

SLOW PHOTOELECTRON VELOCITY-MAP IMAGING (SEVI) SPECTROSCOPY OF CRYO-COOLED ANIONS

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Slow photoelectron velocity-map imaging spectroscopy of cryogenically-cooled anions (cryo-SEVI) is a powerful technique for elucidating the vibrational and electronic structure of exotic neutral species. SEVI is a high-resolution variant of anion photoelectron imaging that yields spectra with energy resolution as high as 1 cm^{-1} . The preparation of cold anions eliminates hot bands and narrows rotational envelopes, enabling the acquisition of well-resolved photoelectron spectra for complex and spectroscopically challenging species.^{1,2}

Recently, cryo-SEVI has been applied as a spectroscopic probe of transition state dynamics on neutral reactive surfaces, through photodetachment of a bound anion similar in geometry to the desired transition state. In the benchmark $\text{F} + \text{H}_2$ reaction, we probe the transition state region through detachment of FH_2^- and directly observe new reactive resonances. Comparison to new theory allows for the assignment of resonances associated with quasi-bound states of the transition state and products.³ We also report spectra of the $\text{F} + \text{CH}_3\text{OH}$ hydrogen abstraction reaction through photodetachment of the CH_3OHF^- van der Waals cluster. We gain insight into the energetics and vibrational structure of transient complexes along the reaction coordinate of this complex polyatomic system.⁴

Finally, we report a new cryo-SEVI study of vinylidene (H_2CC), a high energy isomer of acetylene, which is accessed directly through detachment of H_2CC^- . We find spectroscopic evidence that the isomerization of vinylidene to acetylene is highly state-specific, with excitation of the ν_6 in-plane rocking mode resulting in appreciable tunneling-facilitated mixing with highly vibrationally excited states of acetylene.⁵

¹Hock *et al.* *JCP* **137**, 244201 (2012); ²Weichman *et al.* *PNAS* **113**, 1698 (2016); ³Kim *et al.* *Science* **349**, 510 (2015);

⁴Weichman *et al.* *Nat. Chem.* **9**, 950 (2017); ⁵DeVine *et al.* *Science* **358**, 336 (2017)