Anion Photoelectron Spectroscopy and Thermochemistry of Deprotonated Benzonitrile Isomers

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Introduction

Experimental and theoretical studies involving both linear chain and polycyclic aromatic hydrocarbon (PAH) anions in the interstellar medium (ISM) have continued to be a subject of attention by many computational and experimental researchers due to their closed-shell structure that often result in the formation of anionic resonant structures and reactive neutral radicals upon ultraviolet (UV) photodetachment.[1-5] The recent detection of benzonitrile as the first aromatic molecule in the cold-core Taurus Molecular Cloud 1 (TMC-1) has particularly elicited several theoretical investigations aimed at elucidating not only the nature and structure of the dipole-bound anionic states, but also the accurate determination of the adiabatic electron affinity (EA) along with other thermochemical values.[6-8] The present work builds upon previous studies on the bare benzonitrile anion[6-9] to provide further insights on the nature of the vibrational structure of the neutral radical that arise from the more stable deprotonated ortho, meta, and para benzonitrile isomer.

Research Goals

> Utilize density functional theory (DFT) quantum mechanical techniques to calculate the electron affinities (EAs) and gas-phase acidities (GPAs) of the neutral deprotonated radical and the parent molecule, respectively.

> Use the negative ion thermochemical cycle to estimate the C-H bond dissociation energies for the parent o-, m-, and p-$C_6H_5(CN)$ isomers.

> Utilize the Pescal program to calculate the Franck-Condon (FC) factors of o-, m-, and p-$C_6H_4(CN)$ to determine the active vibrational modes.

Methods

> DFT calculations using the Gaussian 09 program package at the aug-cc-pVQZ level of theory were used to calculate the EAs of the deprotonated neutral radical and GPAs of the parent molecule.

> The negative ion thermochemical cycle (Figure 3) was then utilized to obtain the C-H bond dissociation energies.

> PESCAL program was used to obtain Franck-Condon profiles of deprotonated benzonitrile anionic isomers.[13]

> PESCAL calculated the Franck-Condon-Factors (FCFs) by utilizing a harmonic oscillator approximation including Duschinsky rotation with the Sharp-Rosenstock-Chem method.[14]

Negative Ion Photoelectron Spectroscopy

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

Figure 1: Potential energy profile in negative ion photoelectron spectroscopy
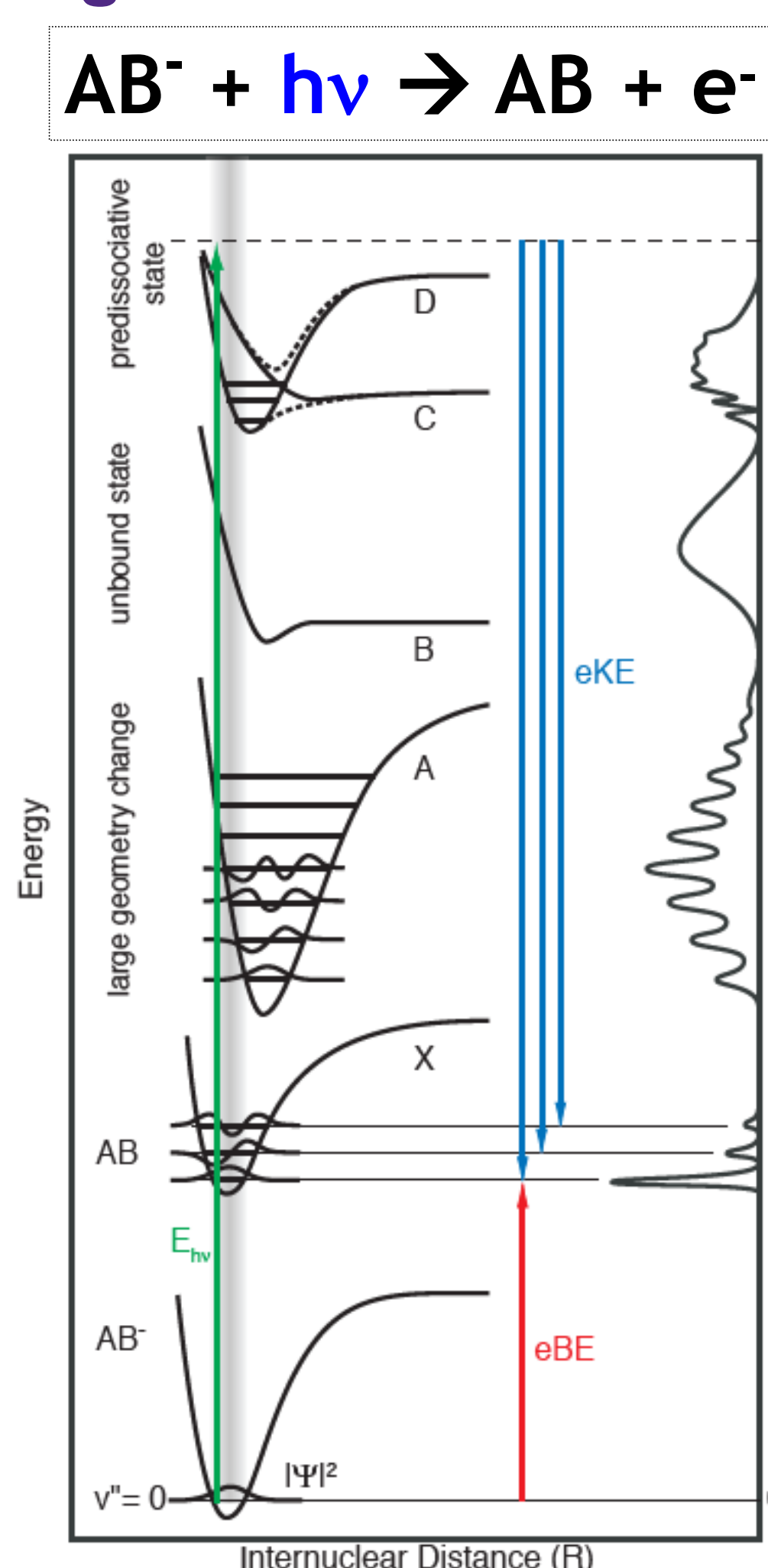
Depending on the photon energy, one can access higher electronic states

