Polyaromatic Radical Anions: Utilization of a Harmonic Model in Simulating Radical Vibrational Structure and Gas-Phase Acidity Determination

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Abstract

Polyaromatic hydrocarbons (PAHs) play a central role in the field of Biochemistry, combustion chemistry, and Astrochemistry. In this work, we show how a harmonic model can be utilized in the Franck–Condon (FC) analysis of the vibrational structure of negative radical anions of PAHs such as naphthalene and anthracene, following the ultra violet (UV) photodetachment of the initially prepared deprotonated anionic species. We utilize the two PAHs as a prototype for the vibronic and FC analysis of the ground-state and lowest lying excited states of similar gas-phase isomers that have rigid, ring structure. The spectra are interpreted based on the comparison with ab initio quantum-mechanical as well as the Franck-Condon (FC) simulations. The geometric and frequency of the optimized of the anion and the neutral radicals are calculated using the GAUSSIAN 09 software package. The FC factors of the anion PES are simulated using the PESCAL program. PESCAL obtains the FC factors using molecular geometry, normal mode vectors, and normal mode harmonic vibrational frequencies of the anion and neutral states. These FC simulations are based on a harmonic oscillator approximation model that utilizes the Duschinsky rotation between the normal mode vectors of the anion and neutral radical species. The calculated adiabatic electron affinity is utilized in the negative ion thermochemical cycle to determine gas-phase acidity values of neutral PAH molecules.

Introduction

Deprotonated Aromatic Hydrocarbons

Brief Overview and Applications

- **Combustion:**
  - Their production is due to inefficient use of fuels
  - Main focus is to understand their properties and their formation pathways
- **Interstellar medium: neutrals, cations and anions have been detected**
  - Carriers of various unidentified IR bands
  - may contribute to mysterious diffuse interstellar bands in the visible

Mechanisms of PAH in interstellar medium mainly speculative

Negative Ion Photoelectron Spectroscopy Technique: A Brief Overview

What information can we obtain from this Technique?

- Energy required to remove electron from radical anion to form a neutral radical to determine electron affinity values (EA)
- Frequencies of vibration in neutral radical upon electron photodetachment
- Geometry change upon photodetachment
- Bond strengths and Gas-Phase acidity (e.g. **O–H** bonds) values using a thermochemical cycle
- Electronic state term energies (Singlet-Triplet splitting) for open-shell reactive intermediates-such as biradicals

