Hydrogen bonding in the $H_2S$ dimer: New insights from experiment and theory

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Hydrogen bonding is a central concept in chemistry and biochemistry and so it continues to attract intense study. Here, we examine hydrogen bonding in the $H_2S$ dimer, in comparison with the well-studied water dimer, in unprecedented detail. We record a mass selective IR spectrum of $H_2S$ dimer in superfluid He nanodroplets. We are able to resolve the rotational substructure of each of the three distinct bands and assign these to the vibration-rotation-tunneling transitions of the para-para, ortho-para, and ortho-ortho dimer of a single IR vibration. Based on a high-level potential energy and dipole moment surfaces, we compute the vibration-rotation-tunneling dynamics and far-IR spectrum with rigorous quantum methods. Calculated rotational constants of the ortho-para $H_2S$ dimer are found to be in good agreement with previously measured microwave values. Six intramolecular mode VSCF/VCI calculations provide the fundamental frequencies and intensities of the four SH-stretch modes, with a focus on the most intensive, the donor bound SH mode which is experimentally observed. Dissociation energies, $D_0$, of the para-para, ortho-para, and ortho-ortho nuclear spin isomers of $H_2S$ dimers are predicted; for para-para also from Diffusion Monte Carlo calculations in full dimensionality. Based on our results, we propose a substantially increased delocalization and strong mixing of intermolecular modes compared to the water dimer. The less directional nature of the hydrogen bonding can be quantified in terms of weaker electrostatic and more important dispersion interaction. The present study reconciles all previous spectroscopic data, serves as a sensitive test for the potential energy and dipole moment surface.

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