

**IONIZATION PROBES OF MOLECULAR STRUCTURE
AND CHEMISTRY**

Final Progress Report
for the Period 2004–2008

Philip M. Johnson

Department of Chemistry
Stony Brook University
Stony Brook, NY 11794

January 2009

Prepared for

THE U.S. DEPARTMENT OF ENERGY
AGREEMENT NO. DE-FG02-86ER13590

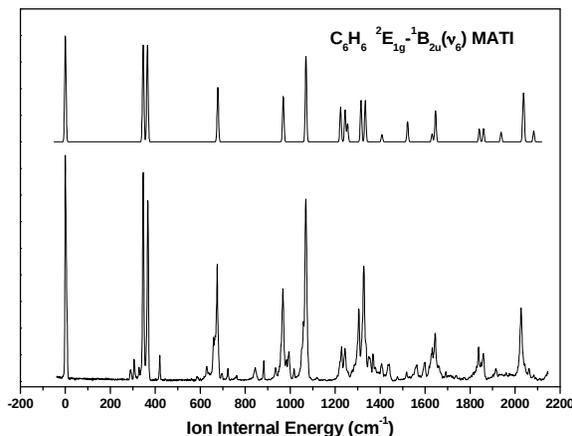
Progress on the Department of Energy project has proceeded along six lines during this grant period: 1)

The Jahn-Teller effect in benzene cation: A benchmark study.

Along with H_3 , Na_3 , and ammonia, benzene cation has been a prototypical system in the study of the Jahn-Teller effect, perhaps the most dramatic type of vibronic coupling. In the development of the modern theory, it has always served as one of the primary examples, having a higher symmetry than the smaller molecules and a richer variety of vibrations to consider. In spite of the interest, it is only recently that detailed experimental vibrational information has begun to emerge, when laser techniques involving Rydberg states provided the means to record cation spectra with adequate resolution to be able to separate out all of the vibrational levels. While these tools have been available for some time, there had been no spectra available that had the combination of resolution, energy breadth, and variety of excitation schemes that would enable definitive analysis of the vibronic structures to be carried out.

There are three low-lying states of benzene cation that are subject to Jahn-Teller interactions, X^1E_{1g} , B^2E_{2g} , and D^2E_{1u} . With the exception of a PIRI study we performed a few years ago on the B^2E_{2g} state, all previous work has focused on the lower energy part of the ground state spectrum, using only pump-probe spectroscopy through the S_1 state. In a series of papers, we have used *ab initio* and classical Jahn-Teller calculations to analyze the Jahn-Teller vibronic coupling in benzene cation as a general example of molecules with multiple active modes. These calculations were applied to further the understanding of our previous PIRI spectra of the B^2E_{2g} state. The present work brings the series to a conclusion by the analysis of new, wider ranging spectra of the cation ground state.

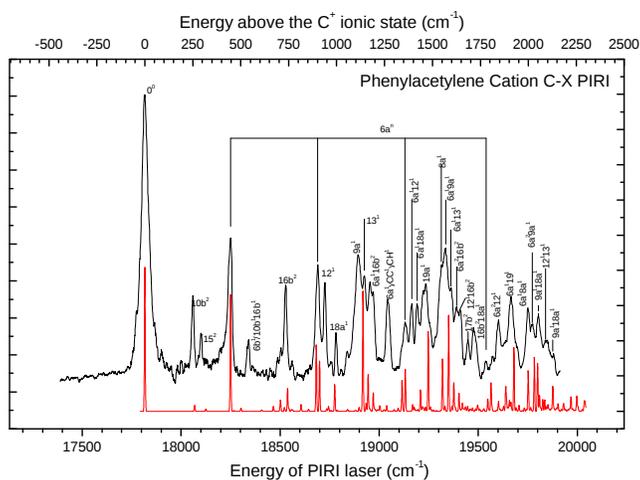
As shown by our theoretical analysis, and by previous studies, one must consider three linearly active vibrational modes in any treatment of the cation ground state. Previous vibrationally resolved spectra had been recorded only using pump-probe techniques through the S_1 state. Over the limited energy range that had been examined, Jahn-Teller calculations could fit the line positions exactly, considering only the linearly active modes ν_6 , ν_8 , and ν_9 . In order to get additional vibrational information that might indicate directions for the improvement of the model, we recorded new $C_6H_6^+$ and $C_6D_6^+$ MATI spectra from different neutral (S_0 , S_1 , and T_1) states over wide energy ranges and analyzed them using multimode Jahn-Teller calculations. Of particular importance in the analysis was the calculation of Franck-Condon factors from the calculated wavefunctions, including effects of geometry change. This enabled a more solid identification of the spectral lines.



