ON THE ORIGIN OF THE BAND STRUCTURE OBSERVED IN THE COLLISION-INDUCED ABSORPTION BANDS OF CO_2

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Two collision-induced (CIA) IR bands of CO_2 are observed in the region of the Raman allowed ν_1- $2\nu_2$ Fermi-dyad monomer bands in the 7 μm region. These bands consist of a featureless CIA component upon which are superimposed very distinctive CO_2 dimer bands. The original observation of band structure in these bands was made by Welsh et al.[a] and was interpreted by Mannik et al. [b] to be the P-, Q- and R-branches of a T-shaped dimer. However, molecular beam studies[c] have subsequently shown that the dimer bands consist of nearly equally intense a-type and b-type transitions and that the dimer structure is a slipped-parallel arrangement with C_{2h} symmetry. Recently Vigasin and Baranov[d] have modeled the dimer profile observed in room temperature CIA spectra using a symmetric-rotor model which leads to a derived C-C separation of 4.46 Å considerably larger than the molecular beam value of 3.3986 Å. In this report, we suggest an alternative explanation for the dimer band profile observed. We have modeled the bands using a Watson asymmetric-rotor Hamiltonian and the rotational constants derived in a molecular beam study. We have varied only the upper-state A rotational constant and the μ_a/μ_b ratio. In this model, the band structure is not due to P- Q, and R-branches but rather to a central sharp a-type Q-branch with broad b-type Q-branches on either side of the band center. All the Q-branch transitions sit on a pedestal of unresolved ^{p}P- and ^{r}R-branch lines. Comparison with observed spectra is good but not perfect and departures from the model will be discussed.

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