HIGH RESOLUTION ANION THRESHOLD PHOTODETACHMENT SPECTROSCOPY BY VELOCITY MAP IMAGING OF SLOW PHOTOELECTRONS

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We have combined Velocity Map Imaging (VMI) and threshold photodetachment (TPD) to obtain a new method for high resolution anion photoelectron spectroscopy. VMI is used to detect slow photoelectrons, generated by photodetachment in a tunable laser. With a maximum kinetic energy of the detected photoelectrons of ca. 10-50 meV and an energy resolution of better than $\Delta E/E$=5 %, we achieve an ultimate resolution of a few cm^{-1}. The sensitivity of the technique is guaranteed by the collection efficiency of VMI, which is close to 100 %, and by the possibility of detecting photoelectrons with low but non-zero kinetic energy, whereby limitations by the Wigner threshold law can be avoided. This renders VMI-TPD spectroscopy more generally applicable than conventional anion zero kinetic energy photoelectron spectroscopy while maintaining the high resolution.

We have applied the new technique to the investigation of Cl-D_2. Franck-Condon overlap between the wave functions of anion and neutral allows the investigation of the shallow potential well located near the transition state of the Cl+H_2 benchmark chemical reaction. This well is deep enough to contain a low number of van der Waals bound states and has been observed in previous photoelectron studies carried out in our lab. At a resolution of ca. 8 meV, these spectra revealed an increased linewidth of Cl-D_2 vs. Cl-H_2. This finding was explained by hindered rotor structure that is observable only in the deuterium cluster but could not be fully resolved by conventional PES. The increased resolution of VMI-TPD allows the resolution of this, and potentially even finer, structure and will help toward a complete understanding of the dynamics of this reaction.