NEW INFRARED SPECTRA OF CO_2-Xe: MODELING Xe ISOTOPE EFFECTS, INTERMOLECULAR BEND AND STRETCH, AND SYMMETRY BREAKING OF THE CO_2 BEnd

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The infrared spectrum of CO_2-Xe is studied in the region of the carbon dioxide ν_3 fundamental vibration (near 2350 cm^{-1}), using a tunable OPO laser source to probe a pulsed supersonic slit jet expansion. We generally think of Xe or Kr isotope effects to be mostly unresolved for infrared spectra of weakly-bound van der Waals complexes. But here we model the Xe isotope dependence of the spectrum by scaling the vibrational and rotational parameters with the help of previous microwave data,[a] using features built into PGOPHER.[b] This model provides a very good simulation of the observed broadening and (partial) splitting of transitions in the fundamental band. More importantly, it is essential for understanding the intermolecular bending combination band, where many transitions are completely split by isotope effects. The combination band is influenced by a significant bend-stretch Coriolis interaction and by the relatively large Xe isotope dependence of the intermolecular stretch frequency. It turns out that K_a = 1 levels of the stretch lie above K_a = 2 levels of the bend for CO_2-^{129}Xe, but below them for CO_2-^{136}Xe. This greatly enhances the Xe isotope dependence of the Coriolis interaction.

The weak CO_2-Xe spectrum corresponding to the (01^11) - (01^10) hot band of CO_2 is also detected and analyzed, providing a measurement of the symmetry breaking of the CO_2 ν_2 bending mode induced by the nearby Xe atom. This in-plane / out-of-plane splitting is determined to be 2.14 cm^{-1}, with the out-of-plane mode lying higher in energy.

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[a] M. Iida, Y. Ohshima, and Y. Endo, *J. Phys. Chem.* **97**, 357 (1993).

[b] PGOPHER, A Program for Simulating Rotational, Vibrational and Electronic Spectra, C.M. Western, University of Bristol, http://pgopher.chm.bris.ac.uk