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

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Pump−probe delayed ionization studies on phenylacetylene and benzonitrile in a supersonic beam reveal the production of a low-ionization-potential (∼5.7 eV) species lasting more than hundreds of microseconds after excitation to the S_1 state. Excitation of the molecules was done with a frequency-doubled, Fourier transform-limited, pulse-amplified cw laser, and the rotationally resolved structure of the S_1-S_0 transition ensures that the excited molecules are monomers. Excited-state photoelectron spectroscopy shows that the long-lived species are formed during the light pulse but not by transfer from the fluorescing S_1 population after the pulse, even though the S_1 spectral signature is present in the long-lived action spectrum. This behavior differs greatly from that found in benzene and with most commonly held pictures of radiationless transitions in large molecules.

Introduction

The evolution of energy in an isolated large molecule excited to its lowest singlet state is usually thought of in terms of a kinetic competition between pathways leading out of the nonstationary state carrying the oscillator strength of the transition. Thus the various pathways leading to fluorescence, a vibrationally excited ground-state surface, or a vibrationally excited triplet-state surface all lead from, and are fed by, the initially pumped singlet state. Here we would like to report on molecules where this simple picture appears to break down.

In radiationless transition theory, it is assumed that the wave function of an isolated excited state of a molecule can mix with the high density of isoenergetic states having the same (internal conversion) or different (intersystem crossing) multiplicity. Following the absorption of light, most aromatic molecules have been found to have emission quantum yield less than unity, indicating that radiationless transitions play an important role in the decay of excited states.[1] Numerous experiments of various types have been performed to illuminate the nature of state interactions in a variety of aromatic molecules.[1−12]

Over the past few decades, two-color pump−probe photoionization techniques have been used to investigate the time evolution of excited states of large molecules under collision-free conditions in the environment of a supersonic beam. In these experiments, the first laser is used to excite the molecules to a singlet vibronic level which evolves in time, crossing over to an isoenergetic point in the triplet manifold. By using another laser with sufficient photon energy to overcome Franck−Condon factor differences, both singlet and triplet molecules can be ionized with about the same efficiency, but molecules that go into the electronic ground state cannot be ionized because the Franck−Condon favorable region of the ionization continuum is above the photon energy. The time evolution of excited-state populations can be measured by varying the delay time between the ionizing laser and the pump laser. Unlike fluorescence spectroscopy, which is only sensitive to the singlet component of the mixed state, photoionization is not constrained by spin selection rules. Therefore, the time evolution of both the singlet and triplet state can both be monitored by detection of either ions[3−9] or photoelectrons[10−12] produced from the ionization.

The intersystem crossing of those aromatic molecules studied previously occurs between the first excited singlet S_1 state and the lowest triplet T_1 state. The triplet lifetimes measured by pump−probe photoionization studies were found to be as much as 9 orders of magnitude shorter than the life of cold triplets.[3,7,9] The reason for this is that the triplet, which is initially formed from the singlet via intersystem crossing, must contain a large amount of vibrational energy to make up for the energy gap between S_1 and T_1 states, a typical value for aromatic molecules being 6000−8000 cm^{-1}. The radiationless decay process that returns the hot triplet molecules to the ground electronic state (and produces a loss of signal) is therefore strongly accelerated by large-amplitude vibrational motions. The typical triplet lifetimes in previous pump−probe studies of isolated monomers were found to be less than one microsecond.[3−7,9] Other experiments on dimers or clusters[6,12−14] show that dissociation of excited-state complexes can drop the molecule downward in the triplet manifold, resulting in much longer triplet lifetimes. For example, a triplet lifetime of more than ten microseconds was observed by Hillenbrand et al.[12] in their pump−probe pulsed field ionization study of pyrazine, and it was interpreted to be the result of relaxed triplet states populated through vibrational dissociation of van der Waals clusters.

In this paper, we report the pump−probe photoionization studies of isolated benzonitrile (BN) and phenylacetylene (PA) in which both molecules evolve into very long lived species (living hundreds of microseconds or more), with low ionization potentials, in an energy region for which short lifetimes would be expected if simple intersystem crossing were taking place. Furthermore, excited-state photoelectron spectroscopy shows that the excited S_1 states do not continue to evolve into this

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long-lived product after the light pulse has ended, a result not expected from the standard kinetic model. To ensure that the properties measured belong strictly to the monomers of these molecules, the present study used a high-resolution pulse-amplified cw laser to excite the molecules to their S_1 states, allowing a comparison between the rotational structure of the action spectra for various ionization processes and the known rotational structure of the monomer. Thus an absolute determination can be made that the signals described here arise from monomers.

