

SYMMETRY BREAKING OF THE BENDING MODE OF CO₂ IN THE PRESENCE OF Ar

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The weak infrared spectrum of CO₂-Ar corresponding to the $(v_1, v_2^{l_2}, v_3) = (01^11) \leftarrow (01^10)$ hot band of CO₂ is detected in the region of the carbon dioxide ν_3 fundamental vibration (~ 2340 cm⁻¹), using a tunable OPO to probe a pulsed supersonic slit jet expansion. While this method was previously thought to cool clusters to the lowest rotational states of the ground vibrational state, here we show that under suitable jet expansion conditions, sufficient population remains in the first excited bending mode of CO₂ (1-2%) to enable observation of vibrationally hot CO₂-Ar, and thus to investigate the symmetry breaking of the intramolecular bending mode of CO₂ in the presence of Ar. The bending mode of CO₂ monomer splits into an in-plane and an out-of-plane mode, strongly linked by a Coriolis interaction. Analysis of the spectrum yields a direct measurement of the in-plane / out-of-plane splitting measured to be 0.8770 cm⁻¹. This aspect of intramolecular interactions has received little previous experimental and theoretical consideration. Therefore, we provide an additional avenue by which to study the intramolecular dynamics of this simplest dimer in its bending modes. Similar results are obtained for CO₂-Ne.