$$eBE = h\nu - eKE$$

A **large** geometry change leads to an extensive vibrational progression

A **small** geometry change with a clear origin

What the technique can measure:

> Electron Affinity (EA)
> Vibrational Frequencies, ω_e
> **Neutral Excited States:**
> All above properties plus term energy, T_0
> Geometry Change, **ΔR,** between the anion and the radical

Results and Discussion

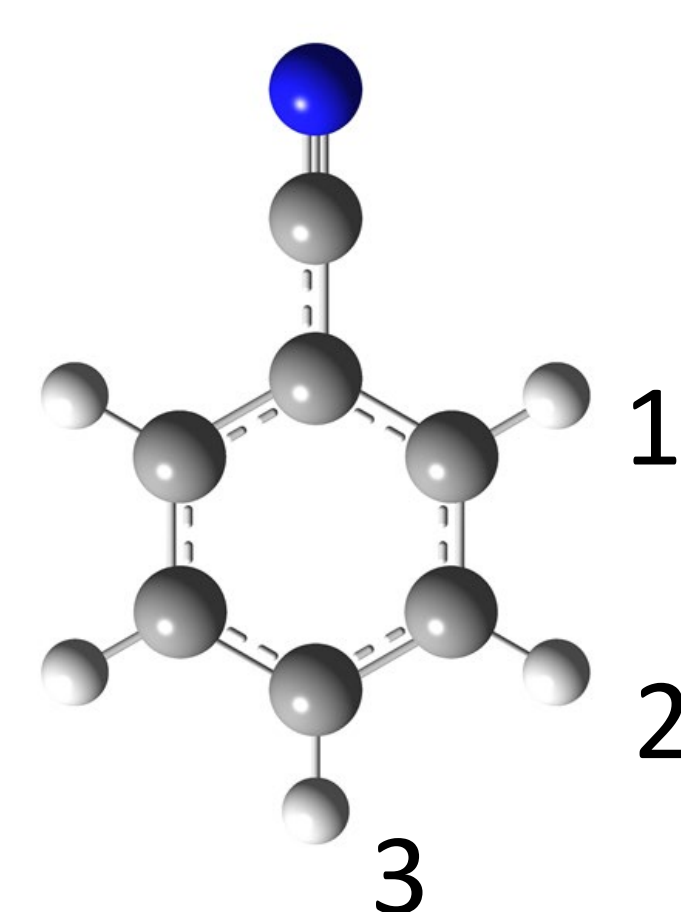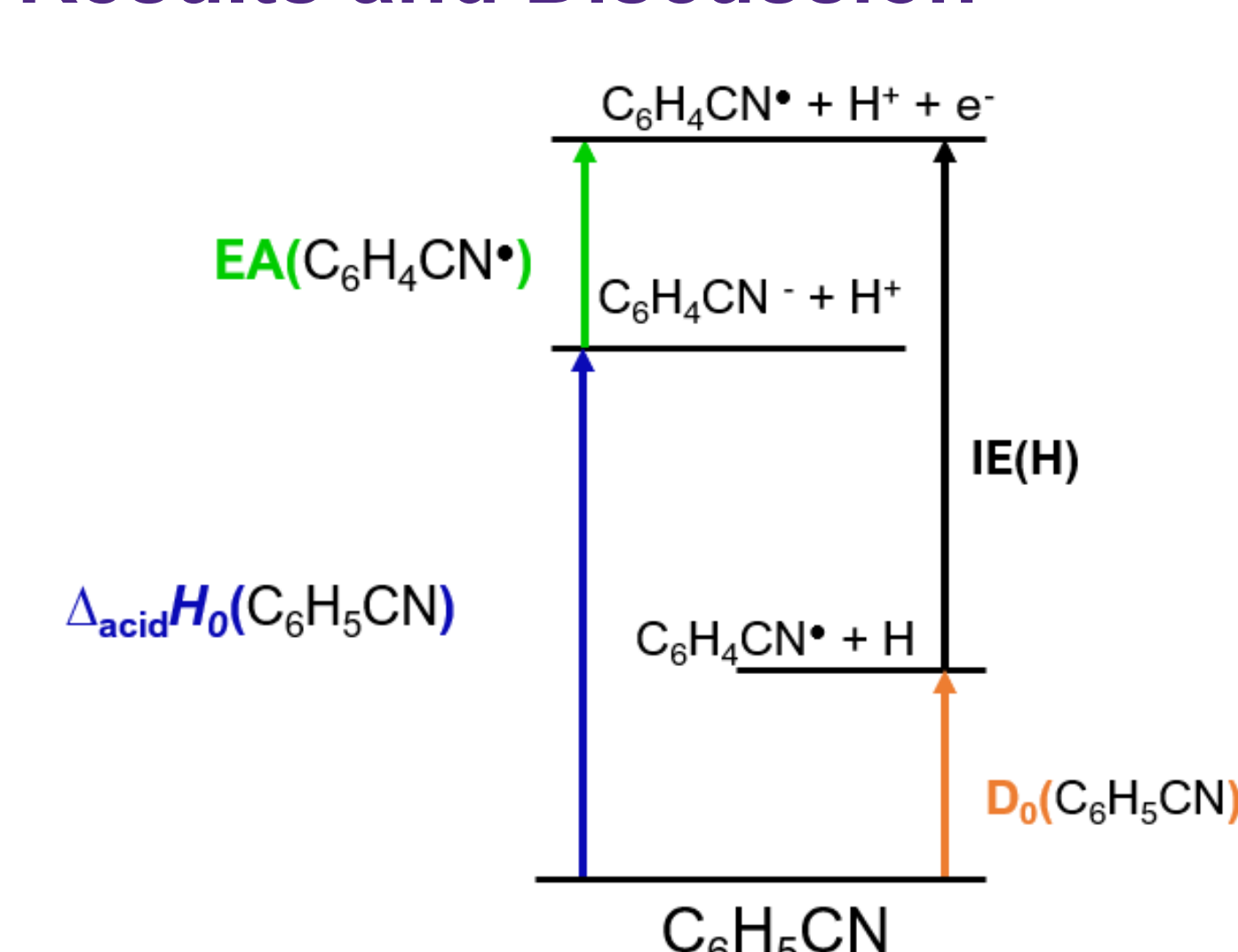**Figure 2**: The optimized structures of BN with labeled deprotonation sites

$$D_0(C_6H_5CN) = \Delta_{acid}H°_{298K}(C_6H_5CN) + EA(C_6H_4CN\bullet) - IE(H)$$

Figure 3: Negative Ion Thermochemical Cycle for BN used to estimate bond dissociation energies

Table 1: Summary of DFT calculated electron affinities, GPAs ($\Delta_{acid}H_{298}$ **(kJmol^{-1})**) and dissociation energies (D_{298}(H–C_6H_4CN–)) for the BN isomers at 298K. For comparison, benzene values are given below.

