Photophysical Properties of Protonated Aromatic Hydrocarbons

Thesis by

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Abstract

Diffuse interstellar bands (DIBs) were first observed in the visible region of the electromagnetic spectrum in the 1920s, with over a hundred features now discovered out to near-IR wavelengths. Since their initial discovery, many attempts have been made to identify the species that are responsible for the DIBs. Polycyclic aromatic hydrocarbons (PAHs) and their derivatives are among the likely candidates for DIB carriers, as demonstrated by the intense unidentified IR emission bands from 3.3 – 11.3 μm that strongly point to their presence of aromatic species in the interstellar medium (ISM). The $S_1 \leftarrow S_0$ electronic transitions for small PAHs lie in the near-UV, however, so only large neutral PAHs with 30+ carbon atoms can absorb at the visible wavelengths characteristic of the DIBs. In diffuse clouds and dense cloud envelopes that are exposed to the harsh interstellar radiation field, molecules are expected to be ionized. Positively charged PAHs are predicted to acquire a hydrogen atom to form thermodynamically stable protonated PAHs in diffuse clouds. These are closed-shell molecular ions with electronic transitions that are red-shifted compared to neutral PAHs, so even small protonated PAHs can, in principle, produce absorption bands in the visible.

Little is known about the photophysical properties of these compounds, however, so this thesis presents an experimental and theoretical analysis of two-, three-, and four-ring protonated PAHs. Theoretically, density functional theory calculations using the B3LYP

functional were used to study protonated PAHs in their ground electronic state. In particular, the energetics of the various potential protonated PAH isomers were calculated along with the proton tunneling or hopping barriers between them. The relative energies of the lowest lying photodissociation pathways were also calculated. It was found that the different isomers of protonated PAHs likely exist in thermodynamic equilibrium under interstellar conditions, thanks to the moderate ($\sim$15 – 20 kcal/mol) barriers to proton migration. Photochemically, the loss of an H atom or H_2 molecule from a protonation site were identified as the most favorable dissociation channels for protonated PAHs. The H and H_2 loss channels were found to be within a few kcal/mol of each other in energy, and about 45 – 60 kcal/mol above the ground state, depending on the parent molecule and isomer.

Following the ground state geometry optimizations and energy calculations, the Configuration Interaction Singles (CIS) method was used to estimate the positions of the electronic transitions for protonated PAHs. Depending on the PAH and isomer, red shifts up to 150 nm were predicted even for small systems, i.e., protonated naphthalene, anthracene, phenanthrene and pyrene. This places the $S_1 \leftarrow S_0$ transitions of essentially all protonated PAHs well into the DIB wavelength region.

In order to investigate these predictions experimentally, a robust hydrogen discharge source was designed to produce protonated PAHs. Laser photodissociation of protonated PAHs was first studied with an excimer laser/reflectron time-of-flight mass spectrometer under ultrahigh vacuum conditions that mimic those in the ISM. Small protonated PAHs were found to be very photostable. Indeed, it was determined that nanosecond pulse length photodissociation is multiphoton even at short wavelengths (193 nm). For protonated anthracene, the dissociation limit was estimated to be 13 – 15 eV, which is much higher than the predicted thermodynamic threshold of 2.5 – 3.0 eV. This was attributed to the onset of

rapid intramolecular vibrational relaxation (IVR) upon electronic excitation.

Thanks to the excellent photostability of protonated PAHs, a cluster photodissociation approach was used to locate the electronic transitions of protonated anthracene between 420 and 540 nm. Clusters with water molecules were produced in a two-valve mixing discharge source. Visible photodissociation spectrum of these clusters was recorded using a novel optical parametric oscillator (OPO) with low beam divergence. The OPO utilizes a hybrid matching scheme involving BBO type I and II crystals in a rotated prism cavity. The observed protonated anthracene absorption bands are very wide (20 nm FWHM) – too wide to account for the DIBs. Again, this spectral broadening most likely results from rapid IVR induced by the high density of states in protonated PAHs. Such strong, wide bands may be important contributors to the overall visual extinction in the diffuse ISM and should efficiently produce infrared emission such as that seen in the Unidentified Infrared emission features, or UIRs.

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