

Vibrational effects on molecular spectra

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1 Objective

Objective for this project was to produce ionization spectrum with vibrations for complex molecule using computational methods and more specifically FHI-AIMS.

2 Methods

There's three main steps in finding the vibrational spectra: finding equilibrium geometry, vibrational frequencies and calculating overlap integrals.

2.1 Equilibrium geometry

To find equilibrium geometry molecules were relaxed with FHI-AIMS using keyword `relax_geometry`. Calculations were also done for molecules in excited electronic state. To accomplish this keyword `force_occupation_projector` was used. Really tight second tier settings were used for atoms and PBE was used as a functional.

2.2 Vibrational frequencies

Vibrational frequencies and corresponding reduced masses were calculated with script provided in FHI-AIMS utilities. Previously found equilibrium geometry was used as a base geometry, but otherwise input files were unchanged.

2.3 Overlap integrals

Calculating the overlap integral follows closely methods used by Gallandi and Körzdörfer [1]. If potential surfaces are approximated as harmonic potentials, integral can be calculated in form

$$\text{FCI}(n_i, n'_i)^2 = e^{-S_i} S_i^{n'_i - n_i} \frac{n_i!}{n'_i!} \left[L_{n_i}^{n'_i - n_i}(S_i) \right]^2$$

$$S_i = \delta_i^2 \mu_i f_i / 2\hbar$$

where μ_i is reduced mass corresponding to frequency f_i . There is two values for each μ_i and f_i , one for the initial state and one for the final state. Values for the final state, which in this case is the excited electronic state, were used. δ_i is obtained by first finding the separation between initial and final geometry, then transforming that separation from cartesian coordinates to vibrational normal mode coordinates, and then taking the component i . n and n' are lists of vibrational quantum numbers for initial and final state. Every mode for which $S_i < S_{min}$ is dropped out as irrelevant. Intensity of delta peaks can then be calculated with equation

$$I(n, n') = \prod_{i=0}^p \overbrace{\text{FCI}(n_i, n'_i)^2}^{\text{Overlap integral}} \underbrace{\exp\left(\frac{-\hbar n_i f_i}{k_B T}\right)}_{\text{Temperature term}}$$

where p is a set of relevant modes. Intensity calculation is then repeated for all combinations of n and n' where $\sum_{i=0}^p n_i < A$ and $\sum_{i=0}^p n'_i < B$. With intensities calculated, peak energies are obtained by adding vibrational energy to the peak without vibrations. Vibrational energy can be calculated with

$$E_{vib} = \sum_{i=0}^p [h f_i (n_i + 1/2)]$$

The peaks without vibrations were calculated using G_0W_0 . In the case of benzene there's also peaks calculated with DCI. All the vibrational calculations and by extension vibrational energies used only PBE.

3 Results

Usually every electronic transition has around 10 – 100 vibrational peaks that have a relative intensity of 0.001 or more, when the largest peak is in the range 0.5 – 1.0. As an example in the Table 1 there's vibrational peaks for one of the benzenes ionizations and in the Figure 1 same peaks plotted.

Intensity	Energy $G_0W_0@PBE$ (eV)	Energy DCI (eV)
0.7107	11.635	12.318
0.2389	11.767	12.450
0.0402	11.899	12.582
0.0045	12.031	12.714
0.0038	12.026	12.709
0.0013	12.158	12.841
0.0012	11.503	12.186
0.0016	11.635	12.318
0.0017	11.767	12.450

Table 1: Relative intensities and positions for the vibrational peaks of the fifth ionization transition of benzene. Zero-zero transition energies calculated with either $G_0W_0@PBE$ or DCI and vibrational energies with PBE.

