THE CO_2–$(N_2)_2$ AND CO_2–Ar_2 TRIMERS: INFRARED SPECTRA, STRUCTURAL CALCULATIONS AND INTERMOLECULAR BEND

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The weakly-bound CO_2–$(N_2)_2$ and CO_2-Ar_2 trimers have been studied in the carbon dioxide ν_3 asymmetric stretch region ($\sim$2350 cm^{-1}). The van der Waals complexes are generated in a supersonic slit-jet apparatus and probed using an optical parametric oscillator.

The interaction of N_2, the most abundant molecule in the Earth's atmosphere, and CO_2 is relevant from the stand point of the overlap of frequencies of the stretching modes of CO_2 with the Earth's emission and its effect on greenhouse. Here, we have observed the fundamental for the CO_2–$(N_2)_2$ trimer. It is composed of c-type transitions establishing that the trimer has C_{2v} point group symmetry with the CO_2 monomer in the ac inertial plane and parallel to the c-axis and the equivalent equatorial N_2 monomers in the ab-plane with molecular axes passing through the center of mass of CO_2 and making an angle of 64°. Theoretical calculations were performed in support of our observations. Several minima on the PES were found. For the most stable isomer, the vibrational corrections to the equilibrium rotational constants were obtained. The rotational parameters at CCSD(T*)-F12c level of theory gives results in very good agreement with those obtained from the observed vibrational fundamental.

Using a dilute mixture of CO_2 and Ar in He, we observed a weak b-type combination band involving an intermolecular mode around 2380 cm^{-1}. This band is assigned to CO_2-Ar_2 trimer which also has C_{2v} point group symmetry and a structure similar to CO_2–$(N_2)_2$ trimer. As such, four of the five combination bands are infrared active. From these only one has b-type transitions which uniquely identifies the intermolecular mode as CO_2 bend with an observed frequency of 32.24 cm^{-1}.