A NEW POTENTIAL ENERGY SURFACE FOR H_2–N_2O AND PIMC SIMULATION PROBING SUPERFLUIDITY AND VIBRATIONAL FREQUENCY SHIFTS IN DOPED $para$-H_2 CLUSTERS

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The existence of superfluidity of $para$-hydrogen clusters doped by the linear molecules[a,b,c] such as CO, CO_2 and OCS stimulated our theoretical study of $(para\text{-}H_2)_N$–N_2O clusters. A new 6D $ab\,initio$ PES for the H_2–N_2O dimer which explicitly included the symmetric and asymmetric vibrational coordinates Q_1 and Q_3 of N_2O was constructed. Four-dimensional global intermolecular PESs were then obtained by fitting the vibrational averaged interactions energies for $\nu_3(N_2O)$=0 and 1 to the Morse/Long Range(MLR) analytical form with theoretically fixed long-range parameters. Using the adiabatic hindered-rotor approximation, effective two-dimensional PESs for the $para$-H_2–N_2O dimer were then generated. Predictions of the infrared spectra of $para$-H_2–N_2O based on these PESs have been in good agreement with the experimental observations.[d] Based on these surfaces, predictions of structural properties, vibrational band origin shifts, rotational dynamics and superfluidity of $(para\text{-}H_2)_N$–N_2O clusters have been generated using bosonic PIMC simulation methods. The evolution of the calculated shifts agreed reasonably with that for the experimental observations.[e] Reduction of the effective moment of inertia is predicted to occur when the dopant is partially surrounded by the $para$-H_2 solvent, which marked the onset of molecular superfluidity in $para$-H_2. Results obtained using our surfaces and PIMC algorithm will be presented.

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[a] H. Li, R. J. Le Roy, P.-N. Roy and A.R.W. McKellar, *Phys. Rev. Lett.* **105**, 133401 (2010).
[b] S. Grebenev, B. G. Sartakov, J. P. Toennies and A. F. Vilesov, *J. Chem. Phys.* **132**, 064501 (2010).
[c] P. L. Raston, W. Jager, H. Li, R. J. Le Roy, and P.-N. Roy , *Phys. Rev. Lett.* **108**, 253402 (2012).
[d] J. Tang and A.R.W. McKellar, *J. Chem. Phys.* **117**, 8308 (2002).
[e] J. Tang and A.R.W. McKellar, *J. Chem. Phys.* **123**, 114314 (2005).