ON THE ELECTRONIC SPECTROSCOPY OF CLOSED SHELL CATIONS DERIVED FROM RESONANCE STABILIZED RADICALS: INSIGHTS FROM THEORY AND FRANCK-CONDON ANALYSIS

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Recent attention has been directed on closed shell aromatic cations as potential carriers of the diffuse interstellar bands. The spectra of mass-selected, matrix-isolated benzylium and tropylium cations were recently reported [Nagy, A., Fulara, J., Garkusha, I. and Maier, J. P. (2011), *Angew. Chem. Int. Ed.*, 50: 3022-3025]. The benzylium spectrum shows an extended progression in a low frequency (510 cm^{-1}) ring distortion mode. Modeling of the benzylium spectrum using (TD)DFT and MCSCF-PT2 methods in concert with multidimensional Franck-Condon (FC) analysis is found to yield excellent agreement with the experimental spectrum. We extended this analysis to larger (2 and 3 ring) PAH cations derived from resonance stabilized radicals, which are predicted to show strong $\mathrm{S}_0 \rightarrow \mathrm{S}_n$ transitions in the visible region. The FC progression is significantly quenched in the larger species, and our results for 1-napthylmethylium are in excellent agreement with very recent experiments [Nagy, A., Fulara, J., and Maier, J. P. (2011), *J. Am. Chem. Soc.*, 133, 19796]. Since carriers of the DIBs should exhibit spectra dominated by a single vibronic transition, our results demonstrate that closed-shell cations may present spectra with the required properties. Furthermore, the calculated ionization energies of a range of CSCs were found to be in the 13-14 eV range, consistent with variations in behaviour of the DIB carriers with respect to various astrophysical environments.