

CHMY 374 (2019): Experiment #2

Electronic Structure and Solvent Effects on Vibronic Spectra of Aromatic Heterocyclic Molecules

Last week we examined the lowest vibronic spectrum of I₂, a diatomic molecule (the simplest kind), which has only one vibrational mode of motion. We only had to consider two molecular orbitals in visualizing that spectrum.

This week we consider a planar, polyatomic molecule, pyrazine (similar to benzene) containing 10 atoms. There are $3N-6$ *normal modes of vibration* for a **non-linear** molecule with N atoms. (This is because there are 3N total degrees of freedom for a system of N atoms, but there are 3 translational degrees of freedom and 3 rotational degrees of freedom. The remaining $3N-6 = 24$ are *the normal modes of vibration*, concerted motions whose frequencies are the eigenvalues of the vibrational Hamiltonian of the molecule viewed as a collection of masses connected by springs. (Linear molecules like I₂ and CO₂ have $3N-5$ vibrational modes because there is “no rotation” around the axis that goes through all the nuclei. (Recall that the nuclei are *10,000 times smaller* than the typical atom “size”. That angular momentum is called nuclear spin). $3N-5 = 1$ if $N = 2$.)

In addition to many more vibrations, there is added complexity in the spectrum due to different classes of molecular orbitals (MOs). Besides the usual π and π^* MOs that have a node in the molecular plane, aromatic nitrogen heterocyclic molecules like pyrazine have as highest (or almost highest) occupied MO (HOMO) so called **non-bonding (n)** MOs of **sigma (σ)** symmetry (no node in plane), mostly involving one or more lone pairs of electrons occupying an **sp²** in-plane atomic orbital (or linear combinations thereof). Such molecules display two kinds of near UV absorption bands called $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. Because the MO from which the electron is promoted in the two cases is so different, these transitions cause quite different changes in electron density. *The electron density changes impact two easily observable properties of the UV spectrum:*

1) *The pattern of bond weakening/strengthening determines the vibrations of the molecule that can be effectively excited along with the electron excitation.* A peak resulting from simultaneous excitation of electrons and vibrations is called a **vibronic peak** (or band). The larger the bond length changes, the higher the vibrational quantum numbers of vibronic excitation that will be observed, and thus a wider overall absorption band associated with excitation to the electronic state. (This is illustrated in the FCFactors.pdf handout from the previous experiment.) Although there are 24 vibrations, only a small number of these can show up in the spectrum. Most of the normal modes distort the symmetry of the molecule and will therefore have vanishing FC factors for transitions from the ground vibrational state and not appear in the spectrum.

2) *How the wavelength of the absorption band will shift in response to a polar solvent.*

Roughly, if the electron density change upon excitation increases the molecular dipole, the excited state will be stabilized more than the ground state, and the transition energy change will be less (shift to longer wavelength, a so-called “red shift”). If the dipole is smaller in the excited electronic state than in the ground state, the polar solvent will stabilize the ground state more, and there will be a “blue shift”.

In this experiment you will:

1. Measure the UV absorption spectrum of pyrazine as a vapor, and in solutions of non-polar and polar solvents.
2. Determine the relative shifts of the bands in response to polar and non-polar solvents, and thereby assign the nature of the electronic transition causing the bands. Here you will draw a rough energy level diagram for the highest occupied n and π MOs, and the π^* LUMO to justify your assignments.
3. From the vibrational structure in the gas phase spectra, you will determine the frequencies of the so called Franck-Condon "active" modes. These modes are the ones that classically would start oscillating in response to changing the force constants of the bonds because of electron density changes associated with the bonding/antibonding nature of the change of the MO by the electron. These also do not change the symmetry of the molecule. With help from the provided literature and orbital handout, you will determine if the active vibrations make sense, given knowledge of the nodes in the MOs, and whether the same vibrations are active in the two transitions.

