INFRARED SPECTRUM AND ENERGY LEVELS OF THE CO DIMER: EVIDENCE FOR TWO ALMOST ISOENERGETIC ISOMERS

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The nature of the CO dimer remains an unsolved problem in spectroscopy. It was first detected twenty years ago in the microwave region by Klemperer's group.[a] More recently the infrared spectrum, which appears in the 2140 cm^{-1} C-O stretch region, was observed in Bonn.[b] Theory indicates that the CO-CO intermolecular potential has a number of minima differing in energy by small amounts and separated by small barriers, so it may not be helpful to think of a unique geometrical structure for the dimer.

We have extended the study of the IR spectrum using a rapid scan diode laser spectrometer with both planar and axisymmetric jet expansions. By probing the supersonic jet at varying distances downstream, we observed the $(CO)_2$ spectra over a range of effective rotational temperatures from about 12 down to 1 K, and were able to identify[c] one perpendicular and two parallel bands with common lower state combination differences. Only even J-values were present in the lower state due to nuclear spin statistics. Since obtaining those results, we have greatly extended the analysis, assigning over 120 lines to 13 subbands involving involving 24 lower state (v_{CO} = 0) and 35 upper state (v_{CO} = 1) rotational energy levels of the complex with total angular momentum values of J = 0 to 9. The energy levels appear to fall into two groups corresponding to distinct (but overlapping) 'isomers' with intermolecular separations of either about 4.09 or 4.35 Å. The 4.35 Å isomer is the ground state of the complex, while the 4.09 Å isomer is a very low-lying (0.88 cm^{-1}) excited state, but this energy ordering is inverted when v_{CO} = 1.

[a] P.A. Vanden Bout, J.M. Steed, L.S. Bernstein, and W. Klemperer, Astrophys. J. **234**, 503 (1979).
[b] M. Havenith, M. Petri, C. Lubina, G. Hilpert, and W. Urban, J. Mol. Spectrosc. **167**, 248 (1994).
[c] M.D. Brookes and A.R.W. McKellar, Chem. Phys. Lett. **287**, 365 (1998).