A mechanism that can produce such a stable and easily ionizable species in a collisionless environment is not immediately obvious, and various possibilities are explored here. These include the following:

1. Intersystem crossing into an isoenergetic set of states in the triplet manifold.
2. Internal conversion into highly excited vibrational levels of the molecular ground state.
3. Intersystem crossing followed by near-IR emission to low vibrational levels of the lowest triplet state.
4. Isomerization.

Various experimental tests have been performed to exclude as many of these mechanisms as possible. The preponderance of evidence currently points to isomerization as the primary mechanism, but the identity of the isomer has yet to be determined

Although we believe the photophysics is similar in PA and BN, this paper primarily focuses on PA, where the quantum yield of the long-lived state is considerably larger and the experimental signals more substantial. The radiative decay of PA has been studied by Hui and Rice[15] in a room-temperature sample. They reported a fluorescence lifetime of 54 ns and a quantum yield of 0.25. The S_1 absorption was analyzed and assigned by King and So,[16−18] and the rotational structure was recorded and fit to constants by Ribblett, Borst, and Pratt[19] and Siglow and Neusser.[20]

The photophysics of PA and BN are compared to that of benzene, a molecule whose properties have been extensively studied and is considered to be prototypical for the “large molecule limit” of radiationless transitions.

Experimental Methods

Two-color pump−probe photoionization experiments were carried out under collision-free supersonic beam conditions. Briefly, jet-cooled PA, BN, or benzene molecules were excited to their S_1 states using a high-resolution pulse-amplified cw laser (for PA and BN) and then, at a variable delay time, a second laser was used to ionize the excited molecules. The ions created at the various laser delays were detected with a time-of-flight (TOF) mass spectrometer, while TOF photoelectron spectra (PES) were recorded using a 30 cm flight tube, doubly shielded with mu-metal for magnetic isolation.

Sample molecules were purchased from Aldrich and were used without any additional purification. A jet-cooled molecular beam was produced from a supersonic expansion of the sample molecules (seeded into He gas at room temperature with a backing pressure of ∼2.7 atm) through a pulsed nozzle (300 μm orifice diameter), and was introduced to the ionization chamber through a skimmer (3 mm diameter) placed about 4 cm downstream from the nozzle. Typical pressure in the source chamber was in the 1×10^{-5} Torr range, and that in the ionization region was between 7×10^{-7} and 2×10^{-6} Torr.

A very high resolution (∼100 MHz) laser system consisting of an Ar^+ pumped cw ring dye laser (Coherent 699-29) pulse amplified in three stages by a seeded Nd:YAG laser (Quanta Ray GCR200) was used as the pump laser to excite the molecules to selected rotational states of the S_1 excited electronic state. Rhodamine 560 dye was used in the cw laser, and fluoroscein 548 dye used in the amplifiers. The dye laser output was frequency doubled in a KDP crystal to obtain wavelengths corresponding to the $S_1 \leftarrow S_0$ 0−0 transition (typically 35877.18 cm^{-1} for phenylacetylene[19] and 36512.94 cm^{-1} for benzonitrile[21]).

An ArF excimer laser (Lambda Physik) was usually used as the probe laser to ionize the excited molecules when measuring excited-state decay curves or doing PES. The 193 nm radiation is of sufficiently short wavelength to ionize both the original S_1 state and any hot or cold triplet states formed by intersystem crossing from the singlet.

For ionization threshold scans, a doubled Lumonics HD300 dye laser (line width ∼0.2 cm^{-1}), pumped by a Quantel Nd:YAG laser, was used as the probe laser, instead of the ArF laser, and all benzene pumping was done with this laser. Stilbene 420 was used in this laser, and the dye output was frequency doubled in a BBO crystal. The output power of each laser was carefully adjusted until there were almost no background ions produced from one-color, two-photon ionization.

For most experiments, the pump laser was introduced into the chamber coaxially counter-propagating to the molecular beam, so that the whole length of the molecular beam was excited. The probe laser was perpendicular to both the molecular beam and the pump laser, and it was fired at a fixed delay with respect to the opening of the pulse nozzle. This ensures that ionization occurs at the same molecular density in the molecule beam, irrespective of the delay between the two lasers. The excited-state decay scans were acquired by moving the time delay of the pump laser with respect to the fixed timing of the pulsed nozzle and the probe laser.

Data collection was done using a National Instruments transient digitizer card having a time resolution of 10 ns. For PES the data was converted to energy units using an $E^{-3/2}$ factor to scale the intensities so that areas in the TOF and energy spectra are consistent. Since it was desired to compare PES intensities in spectra with various time delays between the pump and probe lasers, to eliminate variations caused by long-term condition changes the data acquisition program was set up to cycle through the desired delays on consecutive groups of laser pulses (usually 10). In addition, background signals from single-laser ionization were continually subtracted by using solenoid-operated mechanical shutters to turn the light from individual lasers off and on. It was found that the use of mechanical shutters greatly reduced the amount of electronic interference as compared to changing the timing of the lasers to generate a background signal for subtraction.

