Cold gas-phase spectroscopy of aromatic three-membered-ring carbon and silicon compound ions: correlation between splitting of degenerate ππ* transitions and excited-state structures

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Hückel 2π aromaticity, found in three-membered-ring carbon/silicon cations, is characterized by a π orbital and two degenerate π* orbitals (Fig. 1). UV-vis absorption spectrum of $(C_3Ph_3)^+$ in solution, firstly reported over 60 years ago, exhibits several broad bands (Fig. 2a).[1] However, assignments of these bands still remain unresolved, hiding how the degenerate ππ* transitions are reflected on electronic spectra. In this study, we performed ultraviolet photodissociation (UVPD) spectroscopy of $(C_3Ph_3)^+$ isolated in a cold (~10 K) ion trap.[2] This study reveals the splitting of the degenerate ππ* transitions in the spectrum and its correlation with the excited-state structures.

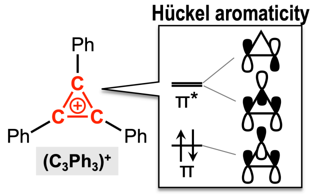

Fig. 1. Structure of target compound and π and π* orbitals at the three-membered-ring.

UVPD spectrum of $(C_3Ph_3)^+$, generated by electrospray ionization of bromide precursor (C_3BrPh_3), exhibited several broad bands even under the cold gas-phase conditions (Fig. 2b). This result indicates that the broad profile is intrinsically determined by excited-state dynamics of $(C_3Ph_3)^+$. Actually, the observed band profile cannot be explained by the degenerate ππ* transitions (Fig. 2c), which is predicted in the vertical transition scheme. DFT calculations suggested that the adiabatic transition energies of the two ππ* states (S_1, S_2) are significantly deviated (ΔE > 5000 cm^{-1}; Fig. 2d), well explaining the spectrum and unveiling the crucial contribution of structural relaxations on the excited-state potential surfaces. In the presentation, we further extend the study to other three-membered-ring carbon/silicon compound ions, $(C_3Ph_2OH)^+$ and $[Si_3(Eind)_3]^+$.[3]

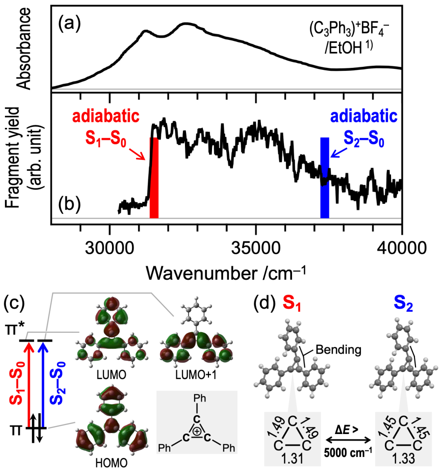

Fig. 2. (a) UV spectrum of $(C_3Ph_3)^+BF_4^-$/EtOH.[1] (b) UVPD spectrum of $(C_3Ph_3)^+$. Bar spectrum represents calculated adiabatic transition energies. (c) Kohn-Sham orbitals of ππ* transitions. (d) Potential minimum structures of $(C_3Ph_3)^+$ at S_1 and S_2.

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