The figure above shows one of the new MATI spectra, a pump-probe experiment through the S_1 state. Care was taken to correct the intensities so they could be compared to a spectral simulation (upper trace) derived from the vibrational wavefunctions arising out of the Jahn-Teller calculations (only the three linearly Jahn-Teller active e_{2g} modes and the lower frequency a_{1g} mode are included in the simulation). It is seen that there is a remarkable agreement between the experiment and a simulation that contained no empirical intensity input, indicating that the classical Jahn-Teller model is working well for the linear interactions.

By virtue of the much larger data set of experimental information, some small but significant discrepancies in the model began to emerge. At higher energies in the spectrum, it would appear to be beneficial to include Fermi interactions between the Jahn-Teller manifolds built upon various totally symmetric vibrational states. The Fermi interactions couple these otherwise isolated manifolds and alter the appearance of the higher energy parts of the spectra. Also, if one is to attain a complete determination of the molecular potential energy surface, all of the quadratically active normal modes should be considered simultaneously. To do this is beyond present technical capabilities, but may become possible as computing technology and quantum chemistry methodology advance.

The PIRI spectra of phenylacetylene and benzonitrile: A new approach to the calculation of vibronic coupling



The revolution caused by the use of electronic structure programs by experimentalists has been impressive. The capability of non-specialists to be able to calculate fairly accurate vibrational frequencies has greatly reduced the guesswork involved in assigning vibrational structure. More recently, good programs have become available that calculate Franck-Condon factors from the vibrational vectors produced by the electronic structure programs.

These have enabled even better results, because now the intensities of the experimental lines provide verifiable information, at least for allowed transitions. We have analyzed the vibrational structure of the allowed $\tilde{C}-\tilde{X}$ transition of phenylacetylene cation recorded by PIRI spectroscopy (above), and find a remarkable agreement between the spectrum and the calculated vibrational positions and intensities.

The PIRI spectrum of the isoelectronic molecule benzonitrile is a greater challenge, however. It turns out that the $\tilde{B}-\tilde{X}$ transition of the benzonitrile cation is forbidden electronically. This is a C_{2v} molecule, and there are 21 different vibrations that can induce transition intensity. We recorded the vibrational structure of the PIRI spectrum of this molecule from three different lower vibrational levels of differing symmetry, and wished to be able to assign the vibrational structure we observe.

However, for forbidden transitions the vibrational frequencies are less reliable, and intensities are greatly affected by the vibronic coupling. For a molecule with as many vibrational modes as benzonitrile, a correct vibrational assignment would be pure luck without having guidance from good theoretical intensity information. We have therefore developed a relatively simple method of calculating vibronic intensities using information from readily available electronic structure and Franck-Condon programs.

Vibronic coupling is an old topic, and over the years many theoretical groups have developed the capability to calculate the effects of vibrational-electronic coupling, even

including sophisticated treatments of conical intersections and Jahn-Teller coupling. In particular there have been many attempts to analyze the vibrational spectral structure of a forbidden electronic transition. However, these have mostly been applied to systems where there are only a few possible inducing modes in the spectrum, such as the $S_1 \leftarrow S_0$ transition of benzene.

