

THE WATER–CARBON MONOXIDE DIMER: NEW INFRARED SPECTRA, AB INITIO ENERGY LEVEL CALCULATIONS, AND A CURIOUS INTERMOLECULAR MODE

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Weakly-bound H₂O-CO has a planar structure with approximately co-linear heavy atoms (O, C, O) and a hydrogen bond between the water and the carbon of the CO. Proton tunneling (H atom interchange) gives rise to two states corresponding to distinct nuclear spin modifications. The magnitude of the splitting in the ground rotational state is about 0.8 cm⁻¹ for H₂O-CO and 0.04 cm⁻¹ for D₂O-CO. Due to the almost linear heavy atom configuration, H₂O-CO has a large A rotational constant, equal to about 19 cm⁻¹ (12 cm⁻¹ for D₂O-CO), so the K quantum number is highly significant. Water-CO was first studied in the microwave and millimeter regions. Infrared spectra have been observed in the regions of the C-O stretch, the O-H stretch, the D₂O bend, and the H₂O bend. Here we study the O-D stretch region (3.6 μm) for the first time, observing D₂O-CO, HOD-CO, and DOH-CO. We also extend the C-O stretch region results to include the K = 1 ← 0 subbands, thus determining A rotational constants for the ν(CO) = 1 excited state. But more significantly, we also observe additional K = 1 ← 0 combination bands in both regions which involve the lowest intermolecular vibration of water-CO. This mode, which lies at 43 – 49 cm⁻¹ depending on isotopologue, can be identified as the in-plane CO bend. It is observed for H₂O-CO, D₂O-CO, and HOD-CO, and exhibits anomalous isotope shifts: even though their A-values are quite different, the D₂O-CO mode is only slightly lower in energy than that of H₂O-CO. Detailed rotational energy level calculations, based on a recent high-level ab initio potential energy surface^a, are in good agreement with experiment, including the newly observed intermolecular mode. As well, the calculations show that the unobserved K = 0 level of this mode lies above the observed K = 1 level, thus explaining the anomalous isotope shifts.

^aY. N. Kalugina, A. Faure, A. van der Avoird, K. Walker, and F. Lique, *Phys. Chem. Chem. Phys.* 20, 5469 (2018).