THE SPECTROSCOPY AND IVR DYNAMICS OF HOCl IN THE $v_{\rm OH} = 6$ REGION PROBED BY INFRARED-VISIBLE DOUBLE RESONANCE OVERTONE EXCITATION.

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We use infrared-visible double resonance overtone excitation to promote HOCl molecules to single, well-characterized rotational levels of high OH stretching states just above the HOCl $\rightarrow$ HO + Cl dissociation threshold on the ground potential energy surface. Double resonance spectra are monitored by laser induced fluorescence (LIF) detection of the OH dissociation products. We present here the results obtained in the $6\nu_1$ region of $HO^{35}Cl$ where we have studied states with J ranging from 4 to 25, K_a from 0 to 5 and energy up to 300 cm^{-1} above the dissociation threshold. In the spectra for $K_a = 0 - 3$ states, the zeroth-order ($v_{\rm OH}$, v_θ, $v_{\rm OCl}$) = (6,0,0) level is split by mixing with a nearby dark state. Because the two states have very different A rotational constants, their separation increases with K_a, but the effects of the mixing remain observable in the spectrum up to $K_a = 3$. Preliminary results from $HO^{37}Cl$ shows the same pattern, except for the perturbing state energy being lowered by the isotope effect. Analysis of the rotational constants and isotope shift allows us to identify the perturbing state as (4,4,2). The lack of further major perturbations compared to the average density of states allows us to infer that most of the matrix elements for couplings between (6,0,0) bright state and other dark states are less than 0.1 cm-1. The average rate of IVR implied by these matrix elements is 2.5×10^9 s, which is 2 orders of magnitude slower than the unimolecular dissociation rate calculated by the statistical adiabatic channel model (SACM). This implies that IVR is likely to be the rate limiting step in the unimolecular dissociation process. The dissociation rates we observe from single eigenstates of the parent molecule are distributed over more than two orders of magnitude and are, on average, three orders of magnitude slower than the SACM predicted rate.