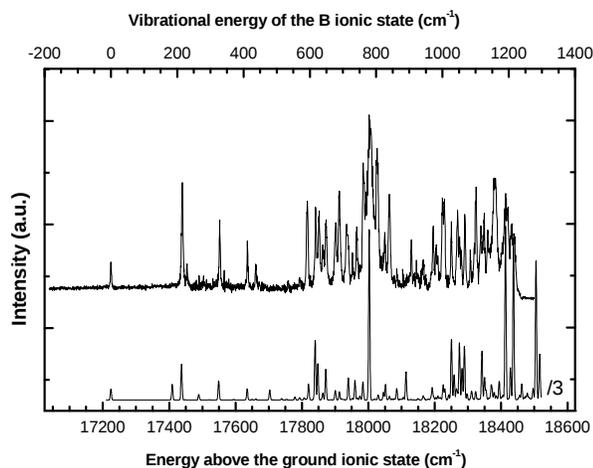
In most cases the intensity in forbidden transitions comes from simple lowering of the symmetry of the molecule by the various non-symmetric vibrational mode. Non-adiabatic coupling by the kinetic energy terms in the Hamiltonian is mostly important in states with conical intersections or degeneracies. Therefore, for non-pathological cases, vibronic intensities should be able to be calculated from simple consideration of the transition moment over the available molecular geometry space.

As is usual in this kind of a problem, one can expand the electronic transition moment in a Taylor series in the normal coordinate space:

$$M(Q) = M(0) + \sum_i \left[\frac{\partial M}{\partial Q_i} \right]_0 Q_i + \frac{1}{2} \sum_{i,j} \left[\frac{\partial^2 M}{\partial Q_i \partial Q_j} \right]_0 Q_i Q_j + \frac{1}{6} \sum_{i,j,k} \left[\frac{\partial^3 M}{\partial Q_i \partial Q_j \partial Q_k} \right]_0 Q_i Q_j Q_k + \dots$$

Almost universally, this series has been terminated after the linear term in previous treatments of vibronic coupling. We have shown, however, that a premature termination precludes the proper treatment of combination bands that contain more than one non-symmetric mode. In order to include the highest order non-zero term for every combination band, one needs to include derivatives up to an order that varies with the point group of the molecule. For example, for C_{2v} , D_2 , and D_{2d} one can safely terminate after the quadratic sum, but for D_{2h} one should include up to the third order cross terms, and D_{6h} needs fourth derivatives if Franck-Condon factors for such complicated combinations are substantial. Somewhat surprisingly, the more symmetric a molecule, the more likely higher order terms are going to be necessary.

For a forbidden transition, the first term on the right side of the above equation is zero, and the intensity of any vibronic transition is simply proportional to the square of the integral of $M(Q)$ over the upper and lower vibrational wave functions, for example: $\langle 000000 | M(Q) | 000100 \rangle$. For each particular set of vibrational states, only one term in the above expansion is generally important. If only one inducing mode is present, the linear term is used, if two are present the quadratic term, etc. The moment derivatives can be pulled out of the integral, so we are left with integrals of the type $\langle 000000 | Q_4 | 000100 \rangle$, where the bra and ket are products of harmonic oscillator wave functions with the quantum numbers listed. Using recurrence properties of harmonic oscillator functions, this latter integral reduces to the particularly simple sum of two Franck-Condon factors,



$\langle 000000 | 000000 \rangle + \frac{1}{2} \langle 000000 | 0000200 \rangle$. States with more quanta of excitation are more complicated, but still the integrals result in sums of Franck-Condon factors, which automatically take into account such difficult features as changes in geometry and rotation of the normal coordinate space between the two electronic states.

