Excited state dynamics of protonated molecules.

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Protonated molecules have the same number of electrons than their neutral homologues, thus at first glance the electronic structure of both species should be quite similar.

How good is this simple assumption?

Up to very recently nearly nothing was known on the excited state properties of protonated species in gas phase, except two papers in 1976[1,2] that report low resolution spectra with no dynamical information. Since 2004, some information has been gathered and some trends are beginning to emerge but the picture is still not clear[3-5].

The contribution will concentrate on simple Polycyclic Aromatic Hydrocarbons (PAH). As attachment of highly abundant H atoms to PAH^+ was measured to be fast, the efficient formation of $(PAH)H^+$ in the interstellar medium has been hypothesized[6]. So far, no comparison of the DIBs (diffuse interstellar bands) with electronic spectra of $(PAH)H^+$ could be made, as the required laboratory spectra were lacking. However, by comparison with the isoelectronic, closed-shell neutral PAH molecules, small $(PAH)H^+$ molecules were not expected to have low-lying electronic states giving rise to absorption in the visible range.

Our experimental set up allows us to characterize the excited states of protonated aromatic molecules at low temperature. For linear $(PAH)H^+$ the electronic absorption is in the visible spectral region, but the transition energy does not decreasing with the size of the system as in neutral molecules but shows an odd/even alternation with the number of aromatic rings[7].

Although the puzzle is far from being complete, with these few pieces some speculative models are beginning to emerge.

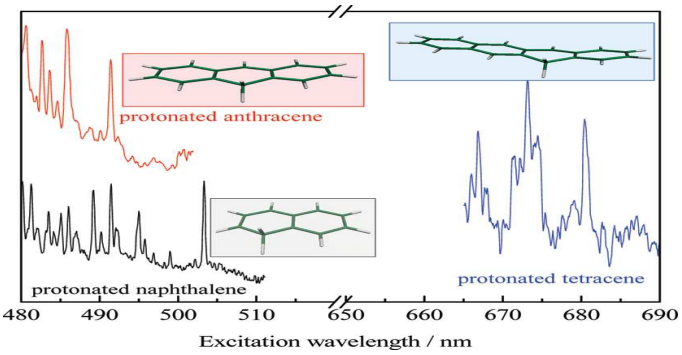

Figure 1: Photofragmentation spectra of protonated linear PAHs.

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