SLOW ELECTRON VELOCITY MAPPING FOR THE STUDY OF CATIONIC STATES OF AROMATIC MOLECULES

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Slow electron velocity mapping (SEVM), a variant of velocity map imaging (VMI), has been implemented to study the vibronic levels of ionized aromatic molecules. The technique of velocity map imaging has been shown to be a powerful method and has gained enormous impetus since its development by Parker et al.\(^a\) SEVM is a versatile photoelectron spectroscopy method that reveals the low energy ionic vibrational structure and also retains the VMI capability to measure angular distributions of the photoelectron. Photoelectron images of the cationic vibrational structure and their angular dependence reflect the character of both the final state and the neutral level from which ionization occurs. Hence, from the photoelectron energies and angular distributions, information on the vibronic character of levels in the first neutral excited state (S1) and the cation state (D0) of molecules can be obtained by resonantly enhanced multiphoton ionization (REMPI). Phenylacetylene (PA) and fluorene were studied and probed using REMPI excitation schemes and the SEVM technique. In the case of PA, the angular distribution of the electrons correlated with ionization via the 6a mode involving the breathing of the benzene ring shows a distinct mode-dependent effect, illustrating the technique. However, in the case of fluorene, only the vibrationless level and stretching vibrational modes in the cation state showed Franck-Condon activity and had nearly isotropic photoelectron distributions. Future work on polycyclic aromatic hydrocarbon systems related to fluorene, such as carbazole, dibenzofuran, and dibenzothiophene is planned.

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