Isomer	Calculated GPA (kJ/mol)		EA (eV)		Dissociation Energy (kJ/mol)	
	6-311	aug-cc-pVQZ	6-311	aug-cc-pVQZ	6-311	aug-cc-pVQZ
1	1595.1	1599.9	1.939	1.901	470.1	471.3
2	1603.0	1607.5	1.812	1.778	465.8	467.0
3	1601.4	1605.8	1.821	1.788	465.0	466.2

For Comparison: In benzene

> GPA ($\Delta_{acid}H_{298}$) =1678.7 ± 2.1 kJ mol^{-1} (Davico et al., **J. Am. Chem. Soc.**, 1995, 117, 9, 2590)

> $D_{298}(C_6H_5–H) = 472.1 ± 2.5$ kJ mol^{-1} (Alecu et al; **J. Phys. Chem. A**, 2007, 111, 19, 3970)

Franck-Condon Analysis

Figure 4 shows the calculated negative ion photoelectron spectra of the ortho-deprotonated isomer at both 0 K and 300 K.
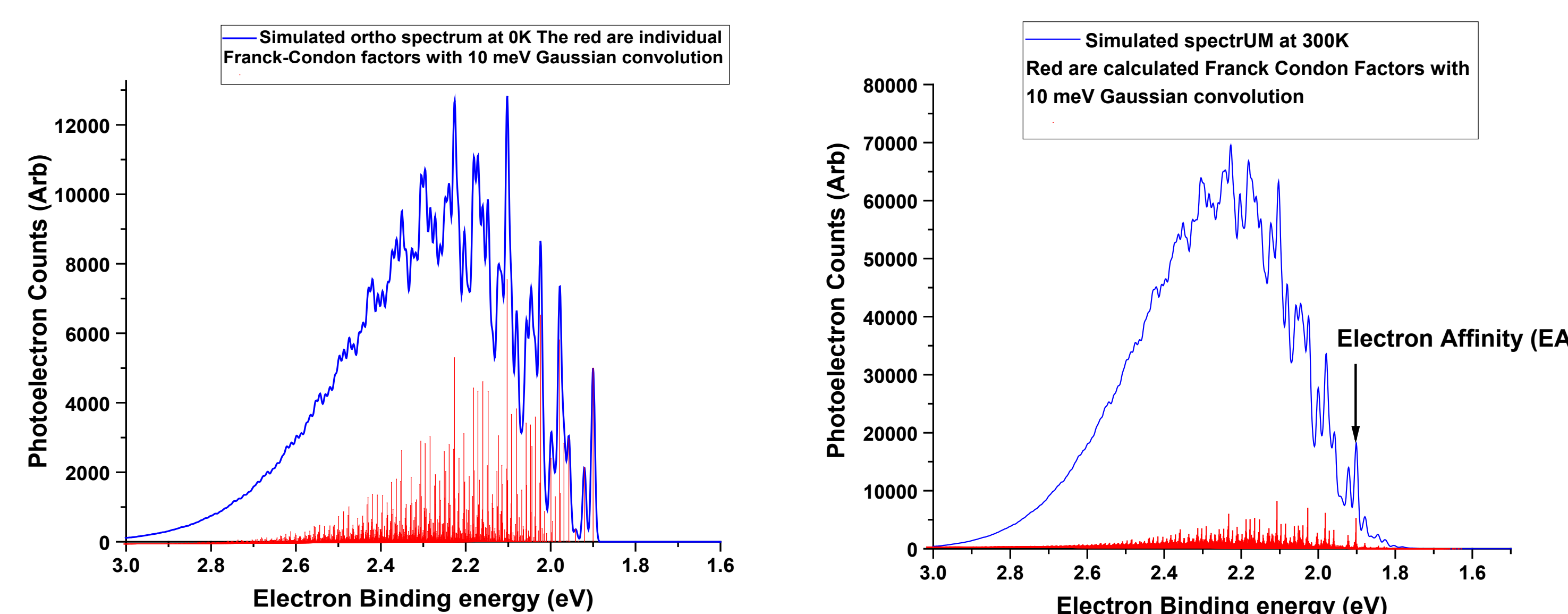

Figure 4: Franck-Condon simulations of BN deprotonated at location 1 at 0K and 300K

> Extensive vibrational progressions at both temperatures are due to the large geometry change that takes place upon photodetachment.