Handouts:

1. [FCFactors.pdf](#): Handed out last week for Experiment 1. Equally useful here.
2. [Exp2_Moomaw_Skiner_VibronicSpectraAndEnergyLevelsOfPolyatomicMolecules-reduced.pdf](#)

We will need only the pyrazine part of this one. You will not need the full depth of this fine article. In most respects, this article does the lab report for you. One challenge will be to phrase your thoughts in your *own* words. ***You will be graded in part on your clever avoidance of plagiarism!***

Procedure:

1. Run spectra on the Shimadzu spectrophotometer. Prior to scans, click the autozero and then baseline with nothing in either path. (Just do this once) You will need to use a fused silica cell, typically Supracil (not glass, plastic, Pyrex ...) to transmit UV to 200 nm.
2. Place a few (small) crystals of pyrazine (a solid with a high vapor pressure) into a fused silica 1-cm path cuvette and take two spectra (350-210 nm, fast, 1 nm slit) and (350-210 slow speed, 0.1 nm slit, take data points every .05nm) and note the difference. Make sure the highest absorbance is > 0.7 and < 2 . These traces should be exported as ascii (i.e., text) files to the hard disc and file names given to the instructor so the data may be posted on the web or emailed. You should also print the two traces together on the same page.
3. Take spectra (350-210 nm fast, 0.1 nm) of three solutions of pyrazine: in hydrocarbon solvent (e.g., hexane or cyclohexane), in isopropanol, and in water. Quick procedure: Dissolve a very small crystal in ~5 ml of solvent in a small beaker. Transfer about 2 ml to the cuvette and check the absorbance at ~260 nm; adjust by intelligent trial and error to get the highest peak to have absorbance between 1 and 2. Dispose of solutions in an organic waste bottle--**AFTER CHECKING THAT THE LABEL SAYS ORGANIC WASTE!**
4. Load the spectra into your favorite spreadsheet program and convert to a cm^{-1} scale. Use the vapor spectrum to locate the vibronic progressions for the sharp, long wavelength) band.

Lab Report

In general, this report is "open ended" as noted in the Moomaw-Skinner article. However, below are suggestions for direction.

1. Make plots of absorbance vs. cm^{-1} from the data files for vapor and each solvent.
2. From the frequency (shifts relative to the gas phase) in different polarity solvents, **assign the electronic transition type to the electronic bands you observed in the spectra.** (Note: the electronic state energies are not determined solely by MO energy differences because electron repulsion always changes when electron configuration is changed, but we use this approximation.)
3. **Include a rough molecular orbital energy diagram, along with pictures and labels; explain the solvent shifts based on the molecular orbitals involved in the transitions.** Here, note that there is no dipole in any state for pyrazine; think about the difference of H-bond energies between ground and excited states. (i.e., think where would H-bonds form, and how would the H-bond strength change when the electron is excited?)
4. **Label the prominent peaks in your vapor phase plot of the transition according to a reasonable assignment or guess. Briefly explain the reasoning behind the assignment.**

The vibrational structure (the vibronic bands) is due to a mixture of Franck-Condon (FC) active modes, hot bands, Herzberg-Teller (HT) bands, and all possible *combinations* of these. In the I_2 spectrum, you encountered FC bands and hot bands, but no combinations because there was only one vibrational mode. For pyrazine, there are $3N-6 = 24$ modes, where N is the number of atoms.

Combination bands arise because two *different* vibrational modes may be excited together. Their frequencies are close to the *sum* of the individual frequencies, and their intensity approximately proportional to the *product* of the individual FC factors.

