DIRECT EXCITATION OF THE REACTION COORDINATE: OVERTONE-INDUCED PREDISSOCIATION OF THE HYDROXYMETHYL RADICAL

HANNA REISLER, MIKHAIL RYAZANOV and CHIRANTHA P. RODRIGO, *Department of Chemistry, University of Southern California, Los Angeles, CA, 90089-0482*.

The overtone-induced vibrational predissociation of the hydroxymethyl radical is achieved following excitation of the radical to the third O-H stretch overtone. The excited O-H stretch is also the bond that breaks; i.e. overtone excitation is in the reaction coordinate. The production of H atoms takes place via tunneling through the barrier to the H + formaldehyde channel. H-atom photofragment yield spectra in the region of the third overtone reveal two mixed bands with contributions from the third OH overtone and a combination band comprised of two quanta of OH stretch and one quantum of CH asymmetric stretch. Using velocity map imaging, sliced images of H-atom products are obtained with kinetic energy resolution sufficient to reveal the vibrational structure in the formaldehyde co-fragment. As expected, most of the formaldehyde molecules are born without vibrational excitation but some exhibit excitation in other modes, such as wagging and CO stretch. The rotational contours of the vibrational bands are well described by temperatures in the range 100-150 K. Slice imaging allows scanning the pump laser while monitoring H fragments in selected kinetic energy ranges, and in this way it is demonstrated that all the observed vibrational levels of formaldehyde have their parentage in the hydroxymethyl radical. The barrier to isomerization to methoxy is comparable to the barrier to direct dissociation and the role of isomerization is investigated by using partially deuterated radicals.