STRUCTURE AND SPECTROSCOPY OF THE CARBON MONOXIDE DIMER: A THEORETICAL APPROACH

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The carbon monoxide dimer is a notoriously difficult system to characterize, both experimentally[a] and theoretically. However, in the last few years, the combined efforts of the NRC Ottawa group and the Cologne spectroscopy laboratory have led to an impressive amount of knowledge on the rovibrational levels of the system. Despite the difficulties in deriving reliable line assignments for the CO dimer spectrum, they were able to assign stacks of accurately known rovibrational energy levels, both for the normal $(^{12}CO)_2$ and for the isotopically substituted $(^{13}CO)_2$.

On the theoretical side, progress has been considerably slower. Until recently the only two potential energy surfaces that were available were unable to explain the observed spectroscopic properties of the dimer. Attempts to improve upon these potentials showed that high-order correlation effects are important,[b] and furthermore that very large basis sets are needed for an accurate description of the intermolecular potential energy surface.[c,d] Nevertheless, we have succeeded in constructing a potential that can explain the observed experimental features.[e] The existence of stacks of rotational levels with different rotational constants is explained in terms of two different isomeric structures that are nearly equal in energy. Also an explanation is presented for the observation of an abnormally large shift in rotational constants upon substitution of ^{12}C by the heavier ^{13}C isotope.

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