THE GEOMETRIC CHANGE OF HF-CO\textsubscript{2} UPON VIBRATIONAL EXCITATION

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HF-CO\textsubscript{2} is quasilinear at the vibrational ground state\textsuperscript{a} and becomes a semi-rigid bent species at $\nu_{HF} = 3$ with the CO\textsubscript{2} intermolecular bending frequency of 24.75(10) cm\textsuperscript{-1}. The ab initio potential surface is very flat from $\theta = 0$ to 40° at $\nu_{HF} = 0$ while at $\nu_{HF} = 3$ the potential energy of linear geometry is about 50 cm\textsuperscript{-1} higher than that at the minimum near $\theta = 40^\circ$. The observed features at 11174.45, 11168.10, and 11181.82 cm\textsuperscript{-1} have been assigned to parallel transition to the K = 0, 1, and 2 levels of the second overtone HF valence band, respectively, indicating a vibrational redshift of 198.36(5) cm\textsuperscript{-1} compared to the HF monomer. The relatively strong transition intensities of the K subbands are due to the inertial axes switching\textsuperscript{b}. The rotational constants of the (3000000) state are $A = 2.96(2)$ cm\textsuperscript{-1}, $(B+C)/2 = 0.0742(10), 0.0717(10),$ and 0.0696(10) cm\textsuperscript{-1} for the K = 0, 1, and 2 levels. The centrifugal distortion $D_K = 0.270(5)$ cm\textsuperscript{-1} is extremely large but in good agreement with the expectation, as a result of very soft CO\textsubscript{2} intermolecular bending. The spectral linewidths are 9.0(9), 7.2(6), and 4.5(6) GHz for the above levels, showing dramatic dependence of vibrational predissociation lifetime upon K. A perpendicular transition of the HF bending combination band at 11538.92 cm\textsuperscript{-1} provides a bending frequency of 362.77(15) cm\textsuperscript{-1}, while $(B+C)/2 = 0.0668(10)$ cm\textsuperscript{-1} and $\Gamma = 4.2(6)$ GHz.

\textsuperscript{b}J. T. Hougen and J. K. Watson, J. Mol. Spectrosc. 43, 298(1965).