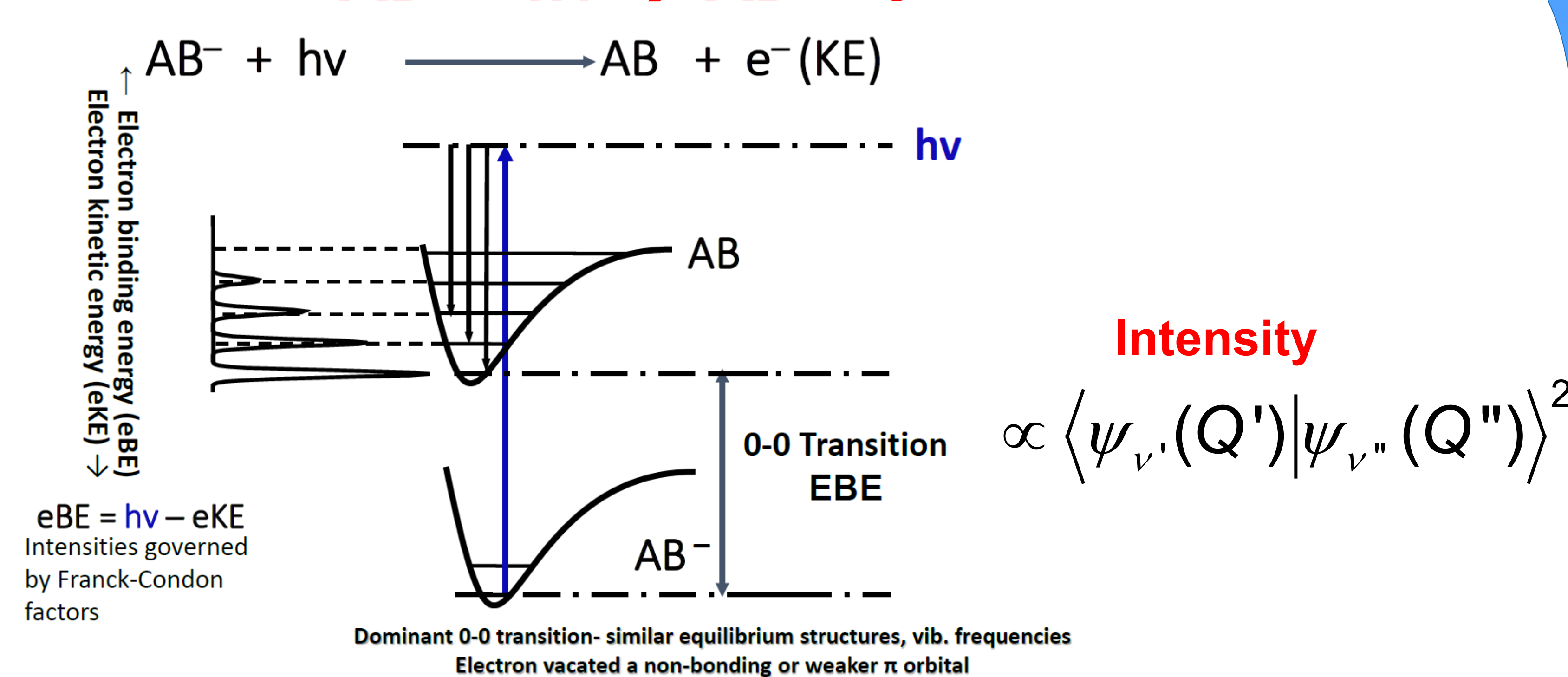## Negative Ion Photoelectron: Spectroscopy

$$AB^- + h\nu \rightarrow AB + e^-$$

Figure 1: Anion photoelectron spectroscopy vibrational spectra

$$eBE = h\nu - eKE$$
$$EA = h\nu - eKE(0-0)$$

Since energy must be conserved in this process, the kinetic energy of the measured photoelectron is equal to the photon energy minus the transition energy between the initial state of the anion and the final state of the neutral molecule.

- Only totally symmetric vibrations are allowed.
- Intensities governed by Franck-Condon factors.

Quantum Mechanical Methods

Franck-Condon Simulations: An overview

- Gaussian 09 at various levels of theory is used to calculate optimized equilibrium geometries and vibrational frequencies of the anion and neutral.[1-4]
- Molecular orbital or density functional theory calculations of geometries, frequencies, force constants using DFT, B3LYP with 6-31+G** basis set.
- Gaussian output is input into PESCAL simulation program to calculates Franck-Condon Factors (FCF) using the Sharp-Rosenstock-Chen method.
  - The method treats vibrational modes as independent harmonic oscillators including full Duschinsky rotation. The non-harmonic oscillators can also be treated using the parallel mode approximation.
- The FC simulation and FCF are essential in assigning the origin peak and vibrational progressions for the radical.

Results and Discussion:

Example 1: O$_2^-$ Photoelectron Spectroscopy:

O$_2^-$ and O$_2$ Electronic Potentials
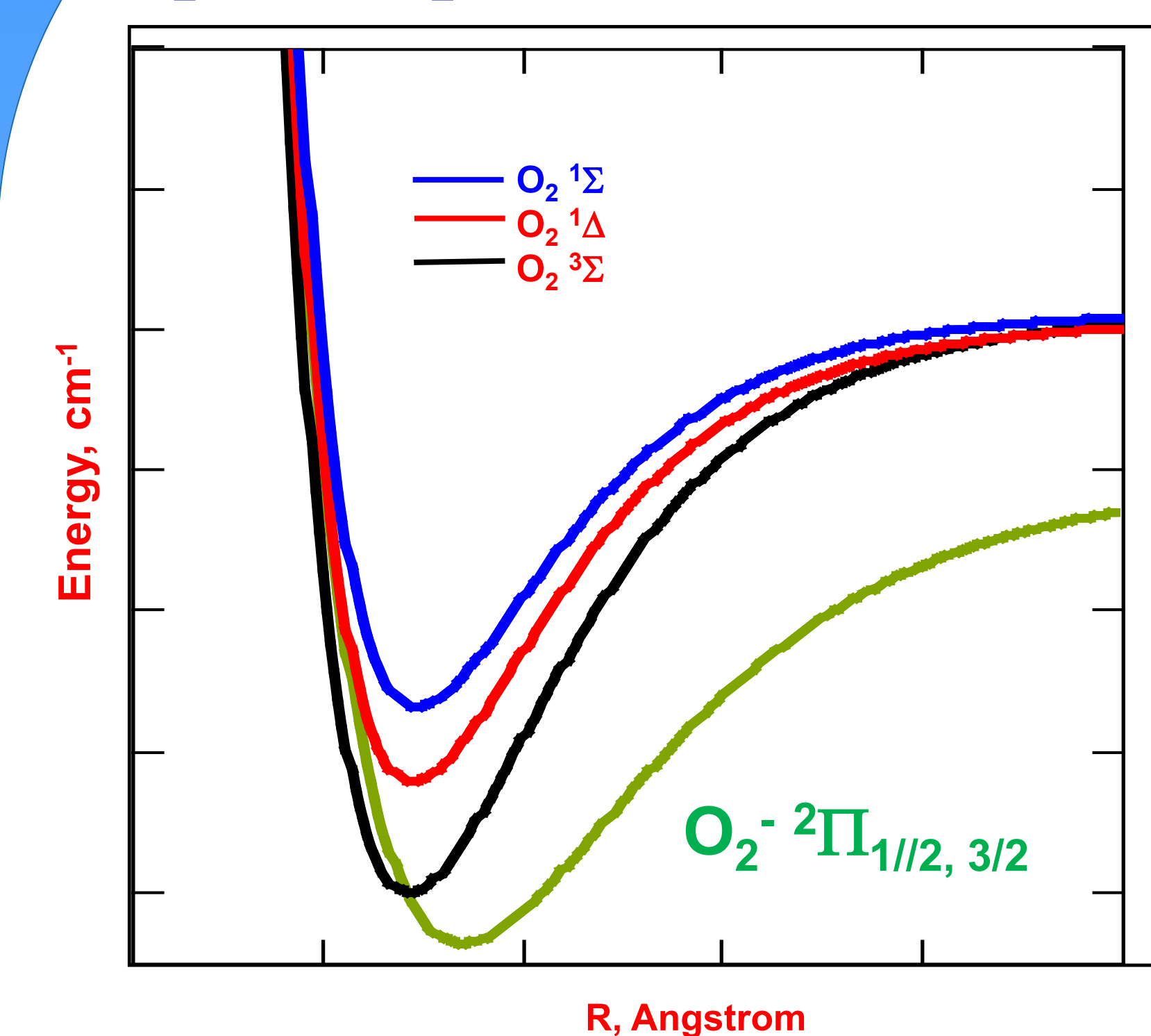
Figure 2: Electronic potentials of **O$_2^-$ and O$_2$**

O$_2^-$ Photoelectron Spectrum

How well can we fit the observed photoelectron spectrum by optimizing O$_2^-$ properties: r$_e$, and EA?

