QUANTUM MONTE CARLO SIMULATION OF VIBRATIONAL FREQUENCY SHIFTS OF CO IN SOLID para-HYDROGEN

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Stimulated by Fajardo's remarkable study of the rovibrational spectra of CO isotopologues trapped in solid $para$-hydrogen,[a] we have performed quantum Monte Carlo simulations to predict his observed vibrational frequency shifts and inertial rotational constants using 2-body potentials based on the best available models for the $p\mathrm{H_2}$-$p\mathrm{H_2}$ [b] and CO-$p\mathrm{H_2}$ [c] potential energy functions. We started by fitting an analytic 'Morse/Long-Range' (MLR) function[d] to the 1D "adiabaic hindered rotor" version of Hinde's 5D $p\mathrm{H_2}$-$p\mathrm{H_2}$ potential developed by Faruk *et al.*[e] We then modified it to take account of many-body effects by scaling it until it yielded the correct equilibrium lattice parameters for the *fcc* and hcp structures of pure solid $para$-hydrogen. A CO molecule was then placed at different interstitial or substitution sites in large equilibrated *fcc* or hcp $para$-hydrogen lattices, and the structural and dynamical behaviors of the micro-solvation environment around CO were simulated with a PIMC algorithm using a 2D effective $p\mathrm{H_2}$-CO potential based on the 5D $\mathrm{H_2}$–CO potential energy surface recently reported by Li *et al.*,[f] with a lattice sum of values of the 2D CO vibrational difference potential being use to predict the vibrational frequency shift. The effective rotational constants B_{eff} for CO in different solid $para$-hydrogen structures were also calculated and compared with the experimental observations and with predicted B_{eff} values for CO in large-sized $para$-hydrogen–CO clusters.[g]

[a] M. E. Fajardo, *J. Phys. Chem. A* **117**, 13504 (2013).
[b] R. Hinde, *J. Chem. Phys.* **128**, 154308 (2008).
[c] H. Li, X-L. Zhang, R.J. Le Roy, and P.-N. Roy, *J. Chem. Phys.* **139**, 164315 (2013).
[d] R.J. Le Roy, C.C. Haugen, J. Tao and Hui Li, *Mol. Phys.* **109**, 435 (2011).
[e] N. Faruk, R.J. Le Roy, and P.-N. Roy, *J. Chem. Phys.* (submitted December 2013).
[f] H. Li, X-L. Zhang, R. J. Le Roy, and P.-N. Roy, *J. Chem. Phys.* **139**, 164315 (2013).
[g] Y. Mizumoto and Y. Ohtsuki, *Chem. Phys. Lett.* **501**, 304 (2011).