Chapter 7

Summary

Several of the properties of protonated PAHs that are important to their abundance and photophysics in the interstellar medium have been explored in this thesis. The key findings are outlined below.

7.1 Structures and Reaction Pathways

In Chapter 2, the results of extensive density functional calculations on protonated benzene, naphthalene, anthracene, phenanthrene and pyrene in their ground electronic state were presented. The original goal of these calculations was to determine the relative energies for protonated PAH isomers and to find their most likely dissociation channels. Loss of a hydrogen atom or a hydrogen molecule from the protonation site were identified as the two lowest energy dissociation channels. The former channel was found to be lower in energy for molecules with a few aromatic rings, although the energy difference between these two channels is not very large. In photodissociation experiments in both [90] and Chapter 5, the mass spectra of the ion product showed the loss of 2 a.m.u., which can be explained either by the loss of H_2 or the sequential loss of two H atoms. The former channel is significantly lower in energy, and is therefore more likely. This photodissociation channel of protonated PAHs would provide a way to generate interstellar molecular hydrogen if the single photon vacuum-UV yield is comparable to that measured in the near-UV multiphoton experiments.

Along with the dissociation channels, barrier heights for unimolecular isomerization of protonated PAHs have been calculated. It was determined that with sufficient vibrational excitation, protonated PAHs may isomerize freely. This process can occur well below the dissociation energy, and is not limited by only one aromatic ring. Indeed, the proton may migrate on the outside rim of PAH molecule, 'hopping' from one carbon atom to another. On cosmic time scales, such proton hopping events would lead to a complete statistical scrambling of the different isomers, and the system would therefore lose all memory about the manner in which it was created.

One significant spectroscopic outcome of the proton mobility in protonated PAHs is a dramatically increased density of vibrational states as is described below.

7.2 Molecular Orbitals and Electronic Transitions

Chapter 3 was devoted to understanding the changes of PAH molecular orbitals upon protonation, and estimating the $S_1 \leftarrow S_0$ transition wavelengths for all isomers of a given protonated PAH. In case of the benzene molecule, all π and π^* orbitals have been considered. The protonation of one of its carbon atoms leads to a change from sp^2 to sp^3 hybridization at this site. Those molecular orbitals of protonated benzene that do not overlap with the protonation site have the same energies as in the benzene molecule; energies of the rest of the orbitals shift to lower values (that is, they are more stable) due to the stabilizing effect induced by the hybridization of the proton σ orbital with the carbon p_z orbital. The immediate result of such changes is to reduce the HOMO – LUMO gap, which leads to a red shifting of electronic absorption bands.

For larger PAHs, the changes in HOMO and LUMO orbitals were more pronounced, although it was still possible to trace their origins to changes in the orbitals of their neutral PAH precursors. Based on the orbital symmetry, the ground and the first singlet excited electronic states of protonated PAHs were assigned. Most protonated PAHs have C_s symmetry, resulting in $\widetilde{X}\ {}^1A'$ and $\widetilde{A}\ {}^1A'$ ground and first excited states.

Wavelengths for the $S_1 \leftarrow S_0$ transitions have been calculated for both neutral and protonated PAHs using the CIS method. The calculated values had a $\sim$25% discrepancy with the experimental data for neutral PAHs, a data set that was used to establish scaling factors for the excited electronic states of protonated PAHs, much as the fairly low level *ab initio* calculations of vibrational spectra must be scaled to agree with experiment. While this manipulation of the predicted energies has no rigorous physical basis, the scaled *ab initio* wavelengths were somewhat red-shifted from experimentally measured values for protonated benzene and isomer 2 of protonated anthracene while being very close to the experimental band position for isomer 1 of protonated anthracene. Such proximity of predicted and experimental wavelengths lend credence to the approach for other aromatic systems.

The predicted red shifts from the analogous transitions in neutral PAHs were some 15 – 200 nm, with a median shift of more than 100 nm. All protonated aromatic hydrocarbons except protonated benzene were found to have strong transitions at visible wavelengths. Many of the calculated values were close to broad bands in the DIB spectrum, a result that encourages the further investigation of protonated PAHs as possible DIB carriers. Although the predicted wavelengths are not sufficiently precise to make conclusions about any exact matches with known DIBs, they do serve as a relatively good guide for laboratory searches for these electronic transitions.

The calculated $S_1 \leftarrow S_0$ transition energies of protonated PAHs turned out to be very close to the predicted thermodynamic threshold for dissociation at the protonated site.

Thus, one might expect them to be photophysically unstable. The opposite behavior has been determined experimentally, as is described next.

7.3 Photostability of Protonated PAHs

Chapter 5 focuses on attempts to record the photodissociation spectra of bare protonated benzene, anthracene and pyrene. The protonation of neutral PAH molecules was performed in a hydrogen discharge source, and mass selected ions were allowed to interact with the pulses from tunable visible/UV nanosecond OPO and excimer lasers. Both the depletion of the parent ion signal and photodissociation products were detected in a reflectron time-of-flight mass spectrometer. No photodissociation by low energy laser pulses was observed, but high energy nanosecond pulses from the excimer laser were found to significantly deplete the protonated PAH ion signal.

The measurements of the photodissociation yield versus radiation intensity revealed the dissociation process to be multiphoton in nature. In the case of protonated anthracene, nanosecond photodissociation required three photons at both 193 and 248 nm. This fact allowed the nanosecond dissociation energy of protonated anthracene to be constrained to 13 – 15 eV. This is significantly higher than the predicted thermodynamic threshold of $\sim$60 kcal/mol, and shows that the lowest excited electronic states of protonated PAHs have poor Franck-Condon overlap with states that lead to C–H bond cleavage.