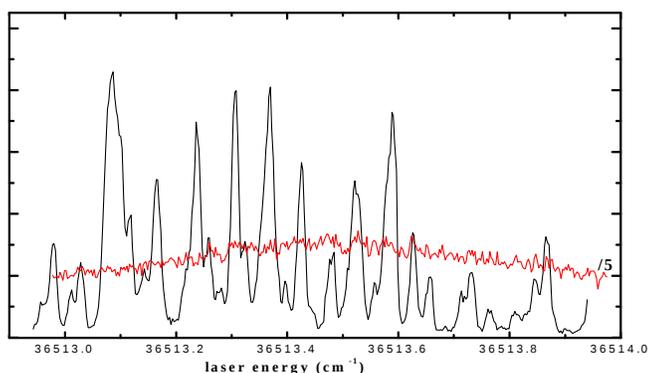
The end result is that vibronic intensities can be calculated by combining available calculations. The transition moments can be obtained from SAC-CI calculations (a module of the Gaussian package), and derivatives estimated by finite differences. Franck-Condon factors are calculated with the program MolFC, written and distributed by Andrea Peluso and Raffaele Borrelli. Geometries and vibrational vectors are produced by a variety of Gaussian and Gamess methods.

We have successfully applied this procedure to understanding the vibrational structure of the B-X transition of benzonitrile cation. It is, of course, subject to the accuracy of the vibrational vectors and transition moments, and is not perfect. However, we feel the procedure should be of great use to experimentalists needing some guidance for difficult assignments. The spectrum above shows the transition from a non-symmetric vibration in the ground state of benzonitrile cation to the ionic B state (upper trace), along with a simulated spectrum below it. Most of the strong lines in this spectrum involve more than one inducing mode. This challenging case has been successfully analyzed, and it would seem that the use of vibronic calculations by experimentalists would greatly promote the reliability of spectral assignments.

Anomalous line broadening in high resolution spectra

A major new tool has been constructed in our laboratory during this grant period, a pulse-amplified CW dye laser capable of a resolution of about 100 MHz, with pulse energies of up to around 20 mJ. With this source we are able to measure rotationally resolved spectra of the S_1 - S_0 transitions of large low-symmetry molecules such as benzonitrile and phenylacetylene, even though the rotational structure is very dense in these asymmetric rotors. Simulated spectra using known rotational constants agree very well with the experimental spectra, viewing the spectra using either fluorescence excitation, MATI excitation, or REMPI, although the temperatures in the best-fit simulations are significantly lower than one would expect in a normal supersonic expansion at the pressures we use. Mostly, however, things appear normal.

However, the amplifying stages of the high resolution laser are pumped by a seeded YAG laser, and an interesting effect appears when the seeder is turned off. Then, as shown at left, for



benzonitrile the resolved rotational spectrum becomes completely diffuse and the overall signal increases substantially (in the figure, the relative intensities are scaled). For phenylacetylene, a high resolution spectrum still appears, but it is on top of a strong broad background. Measurements of the line width of the pulse-amplified laser by either an etalon, or by scanning

an atomic transition, show that the linewidth of the laser is not appreciably different with the seeder on or off, so the effect has to be in the radiation-molecule interaction.

The primary effect of turning off the seed in a YAG laser is to allow multiple longitudinal modes in the laser cavity, which broaden the linewidth and produce beating that creates a random amplitude modulation during the laser pulse. The broader line width has no detrimental effect when pumping a dye, but the amplitude modulation can cause a resultant time variation in the

refractive index of the dye medium that produces a frequency chirp in the high resolution output, in addition to transferring some of the amplitude modulation.

What effect is producing the line broadening? We have examined several possibilities:

