VIBRATIONAL PREDISSOCIATION DYNAMICS OF HF-COMPLEXES AT v_{HF}=3

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We report the lifetimes and rotational distributions of HF products from the vibrational predissociation (VP) of the ArHF and Ar_3HF at v_{HF}=3 by dispersing laser induced fluorescence. The product state distribution of these two complexes has shown that the excess energy resulting from VP ($\Delta v = -1$) is partioned primarily into HF($v = 2$) product rotation. The distribution is extremely sharply peaked near the highest energetically accessible rotational channel ($J^{'}$=13 for ArHF(3000) and $J^{'}$=12 for Ar_3HF). The lifetimes of ArHF(3000) and (3110) states are found to be 4.8×10^{-6} sec and 8.9×10^{-6} sec respectively. Much shorter vibrational predissociation lifetime of 3 nsec is determined for Ar_3HF at $v = 3$, revealed from the Lorentzian component of 60 MHz of the Voigt profile. The correlation of VP lifetime and red-shift for HF-complexes at $v = 3$ will be compared to that at $v = 1$. At the fundamental valence excitation ($v_{HF} = 1 \leftarrow 0$), the VP rate varies as the square of the frequency red-shift.[a] At the present second overtone excitation ($v_{HF} = 3 \leftarrow 0$), based upon $(HF)_2$, N_2HF and Ar_3HF results, the VP rate varies more dramatically as the cube of the frequency red-shift. This suggests that a relatively complex model is required to fully account for the enhancement of VP rates observed for HF-complexes at $v = 3$.

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[a] R. E. Miller, *Science* **240**, 447 (1988)