Fluorescence detection was done with a variety of photomultipliers to span the wavelength range from the UV to the IR. For the UV, EMI 9954QB and RCA 4837 tubes were used, while for the visible region to 1100 nm, RCA C31034 and Hamamatsu R5108 (S1) tubes were used, and from 950 to 1700 nm, a Hamamatsu H9170-75 unit was employed. All the tubes were used in cooled housings. A search for near-IR emission from phenylacetylene was done using an interference filter with a bandpass from 800 to 2500 nm, eliminating the detection of normal fluorescence.

An attempt was made to observe the long-lived state of PA by surface electron ejection by laser-excited metastables (SEELEM)[22] in Prof. R. W. Field’s laboratory. Following S_1 excitation using a frequency-doubled YAG-pumped dye laser

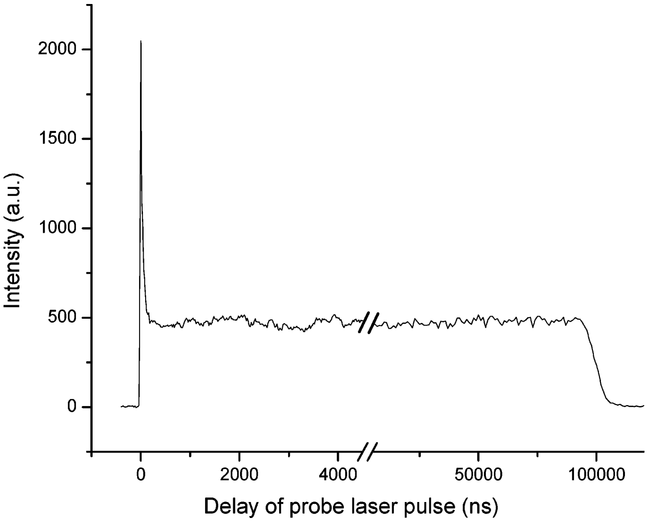

Figure 1. Decay curve of phenylacetylene ions as a function of delay time between pump and probe lasers. The wavelength of the pump laser corresponds to the origin of S_1-S_0 transition, while an ArF laser was used to ionize the molecules. The fast initial decay is due to the decay of S_1. Note that the time scale increases by a factor of 25 at 5 μs.

(Lambda Physik FL3002), a signal from a species apparently living for more than 300 μs was observed. The electronic excitation of a metastable state must be greater than 3.1 eV in order to eject electrons from the yttrium surface of the detector. The T_1 zero level energy is barely at this threshold, and that is the only state of PA expected to have such a long lifetime. However, we are not able to eliminate the possibility of multiphoton effects producing the observed metastables in this experiment, so one cannot consider this evidence of a cold triplet state.

Results and Discussion

Pump−Probe Delay Scans. Figure 1 shows the pump−probe ionization decay curve of phenylacetylene after being excited to the origin of its S_1 state. It is quite clear that the decay is not the exponential or biexponential form expected. The faster decay component is due to the decay of the singlet S_1 state, and it has the same lifetime as the fluorescence. The lifetime of the origin of the S_1 state is thus obtained to be about 73 ns measuring either fluorescence decay or pump−probe ionization. This is somewhat longer than that (54 ns) reported in an earlier fluorescence study[15] at room temperature. It is possible the room temperature measurement displayed effects of hot band excitation and/or pressure quenching.

The rest of the signal is relatively constant, or even rising, over the interval of the measurement. The intensity is about 25% of that of the faster component, indicating a relatively significant quantum yield of a very long lived species. The lifetime is very long indeed; it is so long in fact that it is well beyond the collision free flight time of the supersonic beam, which is about 100−150 μs in our apparatus (depending upon where the nozzle is placed). Since the delays extended over such long times, and therefore long flight distances of the excited species, the time delay scans were very sensitive to the alignment of the pump laser. The shapes of these decay curves over long times were never completely reproducible, and no conclusions can be made from them, except that it is clear that for PA the signal lasts for the entire flight time. Similar decay curves were obtained when pumping an excited vibrational level (A-6b)[1] at 36368 cm^{-1} in S_1.