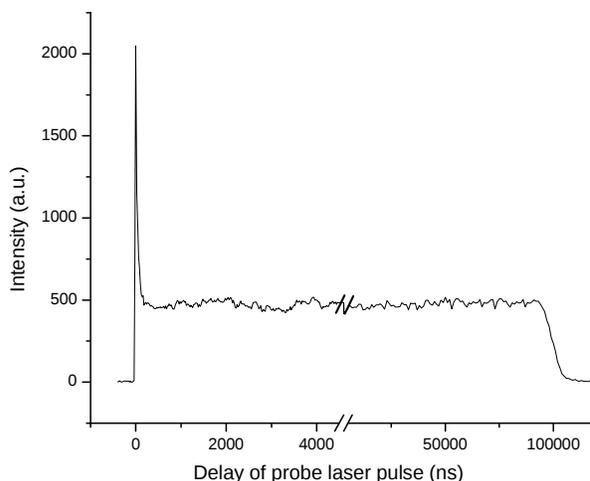
- 1) An effect of the amplitude modulation on radiationless transitions-- If the time structure of the laser pulse were to prepare some superposition state in S_1 that had an effect on radiationless transition rates, mixing of various levels could occur and broadening would be evident. Although it is not clear how such a large observed effect could arise from state mixing, we measured the S_1 state lifetime using both fluorescence and pump-probe techniques, and found no difference with or without the seeder. Any state mixing would affect this decay rate, and we therefore rule out this mechanism.
- 2) AC-Stark broadening-- A random modulation of the light pulse at constant pulse energy would produce higher peak energies, which could broaden lines due to the AC-Stark effect. One picture of this effect is the cycling of the molecule between the state of interest and a real or virtual state one photon higher that moves the states around. Calculations of the higher states of both molecules indicate there are 4p Rydberg states in the right vicinity with large oscillator strengths, so this is not impossible. However, a simple experiment was done to estimate the amount of increase in intensity necessary to produce the observed effect. The original broadening experiments were done without focusing the excitation laser. The experiment was then repeated with the seeder on, but with a lens focusing the light into the molecular beam. It is found that it takes a 75 mm lens to produce the same amount of broadening that is produced by turning off the seeder, a calculated increase in intensity of almost 10^5 . It is exceedingly unlikely that modulation could produce such an extreme peak power.
- 3) Adiabatic fast passage-- A chirped excitation source can sweep across a transition energy, producing a coherent excitation much like a pi pulse in magnetic resonance spectroscopy. This pulse can similarly transfer entire populations to the upper state. Although commonly seen in atomic spectroscopy, the effects on molecules have not been well studied. We are currently trying to estimate the magnitude of this process in our systems, and determine whether it could contribute to the observed broadening, possibly in conjunction with the AC-Stark effect.

There is much left to be done on this project. At the present time we do not even know how general the phenomenon is, since we have only studied phenylacetylene and benzonitrile. The limited wavelength range of the CW ring laser limits the number of molecules that can be studied, but results for other molecules and classes of molecules may shed some light on the causes of this strange effect.

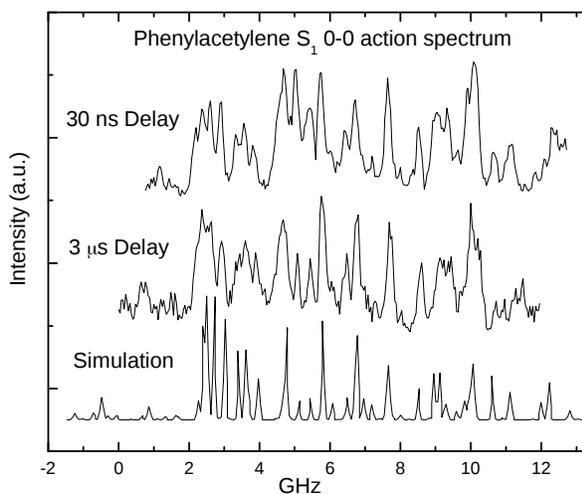
Long-lived species and anomalous photophysics in phenylacetylene

In radiationless transition theory, it is assumed that the wavefunction of an isolated excited singlet state of a large molecule can mix with the high density of isoenergetic triplet and ground singlet states. This mixing can be experimentally followed in time by ionizing the molecule at various times after its excitation, since when the system evolves into the high vibrational levels of the ground state, the Franck-Condon factors prevent ionization and the signal disappears. In this way, one can measure the lifetimes of the triplet states isoenergetic with the pumped singlet state. These are typically on the order of hundreds of nanoseconds to a few microseconds in substituted benzenes.