Figure 3: Negative ion photoelectronic spectrum of O$_2$ anion

O$_2^-$ Photoelectron Spectrum Simulation

Data Consistent with the FC fit

Quantitative fit that help in determining conformers
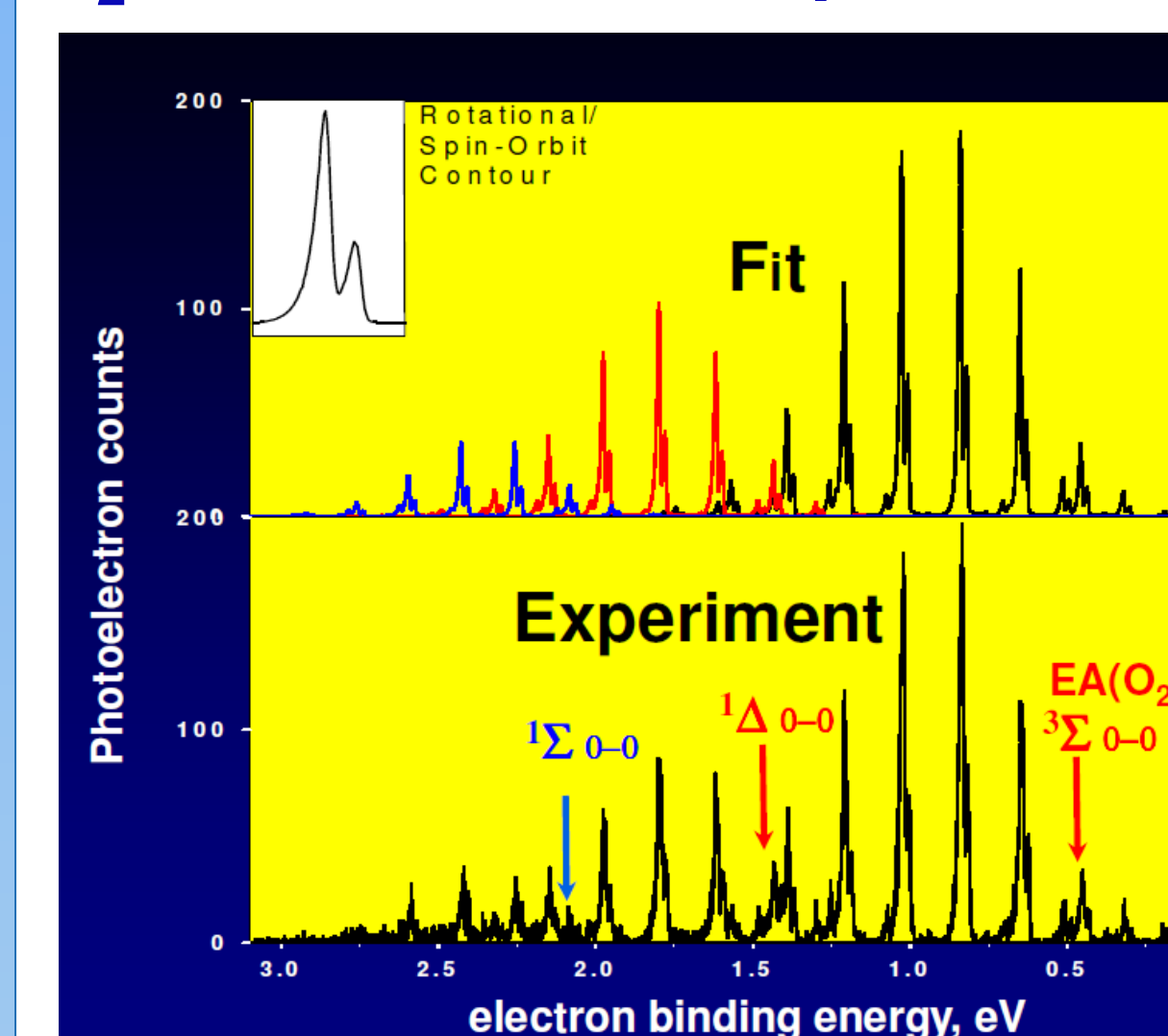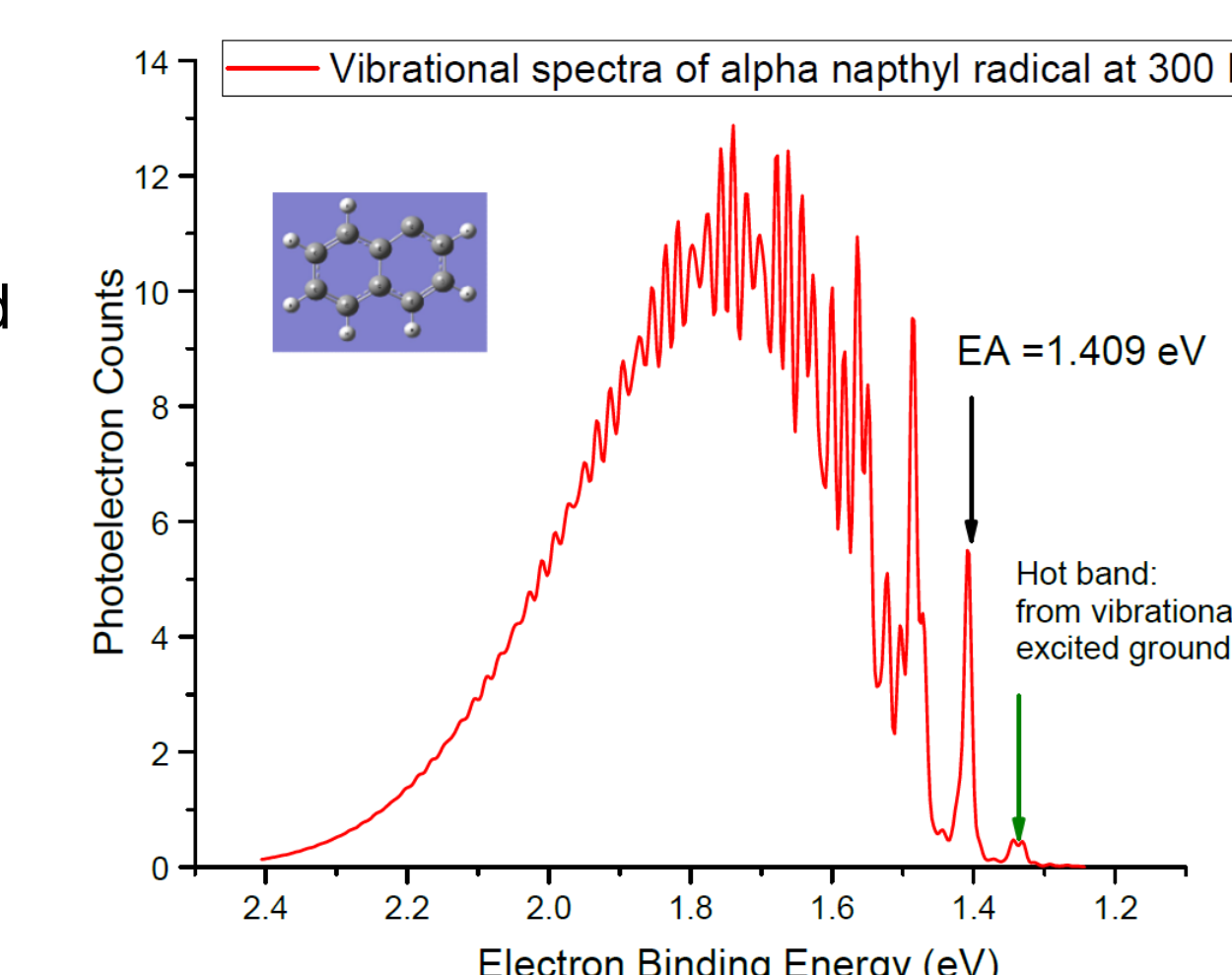
Figure 4: Negative ion photoelectronic spectrum of O$_2$ anion Franck Condon Fit compared with the experimental data

