

Coupled Translation-Rotation Dynamics and Spectroscopy of H₂ and H₂O in C₆₀: Rigorous Quantum Treatment

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The behavior of small molecules, H₂ and H₂O in particular, inside the nanoscale cavities of diverse host materials has attracted a great deal of attention in recent years. In nanoscale confinement, the translational center-of mass motions of the caged molecules are quantized and strongly coupled to the quantized molecular rotations. I will first briefly review our rigorous quantum treatment of the translation-rotation (TR) dynamics of H₂@C₆₀ [1]. These quantum 5D calculations, assuming rigid monomers, have elucidated the TR level structure and revealed distinct spectroscopic signatures of the TR coupling that were later observed experimentally. Recent perturbation-theory treatment of the TR eigenstates of H₂@C₆₀ [2] has allowed connecting specific features of the level structure established in Ref. [1] with specific features of the intermolecular potential energy surface, and provided important new physical insights into the characteristic features of the former.

In another recent study [3], we have reported fully coupled 6D quantum calculations of the TR eigenstates of *para*- and *ortho*-H₂O in C₆₀. They provide a comprehensive description of the dynamical behavior of an asymmetric top, H₂O, inside the fullerene having icosahedral (*I_h*) symmetry. The calculated TR levels have permitted us to assign tentatively a number of transitions in the measured inelastic neutron scattering (INS) spectra of H₂O@C₆₀ [4] that have not been assigned previously.

TR eigenstates of nanoconfined hydrogen-containing molecules can be probed directly by the INS spectroscopy. Several years ago we developed the methodology for accurate quantum simulations of the INS spectra of diatomic molecules in a nanocavity of an arbitrary shape [5]. An unexpected result of this line of work was the discovery and formal proof of the new and surprising selection rule for the INS spectroscopy of H₂ in a near-spherical nanocavity such as that of C₆₀ [6], the first ever to be established in the INS of discrete molecular compounds. This INS selection rule was later confirmed experimentally for H₂@C₆₀ [7], and subsequently generalized [8].

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