The Structure of the Carbon Dioxide-Water Dimer

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In recent years, carbon monoxide has attracted a great deal of attention for its role in atmospheric chemistry. In aerosols, carbon dioxide will dissolve in water and form carbonic acid, and long range interactions lead to the onset of this reaction. Key studies on the interaction between water and carbon dioxide were actually done in the 1970's and 1980's, preceding the current interest on CO_2 in the atmosphere. These studies were partly motivated by a fundamental curiosity about the nature of the interaction between a very polar and a non-polar molecule with bond dipoles. This simple system turned out to be somewhat controversial due to some theoretical results that disagreed with experiment. Here we propose that most of those disagreements were due to an inappropriately low level of theory used in previous theoretical studies.

Microwave and IR experiments point to a planar T-shaped structure, and a barrier of rotation of 3.6 kJ/mol. Calculations on the other hand indicated the existence of as many as eight minima on the surface, with the global minimum being non-planar. Those structures were obtained using SCF or MP2 with fairly small split valence basis sets. In this study, we also use second order perturbation theory, but our observation is that after using larger bases the previously reported structures do not appear to be plausible minima. Furthermore, with the aug-cc-pVXZ basis sets the equilibrium structure is planar, in agreement with experiment. On the other hand, the computed equilibrium structure is not T-shaped as experiment suggests, but the barrier of conversion between the two equivalent global minima is low enough to easily allow for a quick conversion, with the average structure corresponding to the transition state between the global minima. This average structure is T-shaped, in agreement with the experimental average structure.

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