

REASSIGNMENT OF THE  $11537\text{ cm}^{-1}$  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  $(\text{HF})_2$  by intracavity laser induced fluorescence. The fluorescence is monitored with a germanium detector which collects only first overtone emission ( $2 \rightarrow 0$ ) of HF fragments. The band centered at  $11537\text{ cm}^{-1}$  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 ( $\Delta\nu_t=0.6\text{ GHz}$ ). 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  $11402.868(8)\text{ cm}^{-1}$  and rotational constants of  $0.21639(17)$  and  $0.21704(15)\text{ cm}^{-1}$  for the two tunneling components  $A^+$  and  $B^+$ , respectively. The frequency of this intermolecular vibration,  $\nu_4$ , upon  $3\nu_1$  excitation is  $129.36\text{ cm}^{-1}$ , quite similar to that at the fundamental, suggesting only a minor dependence of the hydrogen bond vibration on the free-HF bond length. The predissociation linewidth for  $3\nu_1 + \nu_4$  mode is  $2.5(2)\text{ GHz}$ , which is one order of magnitude larger than the  $0.24(2)\text{ GHz}$  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.