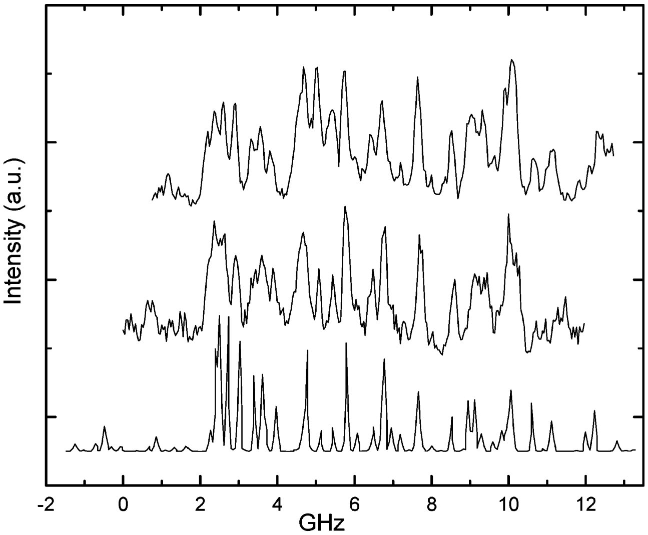

Figure 2. The rotationally resolved structure of the origin band of the phenylacetylene $S_1 \leftarrow S_0$ transition at different pump−probe delay times, (upper) 30 ns and (middle) 3μs. The 193 nm ArF laser was used as the probe laser. The bottom trace is a simulation of the rotational structure of the spectrum using known rotational constants.[19]

Production of the lower vibrational levels of the triplet manifold can easily be produced by the dissociation of clusters,[6,12−14] creating states of long lifetime such as seen here. In the present case, however, we have eliminated that possibility by measuring the action spectrum of the long-lived species using a high-resolution laser to resolve the rotational structure. Figure 2 shows such a spectrum along with a fluorescence excitation spectrum and a simulation of the rotational structure from the known rotational constants. The rotational structures are the same, so the long-lived species must be derived from the excitation of the isolated monomer and is therefore *not* a dissociation-relaxed triplet.

The decay curve of BN also has two components, but with a much weaker long-lived component than PA. However, the same anomalously long lifetime as that of phenylacetylene was still observed. Scanning over the rotational structure of the $S_1 \leftarrow S_0$ transition at different delay times confirms that a long-lived component is formed from monomers in BN as well.

Photoionization Threshold. Because of almost diagonal Franck−Condon factors for aromatic molecules, the probe laser photon in a pump−probe photoionization study must usually meet or exceed the energy necessary to ionize the vibrationless triplet state in order to efficiently ionize the triplet states produced by intersystem crossing.[3−7,9] Figure 3 shows the second photon photoionization efficiency curve of the long-lived PA species with a delay of 30 μs between the pump and probe lasers. The photoionization efficiency curve was recorded by measuring the intensity of molecular ions produced while scanning the wavelength of the probe laser. The photon energy of the pump laser was fixed at 35877.18 cm^{-1}, corresponding to the origin of the S_1 state of phenylacetylene. A relatively slow-rising threshold was observed at a probe laser energy of ∼46500 cm^{-1} (5.77 eV).

Since the ionization energy of phenylacetylene (IP_0) is 71127 cm^{-1} [23], this gives the energy of the state being ionized to be about 24630 cm^{-1} (3.05 eV). This is very close to the triplet energy as reported from previous studies of phosphorescence in isopentane (3.12 eV),[24] EELS in the solid phase (3.15 eV),[25] as well as theoretical calculations (3.04 eV).[26] The rising edge of the photoionization efficiency curve is fairly slow, indicating that the long-lived species could be populated with a distribution

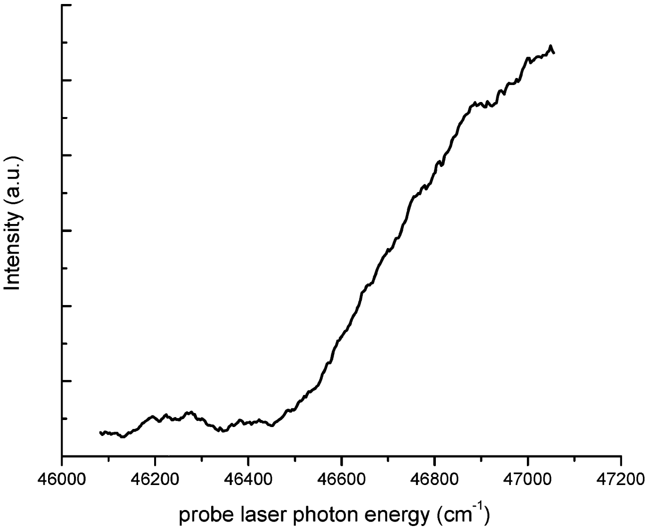

Figure 3. Photoionization efficiency curve of the phenylacetylene long-lived product with a delay of 30 μs between the pump and probe lasers, recorded by measuring the ion intensity while scanning the wavelength of the probe laser. The photon energy of the pump laser was fixed at 35877.18 cm-1, corresponding to the origin of the S_1 state of the phenylacetylene. A threshold was observed at an energy of ∼46500 cm^{-1} for the probe laser. Some background signal appears below this threshold, but this is due to the pump laser only and can be considered a zero level.