Figure 7: Simulated naphthalene anion photoelectron spectrum (alpha isomer) at 300 K

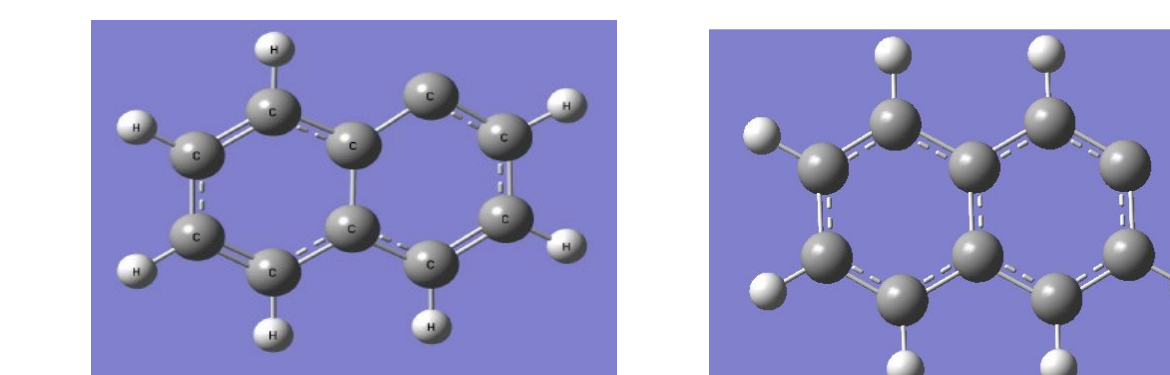### Example 2: Naphthalene Photoelectron Spectroscopy

Figure 5: Alpha and Beta Napthyl Radicals. The two isomers will have different vibrational structures. Only the alpha is considered in this poster.
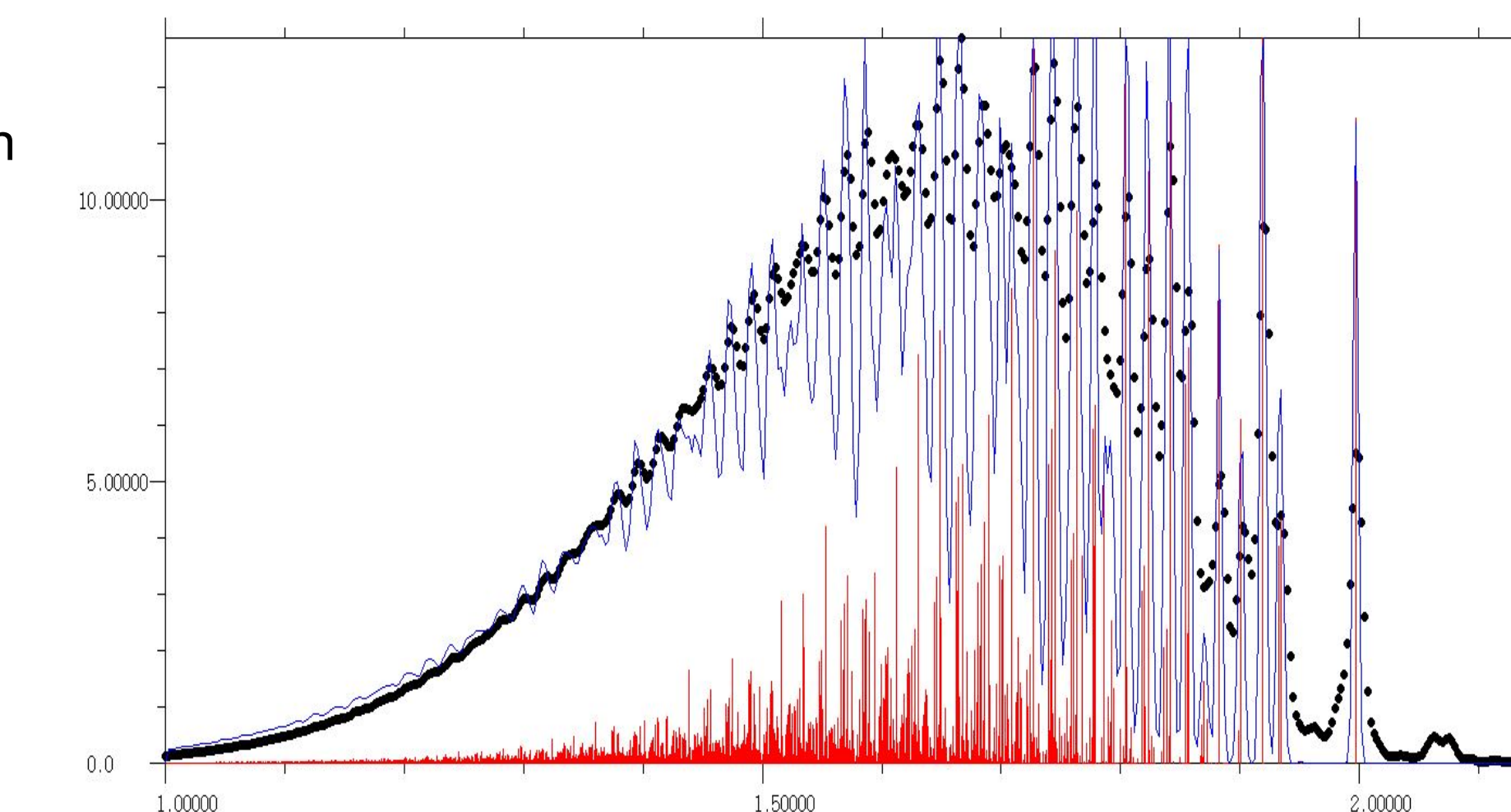

