

THE 4.2 MICRON SPECTRA OF CO₂-CO DIMER FOR BOTH THE C- AND O-BONDED ISOMERS, INCLUDING SPLITTING OF THE DEGENERATE ν_2 BEND IN THE PRESENCE OF CO

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Infrared spectra of the CO₂-CO dimer are observed in the carbon dioxide ν_3 asymmetric stretch region (~ 2350 cm⁻¹) using a tunable infrared optical parametric oscillator to probe a pulsed slit jet supersonic expansion. Both C-bonded and O-bonded isomers are analyzed for the normal isotopologue as well as for ¹³CO₂-CO and ¹⁶O¹³C¹⁸O-CO, the latter being the first observation of an asymmetrically substituted form for which all values of K_a are allowed. A combination band involving the lowest in-plane intermolecular mode (~ 24.5 cm⁻¹) is also studied for the C-bonded form. A weak band near 2337 cm⁻¹ is assigned to the CO₂ hot band transition $(v_1, v_2^l, v_3) = (01^11) \leftarrow (01^10)$, yielding the splitting of the degenerate CO₂ ν_2 bend into in-plane and out-of-plane components due to the presence of the CO. The splitting, an aspect of intermolecular forces which has received little attention in the past, has rather different values of 4.56 and 1.59 cm⁻¹ for the C- and O- bonded isomers, respectively.