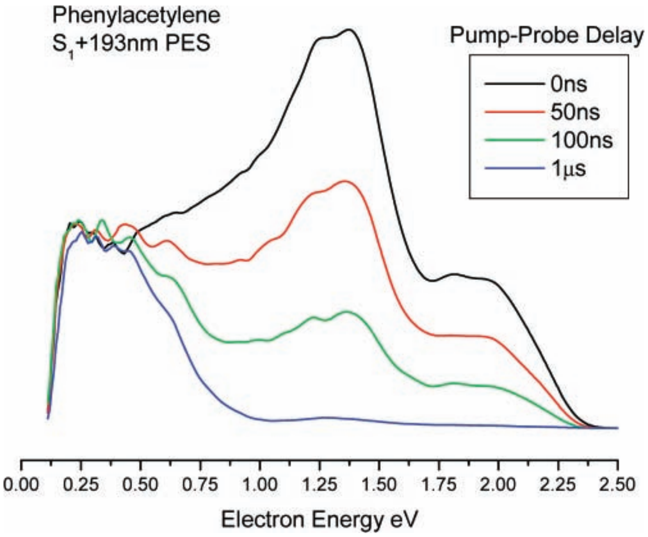

Figure 4. The excited-state PES of phenylacetylene versus the delay time between the pump and the probe lasers using 193 nm as the probe photon. The peaks on the right are ionization of S_1, and decay with the singlet lifetime, while the low-energy peak of the long-lived species appears immediately and does not change during the singlet lifetime. The signal zero of this spectrum is the level at the extreme right of the figure.

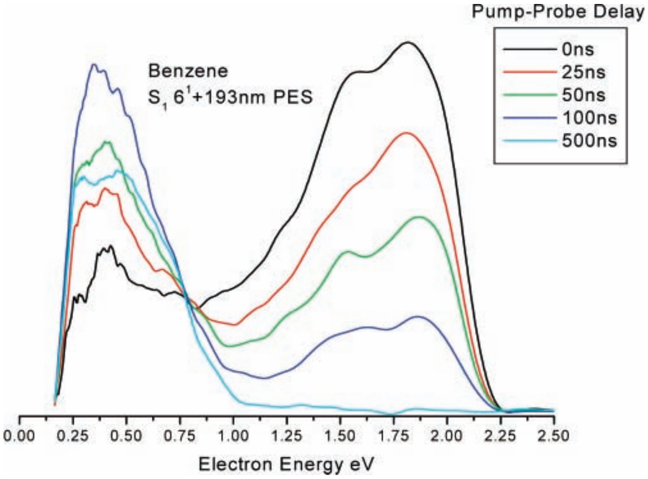

Figure 5. The excited-state PES of benzene versus the delay time between the pump and probe lasers using 193 nm as the probe photon under conditions similar to those used in Figure 4. The isosbestic point demonstrates the simple kinetic process whereby the singlet state is converted to the triplet state. The signal zero of this spectrum is the level at the extreme right of the figure.

of vibrational energies. However, because the Franck−Condon factors for ionization are not known, it is not possible to know the degree of vibrational excitation from the threshold measurement.

Photoelectron Spectroscopy. The pump−probe PES of the vibrationless S_1 state using 193 nm ionization photons is shown in Figure 4 for various time delays between the lasers and can be compared with similar measurements on benzene shown in Figure 5. For PA, three distinct features are present in the spectra at about 2.0, 1.4, and 0.65 eV, with the first two of them dependent upon the laser delay, going away with the fluorescence lifetime. The decaying peaks can easily be assigned as the transitions from singlet S_1 to the ground state ($\tilde{X}$ $^2B_1$) and first excited-state of the ion ($\tilde{A}$ $^2A_2$). The lower-energy electrons are not dependent on the delay and come from the long-lived state, persisting to delays of over 150 μs. The high-energy onset of the 1 μs curve is consistent with the threshold scan described above, and the falloff of all the curves at low energy is due to the loss of low-energy electrons in the flight tube. Spectra using negative repeller voltages show a continuing increase of intensity down to 0.1 eV.

The remarkable feature of the PES in Figure 4 is that the low-energy feature does not change at all with the laser delay, while the singlet is decaying. This means that whatever entity is being ionized is produced independently of the singlet during the laser pulse and is not a daughter product of the singlet. This contradicts the usual concept of an excited state being formed and then decaying along a variety of paths that depend upon a competition between their kinetic rates. The normal kinetic picture is seen in benzene (Figure 5), where the triplet signal initially increases as the singlet decreases and then decays with its characteristic triplet lifetime.[4]

These spectra, in conjunction with the rotationally resolved action spectra, indicate that each different rotational level excited can follow at least two independent routes, leading to either fluorescence or the long-lived species (or other products we cannot detect), and the selection between these routes takes place during the laser pulse or shortly thereafter. A certain population of molecules stays in the singlet state and eventually fluoresces, while another population enters a stabilizing pathway. If these rotational levels were truly homogeneous singlet eigenstates, the selection could take place at any time during the singlet lifetime. The fact that it does not, implies the existence of a set of uncoupled states with the same action spectrum. This behavior does not change when the S_1 excitation is done with a normal dye laser with a bandwidth of fractions of a cm^{-1}, so it is not a feature of high-resolution excitation.