FC activity is observed only for modes that match the change in bond lengths upon excitation due to changes in the bond-order of the bonds. The atom motion during an FC-active mode vibration does not change the symmetry of the molecule. If the bond length changes are large, the mode will exhibit large FC activity, meaning there will be a long progression of peaks, all separated by the FC active mode's frequency. If a $1 \leftarrow 0$ FC band is large, then you should expect to see $2 \leftarrow 0$ and $3 \leftarrow 0$, if resolution allows. **Are the most active FC modes the same for both electronic transitions? You can anticipate the way the intensity changes with increasing v' from the FC-Factors handout.**

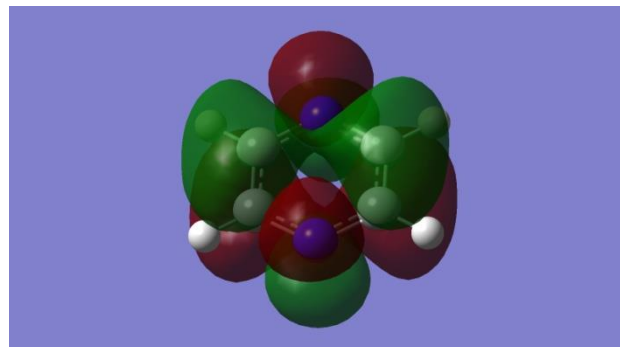
Are the FC active modes consistent with the nature of the MOs involved in the transition?

Herzberg-Teller (HT) active modes are non-symmetric (their motion changes the symmetry of the molecule); they mix orbitals of different symmetry. Only the $1 \leftarrow 0$ transition is observed, even if strong, although combinations of it with other strong lines will be present. There appears to be a fairly strong HT mode evident in the gas phase spectrum of the lowest energy electronic transition. It mixes the n orbital with one of the occupied π MOs by causing hybridization.

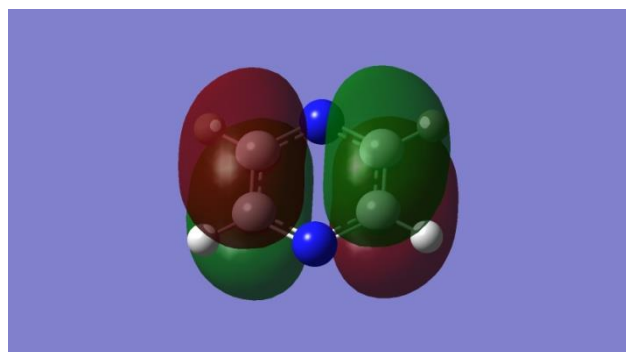
5. Identify any prominent "hot bands". These are bands that involve a transition from an excited vibrational level of the ground state. They will be occupied substantially **only** for those vibrations that

have $h\nu_{\text{vib}}$ on the order of kT or less. Calculate the Boltzmann factors for the hot bands you identify, and comment on whether they are consistent with the strength of these bands.

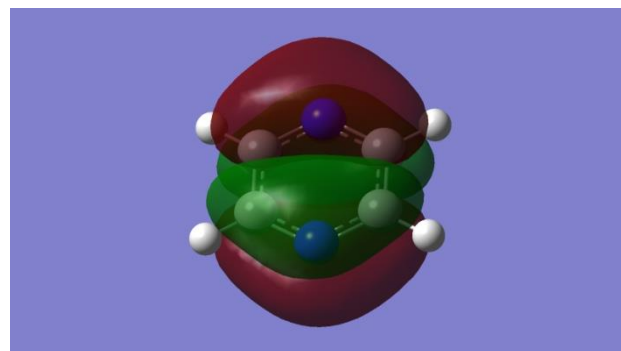
Lumo+1



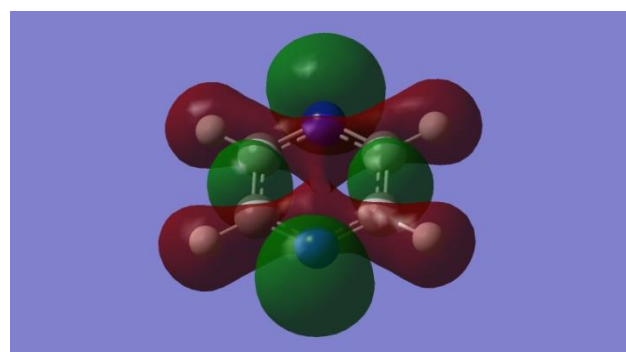
Lumo



Homo



Homo-1



Homo-2