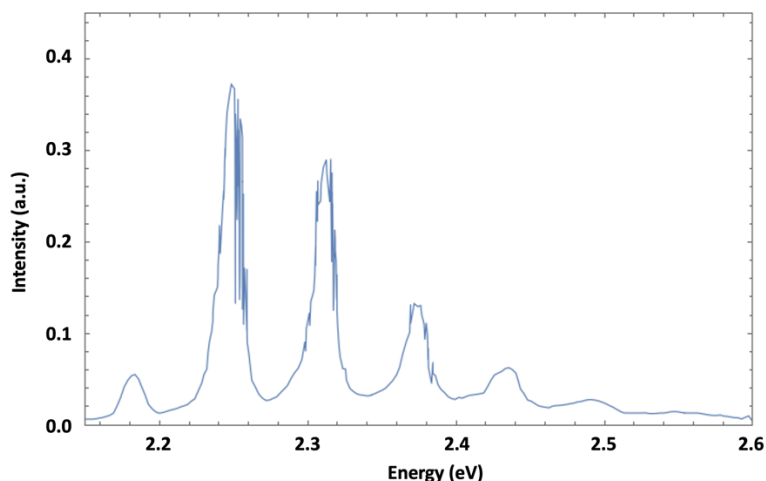


Fig. 2. Photodetachment spectrum of phenolate.

You may have noticed that there are many optional tags and parameters that can be modified in the XML file. This includes parameters modifying the temperature, number of excitations, options to excite only a subspace of vibrational frequencies, or using Duschinsky rotations instead of the parallel approximation. The ezFCF [manual](#) provides information on their meaning and function. Feel free to explore them. You can also learn more from watching the following Q-Chem Webinar: <https://www.youtube.com/watch?v=ZGqij5RY-6M>.

Questions:

1. Show the computed spectrum. Does it agree with the experimental spectrum?
2. How many vibrational modes does the phenolate anion have?
3. Using the initial and target state ω B97X-D/cc-pVTZ geometry optimizations and frequency calculations, what are the $E_{ee}^{a'}$ and $E_{00}^{a'}$ energies for the photodetachment of the phenolate anion? How do those compare to the 2.25 eV value used in ezFCF?
4. You may expect that the $E_{00}^{a'}$ should be close the 2.25 eV value we used in the XML file. What can explain the difference between the value you computed and the 2.23 eV value?
5. Is the harmonic approximation a better approximation for high or low frequency modes? Explain your answer.
6. Why does the agreement between theory and experiments appear better at lower energies and deviates more at higher energy?
7. Repeat the phenolate calculation with temperature set to 0 instead of 300. What changes? Explain the reason for this change.
8. Looking at the filename.xml.spectrum_parallel file, identify the main transition responsible for the hot band in the experimental spectrum.
9. Looking at the filename.xml.spectrum_parallel file, identify the most intense vibronic transitions in the phenolate detachment spectrum. Those intense transitions, alone or in combination with other bands, give the vibronic progression in the photoelectron spectrum. Identify which excited-state vibrational mode is involved in these intense transitions. Use the frequency calculation and IQmol to visualize this vibrational mode. Include a picture of the vibrational mode in your report.

Bonus questions (advanced mode):

1. Repeat the calculation for phenolate using the vertical gradient approximation (see [manual](#)). How does the spectrum compare with the parallel mode approximation approach?
2. Repeat the Franck-Condon factor calculations using the parallel mode approximation for formaldehyde's excitation to the first excited state. You will need to employ TD-DFT calculations to calculate the energetics and geometry of formaldehyde's excited state. Use the ω B97X-D functional and cc-pVTZ basis set again for all calculations. Make sure you obtain all positive frequencies for the excited state of formaldehyde (you may need to turn off symmetry and manually tweak the geometry of formaldehyde in the excited state to break symmetry). How does the computed spectrum agree with the experimental data shown on the next page? Comment on why there is (or isn't) a good agreement. Would you expect the vertical gradient approximation to work for this system?

(hint: what does the potential energy surface of the excited state look like along the out-of-plane pyramidalization mode?)

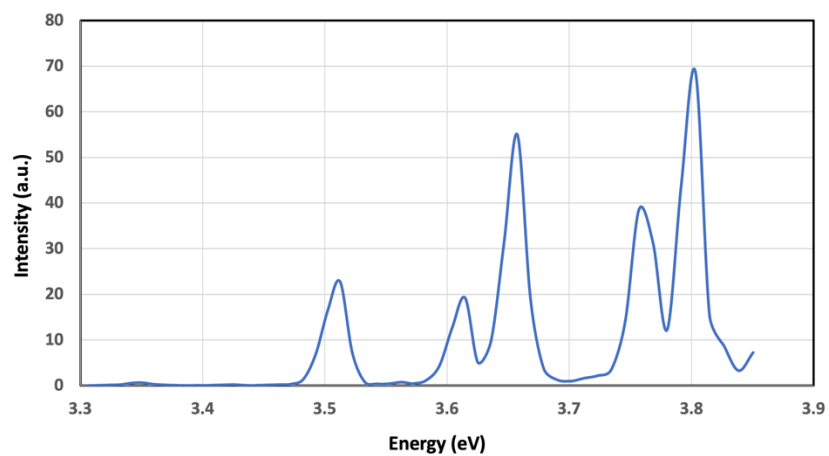


Fig.3. Vibrational progression of S₀-S₁ transition in formaldehyde.