The ionization threshold scan and PES could be consistent with the long-lived component being from a hot lowest triplet state T_1, since Franck−Condon factors may favor transitions to states of the ion with vibrational excitation similar to the lower state. However, with T_1 being about 10,100 cm^{-1} in energy below S_1,[25,27] all triplet states formed initially by intersystem crossing from the S_1 state in a collision-free environment are expected to be very highly vibrational excited, and therefore should not have such long lifetimes.

To examine whether collisions have an effect on the PES spectrum, the pump light was directed across the face of beam valve, irradiating the sample just as it entered the expansion region. This is a location of high pressure and large collision rate. It was found that the long-lived PES signal was identical whether the S_1 excitation was there or in the collisionless region several cm downstream in the skimmed molecular beam. The PES spectrum of a hot molecule would be expected to narrow up as the collisions populate a sparser set of vibrational levels, so this result indicates the long-lived species does not have a particularly large amount of vibrational excitation. This result also did not depend upon the bandwidth of the pump laser.

Cold triplet populations were observed in a previous PES study of pyrazine in this laboratory.[12] In their lifetime measurements using a pump−probe photoelectron technique, Hillenbrand et al. were able to see a slow-decay component with a lifetime more than 10μs.[12] Lacking information about the exact nature of the signal carrier because of a relatively low-resolution pump laser, it was surmised this cold triplet population was produced from dissociation from the van der Waals clusters. In the present study, however, clusters have been excluded from consideration by the rotational structure, and no cluster ions can be observed in the time-of-flight spectrum in the early part of the gas pulse used here.

Mechanisms. *(a) Intersystem Crossing to an Isoenergetic Triplet Level.* In all the molecules previously studied by pump−probe ionization, the signal remaining after the singlet decay has always been ascribed to the ionization of hot triplet levels isoenergetic to the initial S_1 level, having a vibrational energy equal to the S_1-T_1 gap. The lifetime of a collisionless triplet (presumably toward intersystem crossing to S_0) varies dramatically with vibrational energy, typically falling by 5 orders of magnitude from the zero vibrational level to 4000 cm^{-1} of energy.[28] This drop can be attributed to increased intersystem coupling caused by the considerable increase in the density of states, more favorable Franck−Condon factors, IVR,[29] and a smaller gap between the potential energy surfaces of the states.[30] Above 4000 cm^{-1}, the lifetime drops more slowly, and molecules with larger S_1-T_1 gaps have only slightly shorter lifetimes than the smaller-gap molecules for the triplet states isoenergetic to the singlet. The record holder for the longest lifetime of an unrelaxed triplet is aniline at 5.6 μs,[14] having a S_1-T_1 gap of 7200 cm^{-1}.

In the case of pyrazine (which has a very small S_1-T_1 gap), the identity of the long-lived species was definitively confirmed to be the triplet by observing the PES[12,13] and the MATI spectra[31−33] of the state.

PA and BN have roughly 10000 cm^{-1} of vibrational energy in the triplet manifold after intersystem crossing. Therefore one would expect a lifetime of at most a few microseconds for a triplet level isoenergetic to S_1. The observation of a long-lived state with a lifetime at least 2 orders of magnitude larger than other comparable aromatic molecules leads to the conclusion that the species is not a hot triplet isoenergetic to the singlet. The difference between the kinetics of the long-lived PES signal in PA as compared to benzene reinforces that conclusion.

One can also ask the following question. If the long-lived signal in PA is *not* due to the triplet state, where is the triplet signal? If it is not a triplet, then one would have to argue that there is no intersystem crossing in isolated PA, even though the phosphorescence quantum yield is substantial (comparable to fluorescence) in solid solution. To examine this question, we measured the pump−probe time delay curve of styrene as a molecule similar to PA. We found there is no signal at all after the singlet has decayed, neither a triplet component as in benzene, nor a long lifetime component like PA or BN. This is the first molecule to show this characteristic, but it shows that it is possible for a decay curve to lack a triplet component.

(b) IR Emission to a Lower Triplet Level. The long lifetime and the lack of collisional cooling both suggest a lack of vibrational energy in the long-lived species. A cold triplet state would be a candidate, but there has to be some mechanism for relaxation when the excitation is outside the expansion region of the beam.

