

CIVP SPECTROSCOPY OF PYRIDINIUM IONS: SURPRISING PERTURBATION BY TAG MOLECULES

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In cryogenic ion vibrational predissociation (CIVP) spectroscopy, the tag's influence on the spectrum is an important consideration. Whereas for small ions, several studies show that the tag effects can be significant, these effects are less understood for large ions, or for large numbers of tags. Nevertheless, common assumptions are that i) if the investigated molecular ion is large enough, the perturbations arising from the tag are small, and ii) the more weakly bound the tag is, the less it perturbs the CIVP spectrum. Under these assumptions, CIVP spectra effectively represent infrared (IR) absorption spectra of the free molecular ion.

In the Chen group, we have recently started studying IR spectra of large ions in the gas phase.[1] To understand the complicated IR fingerprints of those systems, we employ several theoretical methods. Density functional theory is a common tool for calculating IR spectra. An alternative approach is to calculate the IR spectrum by the Fourier transform of the dipole moment autocorrelation function from a classical trajectory,[2] e.g., from Born-Oppenheimer molecular dynamics (BOMD). In contrast to the harmonic approximation, BOMD includes vibrational couplings and conformational sampling at a given temperature. Having observed unexpected splittings in otherwise unproblematic CIVP spectra of some tagged ions, we calculated IR spectra by BOMD simulations with the semi-empirical GFN-xTB methods.[3,4] Our simulations indicate that mobility among the more weakly bound tags leads to the surprise splittings. We compared the behavior of two tags commonly used in CIVP spectroscopy (H_2 and N_2) with a large pyridinium cation. Our experimental results surprisingly show that the more weakly bound tag can, under the appropriate circumstances, perturb the CIVP spectra more than the more strongly bound tag, by not just shifting, but also splitting the observed bands.

References:

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