A TIER-MODEL OF IVR LIMITED UNIMOLECULAR REACTIONS: THE UNIMOLECULAR DISSOCIATION OF HIGHLY VIBRATIONALLY EXCITED HOCl AND HOBr.

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We present a simple model to interpret the vibrational energy redistribution (IVR) and unimolecular dissociation dynamics of HOCl and HOBr prepared in highly excited OH stretching overtones. We use an approximate vibrational Hamiltonian that has the simplest form compatible with experimental observations and existing *ab initio* calculations of wavefunctions and potential energy surface. While such a model cannot reproduce exactly the experimental results, it does reproduce well their overall features and links them to weak vibrational coupling. The slow dissociation rates observed arise from the slow rate of IVR out of the initially prepared state, resulting from weak coupling. The pure OH stretching overtones are, in this sense, extreme cases, since all the vibrational energy is stored initially in the mode that is least coupled with the dissociation coordinate. The large state-to-state fluctuations of the rates across the range of rotational states investigated are also a necessary consequence of the slow IVR rate combined with the rotational dependence of the vibrational states' relative energy. Faster dissociating states can become "accidentally" nearly-resonant with the bright state at particular J, K values and the resulting mixing, even if small, can be sufficient to increase the observed dissociation rate dramatically. Accordingly, the increasing of the coupling with the number of quanta of OH stretch in the initially excited state results in faster dissociation rates and smaller fluctuations for the higher overtones. Inspection of the $\mathrm{r_{OH}} - \theta$ cut of the potential energy surface reveals that at the energy of $\mathrm{v_{OH}} = 7$ and 8, the highly anharmonic path that leads to the HClO isomer becomes accessible. This suggests that it is mostly the stretch-bend coupling of the OH oscillator that controls the IVR rate and, in turn the unimolecular dissociation dynamics from the initially prepared state. Comparison with the calculated wavefunctions from the Bowman group confirms the increasingly important contribution of the isomer with increasing initial excitation.