Intramolecular Hole−Transfer in Protonated Anthracene

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Abstract

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Introduction

Charge transfer between two different molecules in an excited electronic state is at the heart of photosynthesis. This process is also mimicked in artificial devices which generate solar energy. In both organic photovoltaics (OPV) and dye-sensitized solar cells, following photon absorption, the excited state migrates and undergoes a charge transfer event. A detailed understanding of charge separation in OPV is hampered, in part, by the impossibility of detailed quantum chemical calculations on such a large system. In OPV devices, the electrons and holes are then conducted to metallic electrodes through a series of inter and intramolecular electron and hole-transfer processes.

Gas-phase laser spectroscopy offers the possibility to interrogate a well-defined, cold, isolated chemical system which is tractable at quantitative levels of electronic structure theory. To study photo-induced hole-transfer, a charged species must be studied, which engenders further experimental difficulties. Cations can be introduced into the gas phase by electrospray ionization, but the resulting species are not cold. Jet-cooled molecules can be ionized in the expansion region, but unless the ionization is at threshold, requiring tunable vacuum ultraviolet radiation, excess energy can be deposited in the cation. Techniques capable of studying jet-cooled, isomer-selected, cold cations are thus desirable.

The C_{60}^+ cation was recently studied by the photodissociation of its adduct with helium atoms in a 22-pole cryogenic ion trap. This technique affords a spectrum with a very small shift from the true gas phase spectrum. For C_{60}^+ cation this was sufficiently small to confirm the present of C_{60}^+ in interstellar space.[1] Recently, we reported a triple-resonance technique whereby nascent cations were resonantly photodissociated following preparation by a resonant 2-colour 2-photon photon ionization process, at threshold. The result was an unam-

2

biguous spectrum of protonated naphthalene, isomer selected and vibrationally cold.[2] Here we extend this treatment to protonated anthracene, which demonstrates symmetry-breaking in the excited state along a Marcus-Hush-like charge transfer coordinate.

Protonated anthracene has been studied previously, as its relatively high photostability[3] and abundance in the interstellar medium (ISM) suggest it is a promising diffuse interstellar band (DIB) carrier candidate.[4] However, previous reports are neither at rigorously low vibrational temperature, nor isomer-selected. Alata *et al.* measured the photo-fragmentation spectra of protonated anthracene, which was created (along with other PAHs) in an electrical discharge containing H_2.[5] Through comparison to RI-MP2 calculations, structure observed around 491 nm was assigned to the $S_0 \rightarrow S_1$ transition of the 9H-An+ isomer. A subsequent absorption measurement of protonated anthracene held in a cryogenic matrix by Garkusha *et al.* exhibited several spectral bands across the 400-500nm region.[6] They instead assigned the structure around 491 nm to the $S_0 \rightarrow S_2$ transition of the 1H-An+ isomer, based on TD DFT B3LYP calculations. A recent computational study has suggested the initial assignment to the 9H-An+ isomer was correct, however this discrepancy highlights the need for isomer selectivity.[7] Electronic spectra of protonated anthracene have also been measured via helium-tagging action spectroscopy, however this technique is also limited by isomer non-selectivity and spectral resolution.[4]

In this study, we prepare 9-hydroanthracenium cations exclusively in their vibrational ground state by 2-color resonant ionization of the corresponding 9-dihydroanthracenyl radical. Subsequent resonant photodissociation of the cation reveals the isomer-selected $S_0 \rightarrow S_1$ spectrum of 9-hydroanthracenium. We show that the C_{2v} ground state undergoes symmetry breaking in the excited state along a b_2 (in-plane) mode, effectively localizing the positive charge on one end of the molecule. This coordinate thus represents the abscissa of a Marcus diagram, and the excitation spectrum is interpreted from this standpoint.

Theoretical Considerations

Anthracene protonated at the 9-position is considered C_{2v} until proven otherwise. If the sp^3 carbon is considered as an insulator, the chromophore will consist of two aromatic rings linked by an sp^2-hybridized bridging carbon. The frontier orbitals of the aromatic rings can be taken in even and off combinations, resulting in sets of b_1 and a_2 symmetry. Only the b_1 set can interact with the bridge, which is also b_1. Of the highest occupied aromatic b_1 orbitals, one will have a node at the tertiary carbon atom adjacent to the bridge, and is not expected to be strongly perturbed. The other mixes with the bridging p-orbital and is lowered in energy. This results in two relatively unperturbed aromatic, symmetry-adapted orbitals of a_2 and b_1 symmetry. The lowest-energy unoccupied orbital is largely located on the bridge. The frontier orbitals are shown in Figure.

