

QUANTUM MONTHE CARLO PREDICTION OF VIBRATIONAL FREQUENCY SHIFTS OF $(\text{He})_N\text{-CO}_2$ CLUSTERS

HUI LI and ROBERT J. LE ROY, *Guelph-Waterloo Centre for Graduate Work in Chemistry and Biochemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada*; NICHOLAS BLINOV and PIERRE-NICHOLAS ROY, *Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada*.

High resolution infrared spectra of $(\text{He})_N\text{-CO}_2$ clusters with N up to 60 have been studied by McKellar and co-workers, in the region of the ν_3 fundamental band of CO_2 .^a By fitting to the rotation-vibration transitions for each cluster size, vibrational band origins ν_0 and rotational constants B and D were obtained as functions of N . Quantum Monte Carlo simulation predictions of B and D for $(\text{He})_N\text{-CO}_2$ clusters have been found to agree well with experiment for N values up to 17.^b However, those simulations were based on two-dimensional potential energy surfaces with CO_2 fixed at its equilibrium geometry. While an adequate approximation for describing rotational constants, that approach cannot predict the ν_3 vibrational band origin shift of CO_2 in $(\text{He})_N$ clusters, because of neglect of the dependence of the potential energy surface on the Q_3 asymmetric-stretch motion of CO_2 .

We recently determined a three-dimensional analytical 'Morse/Long-Range' potential energy surface for the $\text{CO}_2\text{-He}$ dimer, which explicitly depends on the Q_3 asymmetric-stretch vibrational motion of CO_2 , and also incorporates the correct angle-dependent inverse-power long-range behaviour.^c We have used this new potential in path-integral Monte Carlo simulations to predict both the effective rotational constant and the shift of the ν_3 band origin for CO_2 doped in $(\text{He})_N$ clusters with N up to 100. Our results will be compared with experiment for clusters formed from both symmetric and asymmetric isotopologues of CO_2 .

^a J. Tang *et al.* *Phys. Rev. Lett.* **92**, 145503 (2004); A.R.W. McKellar, *J. Chem. Phys.* **128**, 044308 (2008).

^b F. Paesani, Y. Kwon and K.B. Whaley *Phys. Rev. Lett.* **94**, 153401 (2005); N. Blinov and P.-N. Roy *J. Low Temp. Phys.* **140**, 314 (2005); F. Mezzacapo, *J. Low Temp. Phys.* **140**, 241 (2005).

^c H. Li and R.J. Le Roy, *PCCP* (2008, in press).