THEORETICAL SPIN-ORBIT SPECTROSCOPY OF Cl DOPANTS IN SOLID PARAHYDROGEN

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Solid parahydrogen (pH_2) matrices containing open-shell (^{2}P) Cl and Br atoms as substitutional impurities exhibit several infrared (IR) absorption features associated with intermolecular interactions between the halogen atom and nearby pH_2 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 pH_2 molecule. The IR spectral features thus contain detailed information about the interaction between the open-shell halogen atom and the surrounding pH_2 molecules, and in particular tell us about the coupling between the atom's electronic degrees of freedom and the nuclear motion of its H_2 neighbors.

Here we present recent progress towards understanding these features in Cl-doped solid pH_2. 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–H_2 pair potential energy functions. Our analysis must account for the fact that the individual pH_2 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.

[a] P. L. Raston and D. T. Anderson, J. Chem. Phys. **126**, 021106 (2007); S. C. Kettwich, L. O. Paulson, P. L. Raston and D. T. Anderson, J. Phys. Chem. A **112**, 11153 (2008).

[b] I .F. Silvera, Rev. Mod. Phys. **52**, 393 (1980).

[c] R. J. Hinde, Comput. Phys. Commun. **182**, 2339 (2011).