> As expected, the 0 K spectrum shows less congestion and more defined peaks

> Vibrational progression resulting from exciting ring deformation vibrational modes are identified as follows:
165 cm^{-1} low freq (butterfly), ~ 456 cm^{-1} ring deformation, ~ 633 cm^{-1} ring deformation, ~ 1000 cm^{-1} ring deformation, ~ 1600 cm^{-1} combination bands (specifics are unclear)
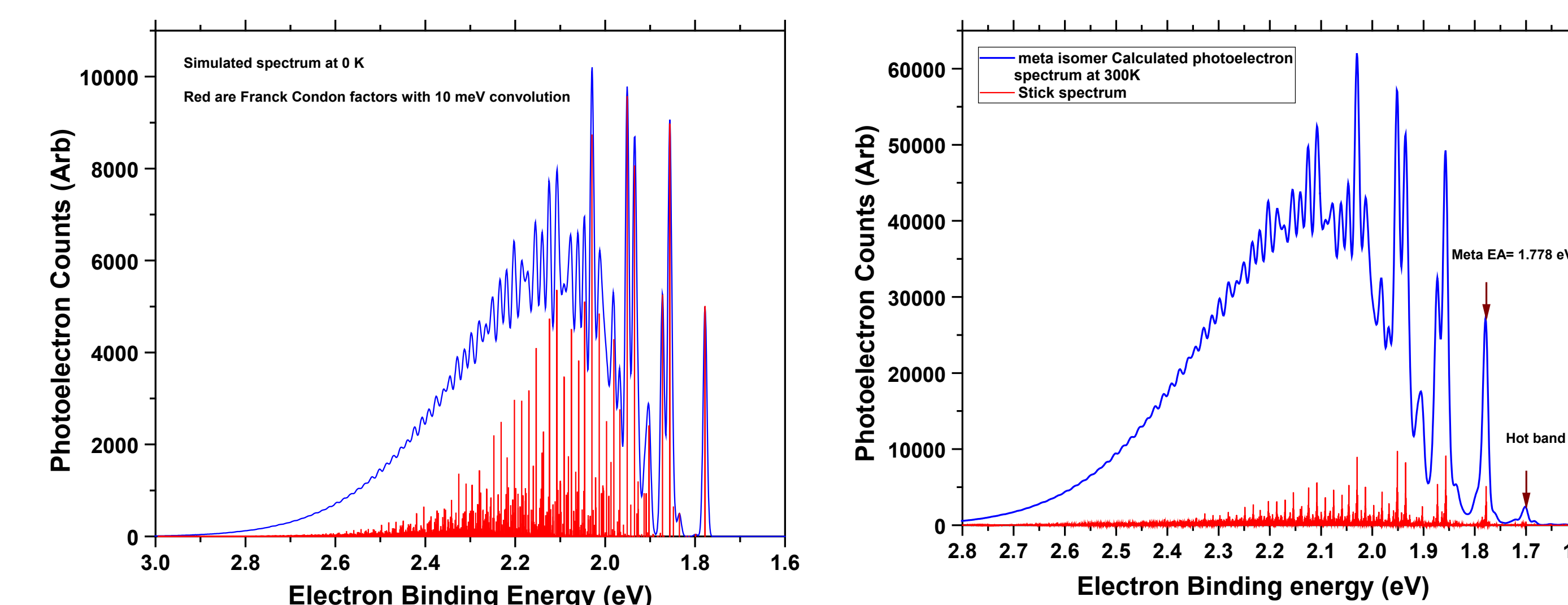

Figure 5: Franck-Condon simulations of BN deprotonated at location 2 at 0K and 300K

> The simulated spectra of m-$C_6H_4(CN)$ can be seen in Figure 5, but an in-depth vibrational analysis has not yet been completed.

> Work is ongoing on the para isomer.

Future Directions

> Complete the Franck-Condon simulations for p-$C_6H_4(CN)$ and complete a vibrational analysis at 0K and 300K.

> Repeat this process for dicyanobenzene isomers.

> Negative ion mass spectrometry experimental studies will be performed to confirm the formation of deprotonated anionic isomers in the gas-phase under different collision energies.

> Investigate the solution effects on the formation of benzonitrile radical anions on the basis of cyclic voltammetry analysis.[15]

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