Rapid internal conversion and intramolecular vibrational energy redistribution processes are likely responsible for the high photostability observed for protonated PAHs. Thus, even small systems of this type have an excellent probability of surviving the UV radiation field in diffuse and translucent interstellar clouds. This is another factor in support of the presence of protonated PAHs in the ISM.

7.4 Visible Spectrum of Protonated Anthracene

The photodissociation spectrum of clusters of protonated anthracene with water was recorded in the visible wavelength region in Chapter 6. Protonated anthracene served as the chromophore, with the cluster method serving to circumvent the high photostability of bare protonated PAHs and enable single photon experiments. Although the cluster spectrum is not identical to that of bare protonated anthracene, the expected shifts are small and the overall nature of the spectrum is expected to be preserved.

The measured spectrum had two very broad ($\sim$1100 cm^{-1} FWHM) absorption bands that were assigned to isomers 1 and 2 of protonated anthracene based on the *ab initio* predictions from Chapter 3. The widths of these bands were quite similar to that measured for protonated benzene in a continuous wave ion trap dissociation experiment [90]. For both species, the broadening may well arise from the extremely high density of vibrational states induced by the proton mobility in such systems, although the degree of internal vibrational excitation in the clusters has not been determined and must be considered as well.

While there is a strong DIB feature near the band origin for the isomer 1 of protonated anthracene, no such close features have been seen in the vicinity of the expected band origin for the isomer 2. Furthermore, the widths of the observed bands were an order of magnitude larger than widest DIB features currently known. Thus, it is unlikely that protonated anthracene is a DIB carrier unless the conditions of our experiment are vastly different than those in the ISM. For larger PAHs, the vibrational density of states and hence, the vibrational energy redistribution rates would be even larger, so the general case for protonated PAHs as DIB carriers would seem to be weakened by our results.

7.5 Conclusions

Perhaps the most important result of this thesis is the high measured photostability of protonated PAHs under nanosecond laser pulse illumination. Thus, if they are created efficiently in the ISM as is suggested by laboratory kinetics experiments [75,82], the chances of their removal by UV radiation are very small. This provides another strong argument in favor of the presence of protonated PAHs in the ISM.

The measured photodissociation spectrum of protonated anthracene – water cluster had very broad absorption bands, however, with only one being in even reasonable proximity to a known DIB. This indicates that protonated anthracene, and by extension the entire class of small protonated PAHs, are not the carriers of the diffuse interstellar bands. The observed spectral widths can naturally be explained by the proton mobility in protonated PAHs.

7.6 Future Research Directions

To further investigate protonated PAHs and to clarify unresolved questions raised by this thesis, a number of experiments or observations come to mind. In the laboratory, more spectra of protonated PAHs should be recorded in the same fashion as that outlined in Chapter 6. This involves measuring the spectrum of protonated anthracene at shorter wavelengths to determine whether isomer 9 contributes to the blue absorption seen, as well as recording the spectra of other protonated PAHs (e.g. protonated naphthalene, phenanthrene, pyrene, and coronene). Protonated coronene would be an especially interesting species to study because it has a larger size, but like benzene, has only one stable isomer. The relative proportion of ring fusion hopping steps needed to scan the PAH periphery is also rather larger than in the small protonated PAHs studied here, and the effect of this on the excited state dynamics could play an important role in the spectral broadening of large protonated PAHs in the ISM.

To minimize the potential broadening due to internal vibrational excitation of protonated PAHs in the discharge source, additional experiments should be performed at cryogenic temperatures. The best way to do this would be to perform visible/UV spectroscopy of protonated PAHs in liquid helium nanodroplets. In such an environment, protonated PAHs would have a temperature 0.38 K, along with a minimal amount of perturbation by the surrounding helium atoms which would permit a better measurement of the band origin positions of the electronic absorption bands. This would be a challenging experiment to perform, and as an easier first step, protonated PAHs could be deposited into rare gas matrices (argon or neon). In this case, the proton may well be confined to only one carbon atom. As a result, the absorption band profiles may be quite different from those in the gas phase or in nanodroplets.

If protonated PAHs do exist in diffuse interstellar clouds, they may produce DIBs that are wider than those measured with current astronomical surveys that are limited to a maximum spectral width of 50 Å for robust feature extraction from complex stellar spectra. Targeted DIB surveys can be conducted that are sensitive to even wider DIB features. Another interesting trend to follow would be to measure the dependence of the DIB width versus environment. For example, DIB profiles from different parts of the same diffuse cloud that are at different temperatures or exposed to different levels of UV radiation could be compared in order to draw conclusions about the rigidity/stability of the absorbing species.

Protonated PAHs have relatively large permanent dipole moments and therefore should be detectable via pure rotational techniques. Indeed, laboratory microwave spectra should in principle be measurable for a wide range of protonated PAHs, including those that are deuterated or that contain heteroatoms. The data obtained may be used in the search for protonated PAHs in the ISM by radio astronomy tools, and the measured frequencies may be compared to those predicted theoretically for improved structure determinations. At the highest resolution achievable, it may even be possible to observe spectral line shifts or splittings that would provide insight into the importance of proton mobility in the electronic ground state of protonated PAHs.

Theoretically, the distribution of the different isomers of protonated PAHs in actual interstellar environments can be calculated based on their relative energies, proton mobilities, UV excitation and IR emission rates. This would permit more accurate estimates of intensity ratios for different protonated PAH isomers that could be compared to astronomical observations. Other effects such as deuteration, dissociative electron recombination, and chemical reactions may be considered as well.