## 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  $1 \text{ cm}^{-1}$ . 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.<sup>1,2</sup>

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  $F + H_2$  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.<sup>3</sup> We also report spectra of the  $F + CH_3OH$  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.<sup>4</sup>

Finally, we report a new cryo-SEVI study of vinylidene (H<sub>2</sub>CC), a high energy isomer of acetylene, which is accessed directly through detachment of H<sub>2</sub>CC<sup>-</sup>. We find spectroscopic evidence that the isomerization of vinylidene to acetylene is highly state-specific, with excitation of the  $\nu_6$  in-plane rocking mode resulting in appreciable tunneling-facilitated mixing with highly vibrationally excited states of acetylene.<sup>5</sup>

<sup>1</sup>Hock *et al. JCP* **137**, 244201 (2012); <sup>2</sup>Weichman *et al. PNAS* **113**, 1698 (2016); <sup>3</sup>Kim *et al. Science* **349**, 510 (2015); <sup>4</sup>Weichman *et al. Nat. Chem.* **9**, 950 (2017); <sup>5</sup>DeVine *et al. Science* **358**, 336 (2017)