The HOMO-LUMO transition of the cation is thus electron transfer from the aromatic rings to the bridge, corresponding to hole-transfer from the bridge onto the aromatic rings. This brings about two near-degenerate transitions to states of A_1 and B_2 symmetry. Distortion along a b_2 mode will reduce the point group to C_s and render both these excited states A'. The interaction between these two states could potentially push the lower state to an energy below that of the C_{2v} geometry.

This was confirmed by quantum chemical calculations presented in this work. The ground state geometry was calculated at both the M06-2X/cc-pvtz and CCSD/cc-pvdz levels of theory, with both calculations converging to a planar C_{2v} geometry. All frequencies were found to be real, indicating a true minimum energy. Corresponding TDDFT and EOM-CCSD excited state calculations were also computed for the S$_1$ state, which converged to a planar C_s geometry. This geometry arises from the charge transfer from the bridge onto one of the aromatic rings, causing an in-plane b_2 distortion. To interrogate this charge transfer process, a transition state search on the S$_1$ surface was also carried out at the M06-2X/cc-pvtz level using the Berny algorithm of Gaussain16. This found a C_{2v} geometry with one imaginary frequency, 35 cm^{-1} above the C_s ground state.

The pathway from the C_{2v} to C_s geometry can be described by the intrinsic reaction coordinate (IRC). This was calculated in both the forward and reverse directions using Gaussian16 software and the HPC algorithm, calculating force constants at each step along the path. This produced a shallow double well potential, shown in Figure. The higher excited state surfaces were also calculated along the IRC coordinate. The surfaces resemble an avoided crossing, which suggests there will be a strong adiabatic interaction between the A and B states. A 2D surface map of both the forward and reverse IRC directions is shown in Figure, showing the C_{2v} saddle point and the two C_s global minima. The coordinate represents the charge hoping between the two aromatic rings.

Electrostatic potential surfaces were also calculated at both the C_{2v} and C_s geometries, as shown in Figure. The surfaces show that the positive charge largely resides on the bridge at the ground state C_{2v} geometry, then hops onto either of the aromatic rings at the excited C_s geometry. This confirms that the shallow double well represents the abscissa of a Marcus charge transfer diagram, making protonated anthracene an excellent prototype for the study of intramolecular hole−transfer.

Results and Discussion

9H-An+

The triple resonant photodissociation spectrum of protonated anthracene is shown in Figure. The cations were prepared by resonantly ionizing the neutrals at threshold, and as such we can be certain that the spectra correspond to protonation (deuteronation) at the 9-position, the C_{2v} species. The spectra reveal a number of progressions, possibly indicating a large geometry change between the ground and excited states of the cation. While the lowest energy geometry for the excited state possess C_s symmetry, as the transition state barrier (35 cm^{-1}) is below the zero point energy, we may treat the excited state as approximately C_{2v}.

The $S_0 \rightarrow S_1$ origin is at xxx cm^{-1}, in agreement with the previous PIMS measurement by Alata *et al.*,[5] confirming their assignment to the 9H-An+ isomer. Multiple narrow transitions are observed up to 1,400 cm^{-1} above the origin transition, that were not resolved in any of the previous studies. Spectral features below ~ 800 cm^{-1} appear sharp, with an average FWHM of $\sim xx$ cm^{-1}, while peaks at higher energies appear broader. This is likely due to the shorter dissociation lifetime of these excited vibrational states. It should also be noted that the relative intensity of peaks may be limited by saturation effects, where all of the resonant ground state cation signal is depleted.

As shown in Figure , most of the structure observed in the experimental spectrum may be accounted for by a standard Franck-Condon (FC) simulation. Vibrational frequency calculations were computed at the M06-2X/cc-pvtz level for both the Ground C_{2v} and excited transition state C_{2v} geometries. Overlaps between the ground and excited state vibrational wavefunctions were then calculated, including Duschinsky rotations, to simulate the vibronic spectrum. The resulting spectrum was dominated by progressions in the 6^n, 8^n, and $17^1 6^n$ modes. Excellent agreement between the simulation and experiment was obtained for the 6^n and $17^1 6^n$ progressions, however the pure FC simulation could not recreate the splitting observed near ~ 230 cm^{-1}.

To evaluate whether the splitting could be caused by a 1-2 Fermi resonance, anharmonic frequency analysis was performed using Generalised 2nd-order Vibrational Perturbation The-ory, with 3rd and 4th derivatives also calculated at the M06-2X/cc-pvtz level. This revealed a large Fermi resonance between modes v_8(366 cm^{-1}) and $2\times v_4$(186 cm^{-1}), with a coupling strength

$$W = \frac{\sqrt{\Delta^2 - \Delta_0}}{2} = 75.5 \text{ cm}^{-1}, \tag{1}$$

where Δ is the splitting with coupling, and Δ_0 is the transition separation without coupling. Therefore, the doublet feature at ~ 230 cm^{-1} is not from a Fermi resonance with mode 6^1 as one may expect, but instead from a large interaction between modes 4^1 and 8^1. The relative

intensity of of the resonant peaks is given by,

$$\frac{I_{v8}}{I_{2\times v4}} = \frac{(\Delta + \Delta_0)}{(\Delta - \Delta_0)} = 1.08. \tag{2}$$

