UNIMOLECULAR DISSOCIATION DYNAMICS OF HIGHLY VIBRATIONALLY EXCITED MOLECULES BY TIME- AND FREQUENCY RESOLVED SPECTROSCOPY: THE CASE OF HOCl AND HOBr.

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We use pulsed, infrared-visible double-resonance overtone excitation to promote HOCl and HOBr molecules to highly excited vibrational states above the HOX $\rightarrow$ HO+ X dissociation threshold, and laser induced fluorescence (LIF) to detect the resulting OH fragments. The initially prepared states are well-characterized, individual rotational levels of high OH stretching overtones of the ground potential energy surface. The simultaneous use of frequency-resolved and time-resolved methods, and the large number of individual rotational states investigated give highly detailed information on the unimolecular dynamics of these molecules. Frequency resolved spectra reveal weak coupling of the OH vibrational coordinate to the remaining vibrational modes. Analysis of the couplings shows that for the lower overtones ($\mathrm{v_{OH}} = 6, 7$) only anharmonic terms up to order four play a significant role. This weak coupling, in turn results in slow and inefficient redistribution of the vibrational energy (IVR) and consequently points to IVR limited unimolecular dissociation. Time-resolved measurements of the OH product appearance give the dissociation rate of each individual initially prepared state. The measured rates are extremely slow at $\mathrm{v_{OH}} = 6$, in the range of $2 \times 10^6 - 3 \times 10^8$ s^{-1}, three to five orders of magnitude slower than the calculated RRKM rate, and increase steadily with $\mathrm{v_{OH}}$, almost but not quite reaching the statistical limit at $\mathrm{v_{OH}} = 8$. The rates measured for a given initially prepared vibrational state show extreme dependence on the rotational quantum number chosen, with up to ten-fold changes observed upon changing J by one unit. These large "fluctuations" of the rates are more pronounced at $\mathrm{v_{OH}} = 6$, where the rates are distributed over more than two order of magnitude, and become progressively less dramatic with increasing $\mathrm{v_{OH}}$.
We show in the next talk how the slow IVR rate and the peculiar features of the observed unimolecular dissociation rates can be related with one another and how the shape of the potential energy surface is likely responsible for them.