While measuring the pump-probe decays of benzonitrile and phenylacetylene, instead of the usual excited triplet decays with lifetimes on the order of a microsecond, we saw very long lived species (with lifetimes longer than we can measure accurately—we are limited to about 150 μ s by the size of our apparatus). This was not unexpected since we have seen similar things in other molecules, where we attributed it to the dissociation of clusters removing energy from the molecules. The dissociation allows them to drop down to the lower vibrational levels of the lowest triplet state where the excited state lifetimes are quite long. This time, however, we were exciting with a pulse-amplified CW laser system and able to scan over the rotational structure of the transition. The pump-probe S_1+193 nm action spectrum of the long-lived component shows that the active molecules are strictly monomers, thus eliminating the cluster mechanism from possibility.

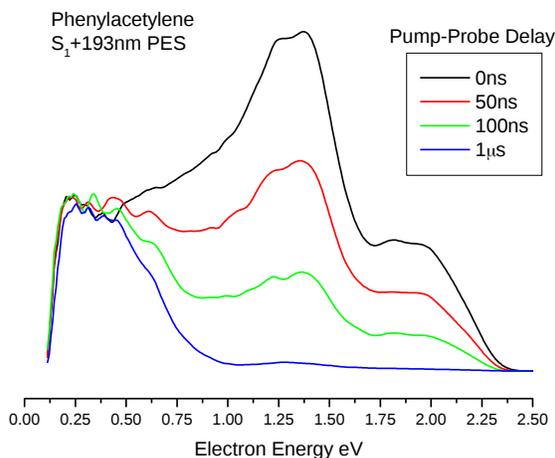


One reasonable mechanism for producing a long-lived state is that the molecules are crossing into the triplet manifold and losing energy by radiation. Emission lifetimes for excited vibrational states are too long for their IR emission to play a part in molecular decay in the triplet manifold. However, there is nothing to prevent an electronic transition from playing a role if there is an excited triplet state just below the excited singlet. We have done calculations to show that there is an excited triplet state in the vicinity of the singlet, with sufficient oscillator strength. Therefore we searched for evidence of a triplet-triplet emission in the vicinity of one micron wavelength using a variety of near-IR photomultipliers. No signals were seen whatsoever, with a sensitivity level several orders of magnitude higher than that able to detect UV fluorescence from phenylacetylene under the same conditions.



To establish whether the long-lived state is a cold or hot triplet, or perhaps some isomer, we have extensively explored the photoelectron spectrum (PES) with respect to delay times. It is seen that, using 193 nm photons, the spectrum evolves from having prominent singlet state transitions (terminating in both the X and the A state of the ion, the two peaks to higher energy in the spectra) to one dominated by low energy electrons. The remarkable thing is that the long-lived component is present immediately, and does not grow during the singlet lifetime. Before or after the singlet decays, the low-energy PES stays unchanged for as long as 90 μ s and is a continuously rising signal from a little below 1 eV to about 0.1 eV, below which there is no information because the electron collection efficiency becomes negligible.

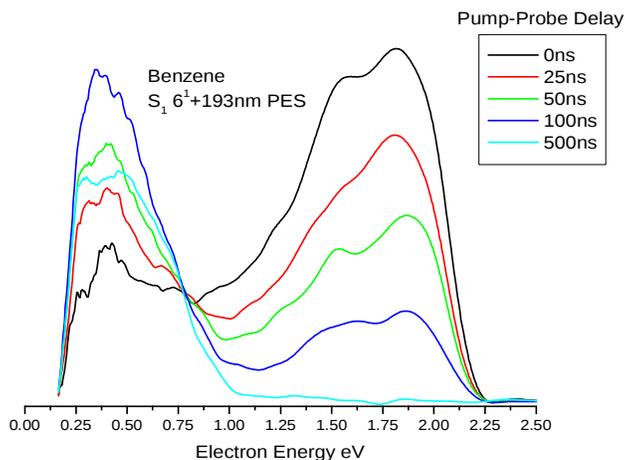
The conclusion one can make from this is that there are two species created during the laser pulse, or perhaps one species or superposition state that collapses rapidly into two populations. One, the singlet, decays by fluorescence ($\tau = 75\text{ns}$), and possibly other pathways, but it does not convert into the other. The long-lived component is spectrally consistent with a hot triplet state, but could be anything with an IP of around 5.5 eV. However, the long lived species bears the spectral signature of the S_1 state. This bifurcation of pathways is at odds with the simple kinetic picture we most often invoke when thinking about excited state evolution.



