VIBRATIONAL PREDISSOCIATION OF WEAKLY BONDED HF COMPLEXES: AN EXPERIMENTAL STUDY WITH FT-IR SPECTROSCOPY

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A high-sensitivity FT-IR spectrosmeter operating at the range of 6000-8000 cm^{-1} was assembled by using a liquid nitrogen-cooled germanium detector and a home-made Michelson interferometer. The valence excitation of HF containing species is carried out with a 40W intracavity Ti-sapphire ring laser.[a] With the detection of HF ν = 2 $\leftarrow$ 0 emission, this method is suitable for analyzing the product distribution for vibrational predissociation of hydrogen bonded HF complexes. The rotational distribution of product HF can be easily measured with our spectral resolution of 1.5 cm^{-1}. The dependence of predissociation dynamics upon the different bound states of Ar-HF and N_2-HF are under further investigation.

The intermolecular potential energy of N_2-HF was calculated using CCSD(T) method with Dunning's tripple-ζ basis function. With HF valence coordinate lying between 0.85 and 1.25 $\AA$, the calculation of vibration-averaged interaction potential was achieved perturbatively through second order using Herman's analytic wavefunction.[b] The vibrational frequncies of intermolecular modes was determined through further adiabatic approximation. the dissociation energy D_0 is predicted to be 370 cm^{-1}, in agreement with the experimental result of 398±2 cm^{-1}.[c] Eighty-seven percent of vibrational redshift at ν_{HF} = 3 level is shown to occur as first order perturbation of the interaction potential.

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[a] H. -C. Chang and William Klemperer, J. Chem. Phys. 98, 2497(1993).

[b] R. M. Herman, R. H. Tipping, and S. Short, J. Chem. Phys. 53, 595(1970).

[c] R. J. Bemish, E. J. Bohac, M. Wu, and R. E. Miller, J. Chem. Phys. 101, 9457(1994).