REASSIGNMENT OF THE 11537 cm^{-1} BAND OF HYDROGEN FLORIDE DIMER AND OBSERVATION OF THE INTERMOLECULAR COMBINATION MODE $3\nu_1 + \nu_4$

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We report a high resolution re-examination of K=1 subband of $3\nu_2+\nu_6$ and the $3\nu_1+\nu_4$ (K=0) combination mode of $(HF)_2$ by intracavity laser induced fluorescence. The fluorescence is monitored with a germanium detector which collects only first overtone emission (2→0) of HF fragments. The band centered at 11537 cm^{-1} is shown to be K=1 of $3\nu_2 + \nu_6$ [previously assigned to K=1 of $\nu_1 + 2\nu_2$, *J. Chem. Phys.* **100**, 1 (1994)]. Hydrogen interchange tunneling is almost completely quenched ($\Delta\nu_t$=0.6 GHz). Vibrational predissociation rate is rapid (4.5 GHz) but half that of 10 GHz observed in $3\nu_2$. The combination mode $3\nu_1 + \nu_4$ is recorded with band origins of 11402.889(4) and 11402.868(8) cm^{-1} and rotational constants of 0.21639(17) and 0.21704(15) cm^{-1} for the two tunneling components A^+ and B^+, respectively. The frequency of this intermolecular vibration, ν_4, upon $3\nu_1$ excitation is 129.36 cm^{-1}, quite similar to that at the fundamental, suggesting only a minor dependence of the hydrogen bond vibration on the free-HF bond length. The predissociaton linewidth for $3\nu_1 + \nu_4$ mode is 2.5(2) GHz, which is one order of magnitude larger than the 0.24(2) GHz of the $3\nu_1$ state. The coupling of this state to the dark state of $3\nu_2 + \nu_4 + \nu_5$ is suggested for the origin of the observed linewidth increase.