There are a large number of isomers of phenylacetylene, some of which require minimal bond rearrangement, and we have considered whether the long-lived state is one of them. It is unlikely that the molecule has undergone a permanent isomerization since that would raise the ionization potential of the molecule enough that 193 nm photons would not have enough energy to produce electrons. However, there could be some dynamic situation where the molecule is floating above a variety of potential wells and the Franck-Condon factors are so low in much of the phase space that there is no substantial coupling to the singlet ground state. If this were the case, there could be some probability of returning to the singlet state. We have searched for this in the PES to no avail, but it is probable that the singlet population would be too small to be detectable.

We are left with the puzzle that there are two populations created in the laser pulse. One fluoresces and the other lives indefinitely, but they do not detectably interconvert. They have different ionization potentials, but have the same rotational excitation signature. One would expect a hot triplet to continue to receive population for the lifetime of the singlet, casting doubt on that candidate unless somehow there are two different types of singlet states excited. A careful examination of the PES spectra with respect to the quantum levels excited in S_1 will be necessary to determine if different levels have differing couplings to the long-lived states. For signal-strength reasons, present PES studies have excited a band-head, with a variety of rotational levels present.

As far as we are aware, no-one had ever studied whether the “triplet” component in pump-probe ionization studies is formed instantly, or continuously during the lifetime of the singlet, for any large molecule. This has to be done by some technique like PES that can distinguish the singlet and triplet, and little excited state PES has been done. Since a kinetic model for intersystem crossing in which IC competes with fluorescence is a general concept in molecular photophysics, it is important to know that answer.



We therefore did a similar time-delay photoelectron study of benzene. As shown above, the PES spectra show exactly what one would expect, with the triplet component (at 0.4 eV) building up as the singlet decays. The “normalcy” shown by benzene makes the anomalous behavior of phenylacetylene even more intriguing.

DOE PUBLICATIONS

Andrew. B. Burrill, You K. Chung, Heather. A. Mann, and Philip M. Johnson, “The Jahn-Teller effect in the lower electronic states of benzene cation: Part III The ground state vibrations of $C_6H_6^+$ and $C_6D_6^+$,” J. Chem. Phys. **120**, 8587-8599 (2004).

Haifeng Xu, Trevor Sears, and Philip Johnson, “Photoinduced Rydberg Ionization spectroscopy of Phenylacetylene: Vibrational assignments of the \tilde{C} state of the cation,” J. Phys. Chem. A, **110**, 7822-7825 (2006).

Philip Johnson, Haifeng Xu, and Trevor Sears, “The calculation of vibrational intensities in forbidden electronic transitions,” J. Chem. Phys. **125**, 164330 (2006).

Haifeng Xu, Philip Johnson, and Trevor Sears, “Photoinduced Rydberg ionization spectroscopy of the \tilde{B} state of benzonitrile cation,” J. Chem. Phys. **125**, 164331 (2006).

Jason Hofstein, Haifeng Xu, Trevor Sears, and Philip Johnson, “The fate of excited states in jet-cooled aromatic molecules: Bifurcating pathways and very long-lived species from the S_1 excitation of phenylacetylene and benzonitrile,” J. Phys. Chem. A **112**, 077367 (2008).