Under collision-free conditions, one viable mechanism to quench phenylacetylene monomers from the excited S_1 state to the low vibrational levels of the T_1 state is radiative emission. Conventional wisdom is that emission between vibrational levels of the same electronic state has too long a lifetime to play a part in energy relaxation 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. There is no experimental data about the energy of excited triplet states in the gas phase in the literature. However, in their electron-energy-loss spectroscopy (EELS) study of solid phenylacetylene, Swiderek et al.[25] found the lowest triplet ($^3A_1$) to be at 3.154 eV and the lowest excited singlet ($^1B_2$) at 4.41 eV (the gas-phase value is 4.45 eV). They also observed a second singlet−triplet transition at 4.26 eV, which was assigned as a spin-forbidden transition from the ground singlet state to two nearly degenerate triplet excited states, $T_2(^3B_2)$ and $T_3(^3A_1)$. This was corroborated later by Serrano-Andres et al. in their theoretical studies, where the $T_2(^3B_2)$ state has been computed at a vertical energy of 4.22 eV with band origin at 4.08 eV, and the $T_3(^3A_1)$ state is placed at 4.31 eV.[26] We have performed SAC-CI calculations[34] which indicate that transitions between the ground triplet T_1 state and the excited triplet $T_{2,3}$ states have sufficient oscillator strengths. It is therefore possible that in phenylacetylene there could be considerable radiative decay in the triplet manifold. The cold triplets would be populated by photon emission to the ground triplet T_1 state from the excited triplet T_2 or T_3 state that is produced by intersystem crossing from the excited singlet S_1 state.

As appealing as this mechanism is, it has not held up to experimental verification. An exhaustive search for IR emission was performed. The emission would be expected to be at around 1000 nm, so a specialized photomultiplier designed for that region was employed, as well as standard S1 photomultipliers. No emission was seen, and it can be estimated that the available sensitivity level was good enough to observe emission at least 2 orders of magnitude below the flux of normal UV emission in PA. Second, if there were IR emission, one would expect there to be significant population in the lower vibrational levels of T_1. This would lead to a sharp onset and possibly vibrational structure in the PES and the photoionization efficiency curve, which are not seen. And finally, if intersystem crossing is taking place, one would expect to see a buildup of the long-lived PES signal as the singlet decays.

(c) Direct Internal Conversion from S_1. Internal conversion of S_1 to high vibrational levels of S_0 would create a state that has an indefinitely long lifetime, barring dissociation or isomerization. However, the Franck−Condon factors for 193 nm ionization of a state with 38000 cm^{-1} of vibrational energy would be insignificantly small, and other molecules that have been studied[3−9,14] do not show any ionization signal from the hot ground state. PA and BN are somewhat unique in that they

have skeletal modes involving the triple bond that are higher in frequency than the skeletal modes in other substituted benzenes, so it could be conceivable that energy could be transferred to a high-frequency local mode, but even that would be a high harmonic, so direct ionization is still improbable.

Another possibility is that the 193 nm photon causes a transition from the hot S_0 state to a hot neutral excited state, which then autoionizes. This sort of phenomenon is seen in large molecules like fullerenes,[35−38] where it manifests itself in the appearance of delayed ionization because the energy reorganization from vibrational to electronic excitation takes a significant time.

Delayed ionization was searched for by using a high voltage (300 V/cm) to drive the electrons rapidly to the detector, while looking for electrons arriving after the primary pulse. A few delayed electrons were seen, but were much less than 1% of the total signal. This seems too little to account for the production of long-lived states seen in PA, but since we know nothing about the rates of the autoionization of hot PA, this mechanism must be deemed unlikely but not completely discounted.

(d) Isomerization. There are many ways in which PA can isomerize. The most facile way, one where there do not even have to be any hydrogen shifts, is to go to cyclooctyne (1,2-dehydrocyclooctatetraene). The anion photoelectron spectroscopy of this molecule is known,[39] and it is found that the ground state moves up to only 0.7 eV below the triplet because of loss of aromaticity. One could therefore envision that the density of cyclooctyne S_0 states at the level of T_1 is low enough that intersystem crossing is suppressed between those states. Preliminary calculations at the DFT-B3LYP 6-31G(2d,p) level indicate that the T_1 state of cyclooctyne will be about 0.3 eV below that of PA, allowing for easy conversion in a hot molecule. The ionization potential of cyclooctyne triplet is calculated to be 6.7 eV, which is just above the 193 nm photon energy of 6.42 eV. The IP could shift with better calculations, and excited vibrations could make up the extra energy, so stabilization by isomerization remains a possibility for explaining the very long lifetime.

