QUANTUM MONTH CARLO PREDICTION OF VIBRATIONAL FREQUENCY SHIFTS OF $(\mathrm{He})_N$-CO_2 CLUSTERS

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High resolution infrared spectra of $(\mathrm{He})_N$-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 $(\mathrm{He})_N$-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 $(\mathrm{He})_N$ 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 CO_2-He bimer, 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 $(\mathrm{He})_N$ 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.

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[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).