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To be or not to be hydrogen-bonded: Supercritical water and (H2S)2

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Water also serves as the prototype for directional hydrogen bonding at ambient conditions. However, the question of whether supercritical water is still hydrogen-bonded or how water molecules interact in the supercritical regime is a matter of controversial discussions. We present terahertz (THz) spectra, which directly probe the intermolecular interactions of water under these extreme conditions [*Sci. Adv.* 11, eadp8614, 2025]. While we spectroscopically detect the liquid-gas phase transition just below the critical point, THz spectra of the high-temperature gas phase are indistinguishable from those of supercritical water at the same density. The accompanying ab initio simulations provide the molecular underpinnings: The water-water contacts at supercritical conditions are essentially orientationally random.

Furthermore, we examine hydrogen bonding in the H2S dimer, in comparison with the well-studied water dimer, in unprecedented detail [*Nat. Commun.* 15, 9540, 2024]. We record a mass-selected IR spectrum of the H2S dimer in superfluid helium nanodroplets. We are able to resolve a rotational substructure in each of the three distinct bands and, based on it, assign these to vibration-rotation-tunneling transitions of a single intramolecular vibration. With the use of high-level potential and dipole-moment surfaces, we compute the vibration-rotation-tunneling dynamics and far-infrared spectrum with rigorous quantum methods. We show that the intermolecular modes in the H2S dimer are substantially more delocalized and more strongly mixed than in the water dimer. The less directional nature of the hydrogen bonding can be quantified in terms of weaker electrostatic and more important dispersion interactions. The present study reconciles all previous spectroscopic data and serves as a sensitive test for the potential and dipole-moment surfaces.

Keywords

This abstract is submitted for....

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