

## QUANTUM MONTE CARLO PREDICTION OF VIBRATIONAL FREQUENCY SHIFTS FOR CO-(p-H<sub>2</sub>)<sub>n</sub> CLUSTERS

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Since *para*-H<sub>2</sub> molecules are spin zero bosons (like <sup>4</sup>He atoms) they might also show superfluid behavior at low temperatures. Results of recent spectroscopic studies of molecules embedded in helium droplets suggests that a new route for investigating superfluidity of *para*-hydrogen (p-H<sub>2</sub>) would be to consider p-H<sub>2</sub> clusters doped with a single chromophore molecule (such as CO, CO<sub>2</sub>, N<sub>2</sub>O, or OCS). High resolution infrared spectra of CO in (H<sub>2</sub>)<sub>n</sub> cluster have been studied by the McKellar and coworkers,<sup>a</sup> who observed *R*(0) transitions which have been assigned for *n* up to 9 for *b*-type transitions and to *n* = 14 for *a*-type series, with the help of reptation Monte Carlo simulations. Recently, Raston and coworkers indirectly determined band origin shifts for C-O stretching in small clusters with *n* up to 7.<sup>b</sup> Such studies stimulated our efforts to predict vibrational frequency shifts for larger clusters, and to perform critical comparisons between experimental and theoretical shifts in smaller clusters.

Predicting vibrational band origins shifts requires a potential energy surface which depends on the monomer vibrational coordinate(s). We recently determined a five-dimensional ‘Morse/Long-Range’ potential energy surface for CO-H<sub>2</sub> which explicitly depends on the C-O vibrational coordinate, and also incorporates the correct angle-dependent inverse-power long-range behaviour.<sup>c</sup> We have now used this new potential in quantum Monte Carlo simulations to predict both the rotational dynamics and the shift of the C-O band origin for CO doped in p-H<sub>2</sub> clusters, in order to provide definitive theoretical evidence regarding whether superfluidity occurs for p-H<sub>2</sub> cluster doped with CO, and if so, at what cluster size it begins.

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<sup>a</sup> S. Moroni, M. Botti, S. De Palo and A.R.W. McKellar, *J. Chem. Phys.* **122**, 94314 (2005).

<sup>b</sup> P.L. Raston, W. Jäger, H. Li, R.J. Le Roy, and P.-N. Roy (2010, ms. in preparation).

<sup>c</sup> H. Li, P.-N. Roy and R.J. Le Roy (2010, ms. in preparation).