

THEORETICAL SPIN-ORBIT SPECTROSCOPY OF Cl DOPANTS IN SOLID PARAHYDROGEN

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Solid parahydrogen (pH₂) matrices containing open-shell (²P) Cl and Br atoms as substitutional impurities exhibit several infrared (IR) absorption features associated with intermolecular interactions between the halogen atom and nearby pH₂ molecules.^a These dopant-induced IR absorption features are associated with (i) spin-orbit (SO) excitation of the halogen atom, and (ii) cooperative excitations in which a single IR photon both triggers SO excitation of the halogen atom and excites the H-H stretching coordinate of a nearby pH₂ molecule. The IR spectral features thus contain detailed information about the interaction between the open-shell halogen atom and the surrounding pH₂ molecules, and in particular tell us about the coupling between the atom's electronic degrees of freedom and the nuclear motion of its H₂ neighbors.

Here we present recent progress towards understanding these features in Cl-doped solid pH₂. This system represents an arena for testing theoretical approaches that generate many-body, non-pairwise-additive potential energy functions for the dopant-matrix interaction by combining multiple low-lying Cl-H₂ pair potential energy functions. Our analysis must account for the fact that the individual pH₂ molecules in the doped solid undergo large amplitude zero-point motions;^b we use quantum Monte Carlo simulations^c to model these zero-point motions. We interpret our findings in terms of a reduced dimensionality model that provides a qualitative understanding of the role that matrix zero-point motions play in the observed spectra.

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^bI. F. Silvera, *Rev. Mod. Phys.* **52**, 393 (1980).

^cR. J. Hinde, *Comput. Phys. Commun.* **182**, 2339 (2011).