

Electronic Structure Calculations on Excited States of Polycyclic Aromatic Hydrocarbon Ions

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Over the past several years, with work from our group and others, it has become possible to perform electronic structure calculations on excited states of large radicals and ion radicals, of relevance to interstellar chemistry. These calculations, based on time-dependent density functional theory within the adiabatic approximation, are often capable of yielding excitation energies within about 0.3 eV of experiment. Oscillator strengths are generally in qualitative agreement with experiment. There are still some aspects of the theory that could benefit from improvement but this is a qualitative step forward from the situation a few years ago when reliable excited states calculations on large molecules were simply not possible.

The combination of TDDFT excitation energy and oscillator strength calculations is often enough to permit assignment of electronic transitions observed in laboratory spectra. We shall show examples of calculations of this type that we have performed on the radical ions of perylene, terrylene and quaterrylene. These species have recently been studied experimentally at NASA Ames, and our calculations permit unambiguous assignment of the strongest spectral feature. Other systems that we have looked at are PAH ions that are possible candidates as carriers for the diffuse interstellar bands, based on their observed stability in combustion systems, but for which no laboratory spectra is yet available. Here our calculations can help to indicate whether or not experimental study is justified by predicting whether or not strong transitions are expected in the visible.

Beyond numbers of reasonable accuracy, the other important feature of calculations of this type is that they can sometimes provide thought-provoking insight into the origin of the key electronic transitions in reactive species, and why they are strong (or weak). This is done by visualizing the electronic transition as a rearrangement of electron density, which can then be related to the electronic structure of the species. We shall illustrate this possibility by explaining the origin of the strong oscillator strength in the large PAH ions mentioned above, and explaining the striking link between features of the electronic spectrum of the neutral, positive and negative ions. Perhaps future calculations will help to stimulate new thinking about carbon clusters in the interstellar medium, and their link, or lack of it, to spectral measurements such as the diffuse interstellar bands.