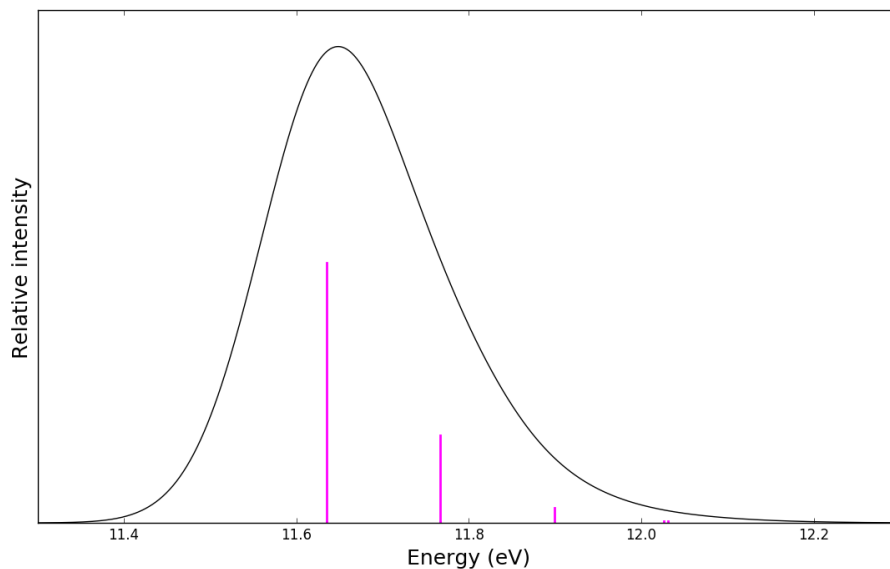


Figure 1: Fifth ionization peak of benzene with gaussian broadening of 0.08 eV. 0-0 peak position with $G_0W_0@PBE$.

In the Figure 2 is the ionization spectra the of benzene with ten first transitions. From top to bottom, experimental, $G_0W_0@PBE$ without vibrations, and $G_0W_0@PBE$ with vibrations. In the Figure 3 is the same spectra, but with DCI values and only five first transitions.

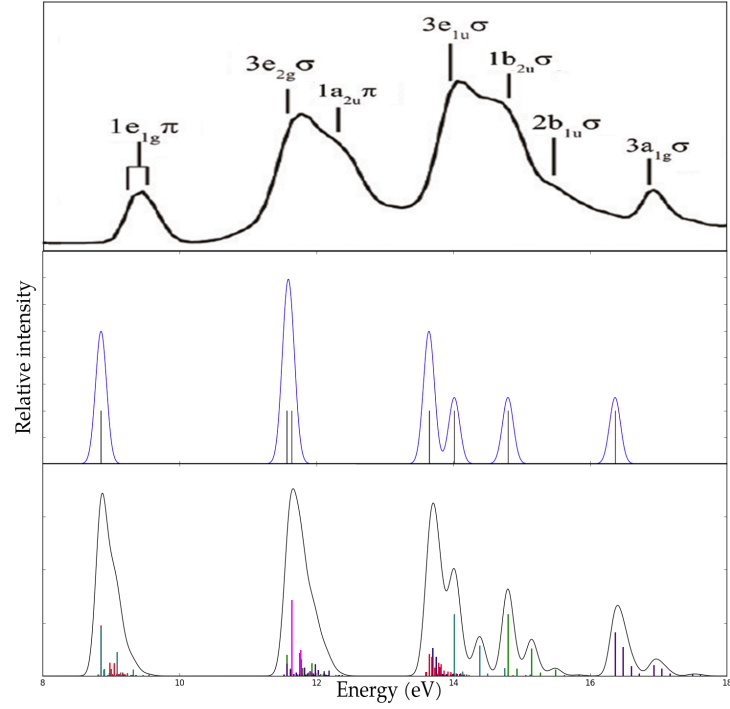


Figure 2: Ionization spectra of benzene with gaussian broadening of 0.08 eV. 0-0 peak position with $G_0W_0@PBE$. Experimental spectrum is taken from [2]

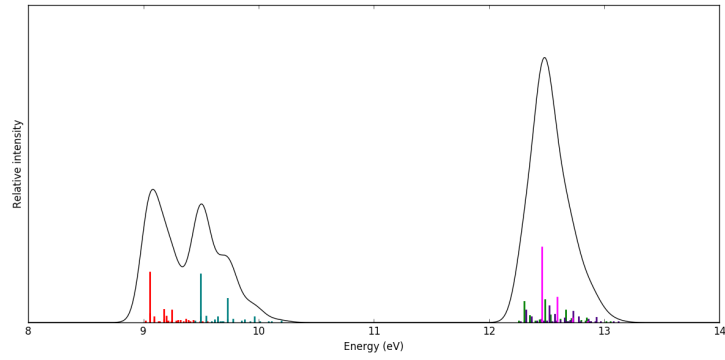


Figure 3: Ionization spectra of benzene with gaussian broadening of 0.08 eV. 0-0 peak position with DCI.

References

- [1] Lukas Gallandi and Thomas Körzdörfer. Long-range corrected dft meets gw: Vibrationally resolved photoelectron spectra from first principles. *Journal of Chemical Theory and Computation*, 11(11):5391–5400, 2015.
- [2] Suet-Yi Liu, Koutayba Alnama, Jun Matsumoto, Kiyoshi Nishizawa, Hiroshi Kohguchi, Yuan-Pern Lee, and Toshinori Suzuki. He i ultraviolet photoelectron spectroscopy of benzene and pyridine in supersonic molecular beams using photoelectron imaging. *The Journal of Physical Chemistry A*, 115(14):2953–2965, 2011.