High-resolution vibrational spectroscopy of transient species is important for determining their molecular structures and understanding their chemical reactivity. However, the low abundance and high reactivity of molecular radicals pose major challenges to conventional absorption spectroscopic methods. The observation of dipole-bound states (DBS) in anions extend autodetachment spectroscopy to molecular anions whose corresponding neutral radicals possess a large enough dipole moment (>2.5 D). However, due to the difficulty of assigning the congested spectra at room temperature, there have been only a limited number of autodetachment spectra via DBS reported. Recently, we have built an improved version of a cold trap coupled with high-resolution photoelectron imaging. The first observation of mode-specific autodetachment of DBS of cold phenoxide have shown that not only vibrational hot bands were completely suppressed, but also rotational profile was observed. The vibrational frequencies of the DBS were found to be the same as those of the neutral radical, suggesting that vibrational structures of dipolar radicals can be probed via DBS. More significantly, the DBS resonances allowed a number of vibrational modes with very weak Frank-Condon factors to be “lightened” up via vibrational autodetachment. Recently, our first high-resolution vibrational spectroscopy of the dehydrogenated uracil radical, with partial rotational resolution, via autodetachment from DBS of cold deprotonated uracil anions have been reported. Rich vibrational information is obtained for this important radical species. The resolved rotational profiles also allow us to characterize the rotational temperature of the trapped anions for the first time.

Reference