

ON THE ORIGIN OF THE BAND STRUCTURE OBSERVED IN THE COLLISION-INDUCED ABSORPTION BANDS OF CO₂

Y. I. BARANOV, W. J. LAFFERTY, AND G. T. FRASER, *Optical Technology Division, NIST, Gaithersburg, MD 20899*; A.A. VIGASIN, *General Physics Institute, Russian Academy of Sciences, Vavilova 38, Moscow, 119991, Russia*.

Two collision-induced (CIA) IR bands of CO₂ are observed in the region of the Raman allowed $\nu_1 - 2\nu_2$ Fermi-dyad monomer bands in the 7 μm region. These bands consist of a featureless CIA component upon which are superimposed very distinctive CO₂ 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 Vigin 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 ^pP- and ^rR-branch lines. Comparison with observed spectra is good but not perfect and departures from the model will be discussed.

^aH.L. Welsh, M.F. Crawford and J.L. Locke, Phys. Rev, 76, 580 (1949)

^bL. Mannik, J.C. Stryland and H.L. Welsh, Can. J. Phys. 49, 3056 (1971).

^cK.W. Jucks et al., J. Chem. Phys., 88, 2185(1988); M.A. Walsh et al., Chem. Phys. Lett. 142, 265 (1987).

^dY.I. Baranov and A.A. Vigin, J. Mol. Spectrosc. 193, 319 (1999); A.A. Vigin, J. Mol. Spectrosc. 200, 89 (2000).