Further features missing from the pure FC simulation may be accounted for by considering potential Herzberg-Teller vibronic coupling between the $S_1(^1A_1)$ and $S_2(^1B_2)$ excited states, as predicted from Figure x. Coupling would occur through b_2 vibrational promoter modes, as for C_{2v} symmetry

$$^1A_1 \otimes b_2 = ^1B_2. \tag{3}$$

To account for the nuclear-electronic interactions, the Herzberg-Teller expansion may be applied to the vibronic wavefunction of the S_1 state $\Psi_{S_1 j}(r, Q)$. By expanding around the equilibrium geometry Q_0, the wavefunction may be rewritten as

$$|\Psi_{S_1 j}\rangle = |\psi_{S_1}\chi_{S_1 j}\rangle + \gamma_{S_2 k, S_1 j} Q_n |\psi_{S_2}\chi_{S_2 k}\rangle, \tag{4}$$

where ψ_{S_1} is the electronic wavefunction of the S_1 state, $\chi_{S_1 j}$ is the vibronic wavefunction, Q_n is the coupling coordinate, and $\gamma_{S_2 k, S_1 j}$ is the vibronic mixing coefficient.

The strength of the vibronic coupling constant may be determined from examining the transition dipole moment. Substituting the S_1 state wavefunction from Eq. (4) into the $S_0 \rightarrow S_1$ transition dipole moment gives,

$$\mu_\alpha = \langle \Psi_{S_0} | \vec{\mu}_\alpha | \Psi_{S_1} \rangle \tag{5}$$

$$= \langle \psi_{S_0} | \vec{\mu}_\alpha | \psi_{S_1} \rangle \langle \chi_{S_0 m} | \chi_{S_1 j} \rangle + \gamma_{S_2 k, S_1 j} \langle \psi_{S_0} | \vec{\mu}_\alpha | \psi_{S_2} \rangle \langle \chi_{S_0 m} | Q_n | \chi_{S_2 k} \rangle \tag{6}$$

$$= \mu_{\alpha:0}^{S_1 - S_0} \langle \chi_{S_0 m} | \chi_{S_1 j} \rangle + \gamma_{S_2 k, S_1 j} \mu_{\alpha:0}^{S_2 - S_0} \langle \chi_{S_0 m} | Q_n | \chi_{S_2 k} \rangle, \tag{7}$$

where the term $\mu_{\alpha:0}^{S_1 - S_0} = \langle \psi_{S_0} | \vec{\mu}_\alpha | \psi_{S_1} \rangle$ represents the electronic transition moment at the ground state geometry.

Another way to describe the vibronic coupling dependence on the transition moment would be to expand the general $\mu_{\alpha:0}^{S_1-S_0}$ transition dipole function as a Taylor series in Q_n about the ground state geometry,

$$\mu_\alpha = \mu_{\alpha:0}^{S_1-S_0}\langle\chi_{S_0m}|\chi_{S_1j}\rangle + \left(\frac{\partial\mu_\alpha^{S_1-S_0}}{\partial Q_n}\right)_0 \langle\chi_{S_0m}|Q_n|\chi_{S_2k}\rangle + \dots \tag{8}$$

Comparing Eq. (??) and Eq. (8) one obtains,

$$\left(\frac{\partial\mu_\alpha^{S_1-S_0}}{\partial Q_n}\right)_0 = \gamma_{S_2k,S_1j}\mu_{\alpha:0}^{S_2-S_0}. \tag{9}$$

Therefore, the strength of the possible Herzberg-Teller transitions may be estimated, by calculating the derivative of the transition dipole moment along each b_2 normal mode coordinate. This was calculated for all xx modes in protonated anthracene along each axis, with the dipole derivatives given in the Supplementary information. Two vibrational modes were found to have large transition dipole moment slopes, va and vb. The transition strengths of the Herzberg-Teller coupled modes were computed from the harmonic frequency calculations at the ground and excited transition state C_{2v} geometries, implementing a linear variation of the dipole moment to include the first order term of the Taylor expansion about the equilibrium geometry. The calculated transitions included dominant progressions 14^16^n and 41^16^n, as shown in Figure.

By combining the information from the harmonic Franck-Condon, anharmonic resonances, and Herzberg-Teller calculations, the complete $S_0 \to S_1$ spectrum could be simulated, as shown in Figure. The simulated spectrum resembles a close match to the experimental triple resonance spectrum, validating the shallow double well framework used in this work to describe the system.

Acknowledgement

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TOC Graphic - For Table of Contents Only