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

LECHENG WANG, ROBERT LE ROY, PIERRE-NICHOLAS ROY. Department of Chemistry, University of Waterloo, Waterloo, ON, Canada.

Stimulated by Fajardo’s remarkable study of the rovibrational spectra of CO isotopologues trapped in solid para-hydrogen, 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 $pH_2$-$pH_2$ and CO-$pH_2$ potential energy functions. We started by fitting an analytic ‘Morse/Long-Range’ (MLR) function to the 1D “adiabatic hindered rotor” version of Hinde’s 5D $pH_2$-$pH_2$ potential developed by Faruk et al. 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 $pH_2$-CO potential based on the 5D $H_2$–CO potential energy surface recently reported by Li et al. 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 $B_{\text{eff}}$ for CO in different solid para-hydrogen structures were also calculated and compared with the experimental observations and with predicted $B_{\text{eff}}$ values for CO in large-sized para-hydrogen–CO clusters.

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