(e) Light-Induced Coupling. The fact that the long-lived signal appears immediately in the PES and therefore does not result from a singlet population indicates there may be some intrastate coupling caused by the radiation field. In pulsed laser experiments such as this, where substantial populations get transferred between states, there is always the possibility of higher-order processes taking place. Some multiphoton ionization from the first laser is always present in time delay experiments in order to get enough population transfer to have adequate signal-to-noise. In PA, the two-photon energy of light resonant with the S_1 origin is only 0.076 eV above IP_0, in a region that is full of both Rydberg states and other neutral excited levels. It is not hard to envision a resonant cycling up and down through a Rydberg state. A characteristic of Rydberg states is that their singlets and triplets are very close in energy, and the spin functions are not very well defined. Thus one could imagine this being a mechanism for the coupling of singlet and triplet states. Similarly, cycling through a neutral excited state such as a charge-transfer state could enhance internal conversion or isomerization by relieving the stringency of Franck−Condon factors.

Again, this does not bear up under experimental scrutiny. Figure 6 shows the pump intensity dependence for the long-lived signal. This is found to be quite linear, in contrast to the quadratic dependence seen for two-photon ionization at the same laser intensities.

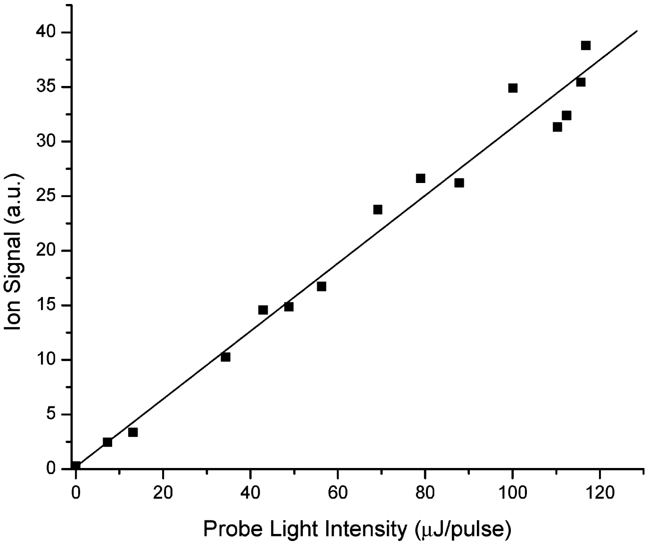

Figure 6. Intensity of the long-lived signal of phenylacetylene ionization versus the intensity of the pump laser, which precedes the 193 nm probe laser by 20 *μ*s. This demonstrates the single-photon nature of the S_1 excitation.

Conclusions

The identity of the long-lived species in phenylacetylene and benzonitrile cannot be conclusively determined from the current data. The most likely candidates would be either a low-lying vibrational level of T_1 or some isomer.

For the former, the only obvious mechanism for its population, nearinfrared emission, was not confirmed. However, a null experiment is always subject to uncertainties with regard to whether the experimental requirements were properly fulfilled. In this case, perhaps the emission is at a longer wavelength than the photomultipliers could detect, for example. Other results, such as the very long lifetime, the SEELEM experiment, and the lack of collisional cooling are consistent with a cold T_1 state. However, one would expect that a relaxation in the triplet manifold would exhibit normal kinetics as seen in benzene, rather than a direct production of the long-lived species as seen in PA.

If the long-lived species is an isomer, the only requirement is that it has a low ionization potential. The isomerization can soak up a considerable amount of energy, leaving the product in a cold vibrational state consistent with the lack of collisional changes in the PES. Since the structure of the isomer is not known, the energetics involved in the transformation and ionization cannot be determined. Higher-level electronic structure calculations on the various possible products would be very valuable in assessing the probability that one of the possible isomers has the right energy levels to be involved.

The unexpected fact that the long-lived product is formed during the light pulse, but not from fluorescing part of the singlet, also does not have an easy explanation. Any isomerization may take place on the ground-state surface, following internal conversion, and an interesting possibility is that internal conversion always proceeds directly during the light pulse. One would have to envision that the non-stationary state initially formed by the light dephases immediately into either pure excited-state singlet or ground-state singlet forms, which then do not interconvert. In most molecules the hot S_0 states following internal conversion cannot be ionized with the lasers employed to date, so this behavior has never been seen before because it has never been explored. Among other ramifications of the immediate bifurcation between the fluorescing molecules and molecules proceeding to the long-lived species is the impossibility of seeing the effects of the newly seen pathway in any fluorescence excitation experiment. Since most previous high-resolution studies of radiationless transitions have used fluorescence detection, there appears to be a need for the further exploration of large-molecule photophysics using either direct absorption or ionization techniques.

Regardless of the mechanism, an explanation for the lack of production of the long-lived species after the light pulse would be more palatable with an isomerization product than with a lower triplet product.

We are left with the situation that the photophysics of phenylacetylene (and benzonitrile by inference) has exposed a new set of properties that have not been seen previously in any of the aromatic molecules that have been studied in detail. A definite determination of the cause of these properties awaits the positive identification of the long-lived product, but hopefully further study will lead to further understanding of excited-state evolution.

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