Figure 6: Snapshot of naphthalene anion photoelectron spectrum (alpha isomer) from Pescal program. (Dotted line is an experimental spectra obtained from Reference 3)

- At 300 K, there is contribution from excitation resulting from vibrational excited ground state of the anion, resulting in hot bands
- The hot band vibrational progression congests the vibrational spectra of the radical
- Spectra shows an extensive FC activity, which is a result of large change in geometry upon photodetachment.
- The electron is detached from an s-p hybrid orbital that is localized on the deprotonated site of the anion

Conclusions and Future Directions

Following the preliminary negative ion photoelectron spectroscopy studies presented in this poster, related collision induced dissociation studies will be carried out and the deprotonated anions of interest investigated via FC analysis. In summary:

- Benjamin Headrick will carry out negative photoelectron studies of Naphthalene anions and the associated derivatives. This will aid in revealing the radical vibrational structure and obtaining gas phase acidity values through the negative ion thermochemical cycle
- Taylor Dimino will pursue similar research albeit with a focus on biomolecular applications, starting with histidine anion spectroscopy as a prototype
- Rebecca Firth will apply the techniques outlined in this poster to study PAHs that are of astrochemistry significance such as mono and dicyanobenzene.

Selected References

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2) Branton, G. R.; Frost, D. C.; Makita, T.; McDowell, C. A.; Stenhouse, I. A. Photoelectron Spectra of Some Polyatomic Molecules. Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences 1970, 268, 77-85.
3) Ervin, K. M.; Ramond, T. M.; Davico, G. E.; Schwartz, R. L.; Casey, S. M.; Lineberger, W. C. Naphthyl Radical: Negative Ion Photoelectron Spectroscopy, Franck−Condon Simulation, and Thermochemistry. The Journal of Physical Chemistry A 2001, 105, 10822-10831.
4) Weichman, M. L.; Kim, J. B.; DeVine, J. A.; Levine, D. S.; Neumark, D. M. Vibrational and Electronic Structure of the α- and β-Naphthyl Radicals via Slow Photoelectron Velocity-Map Imaging. Journal of the American Chemical Society 2015, 137, 1420-1423.