THE CO–$(D_2O)_2$ AND CO–$(D_2O)_3$ COMPLEXES: INFRARED SPECTRA AND STRUCTURAL CALCULATIONS

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The weakly-bound CO–$(D_2O)_2$ and CO–$(D_2O)_3$ complexes have been studied in the C-O stretching fundamental of the CO monomer. The van der Waals complexes are generated in a supersonic slit-jet apparatus and probed using a quantum cascade laser. One band was observed and analysed for each complex. The trimer, CO–$(D_2O)_2$, band is composed of a/b-type transitions establishing that the CO monomer lies nearly in the a-b inertial plane. The observed rotational constants lead to a small value of the inertial defect indicating that the heavy atoms in the trimer are co-planar. We observe no evidence of tunneling splitting and conclude that the large amplitude tunneling that exists in the free D_2O dimer is quenched by the presence of the CO monomer. The CO–$(D_2O)_3$ band is also composed of a/b-type transitions establishing that the CO monomer lies nearly in the a-b inertial plane.

Theoretical calculations were performed to find minima on the potential energy surfaces for both complexes at B2PLYP-D3BJ level of theory and applying counterpoise correction for the basis set superposition error. Further optimisations were then carried out at different coupled cluster levels of theory and extrapolating to the complete basis set limit. The rotational parameters at CCSD(T*)-F12c level of theory give results in very good agreement with those obtained from the observed spectra. In both complexes, the experimental structure corresponds to the lowest energy isomer.

The corresponding bands for CO–$(H_2O)_2$ and CO–$(H_2O)_3$ are significantly predissociated which hampers their detailed rovibrational analysis.