THE GEOMETRIC CHANGE OF HF-CO_2 UPON VIBRATIONAL EXCITATION

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HF-CO_2 is quasilinear at the vibrational ground state[a] and becomes a semi-rigid bent species at ν_{HF} = 3 with the CO_2 intermolecular bending frequency of 24.75(10) cm^{-1}. The *ab initio* potential surface is very flat from θ = 0 to 40° at ν_{HF} = 0 while at ν_{HF} = 3 the potential energy of linear geometry is about 50 cm^{-1} higher than that at the minimum near θ = 40°. The observed features at 11174.45, 11168.10, and 11181.82 cm^{-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^{-1} compared to the HF monomer. The relatively strong transition intensities of the K subbands are due to the inertial axes switching[b]. The rotational constants of the (3000000) state are A = 2.96(2) cm^{-1}, (B+C)/2 = 0.0742(10), 0.0717(10), and 0.0696(10) cm^{-1} for the K = 0, 1, and 2 levels. The centrifugal distortion D_K = 0.270(5) cm^{-1} is extremely large but in good agreement with the expectation, as a result of very soft CO_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^{-1} provides a bending frequency of 362.77(15) cm^{-1}, while (B+C)/2 = 0.0668(10) cm^{-1} and Γ = 4.2(6) GHz.

[a] D. J. Nesbitt and C. M. Lovejoy, J. Chem. Phys. 93, 7716(1990).
[b] J. T. Hougen and J. K. Watson, J. Mol. Spectrosc. 43, 298(1965).