QUANTUM SOLVATION OF $CO_2$ BY He ATOMS: FROM ONSET TO NANODROPLET

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Spectroscopic studies of molecules embedded in helium droplets provide a unique opportunity to investigate a superfluid. High-resolution infrared spectra of $CO_2$-$(He)_N$ clusters ranging in size from 'small' ($N \simeq 1 - 17$) to 'intermediate' ($N \sim 60$) have been reported recently by McKellar and co-workers.[a] However, they have not yet been able to extend this range to clusters large enough that the observed vibrational band origins shifts $\Delta\nu_3$ and rotational constants $B_0$ and $D_0$ approached the nanodroplet limit values.[b] This paper describes the use of modeling techniques to explore the domain between intermediate and 'larger' ($N \sim 10^2 - 10^3$) clusters, seeking to characterize the onset of nanodroplet behaviour.

Path integral Monte Carlo (PIMC) simulations using the worm algorithm can in principle provide reliable quantitative results for "larger" clusters approaching the nanodroplet limit. We have recently determined a three-dimensional analytical 'Morse/Long-Range' potential energy surface for $CO_2$-He, which explicitly depends on the $Q_3$ asymmetric-stretch vibrational motion of $CO_2$, and takes account of change in the average value of $Q_1$ when $\nu_3$ is excited.[c,d] Using this potential, predicted vibrational frequency shifts have been found to be in excellent agreement with experiment across the range $N = 1 - 40$,[d] so it is expected to provides a good description of larger clusters. This paper describes results obtained on using this potential in PIMC simulations to predict the effective rotational constant $B_0$ and the $\Delta\nu_3$ band-origin shift for $CO_2$ in $(He)_N$ clusters with $N > 10^2$. The importance of identical-particle exchange effects will be examined by comparing results obtained using both Boltzmann and Bose-Einstein statistics.

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[c] H. Li and R.J. Le Roy, *J. Chem. Chem. Phys.* **10**, 4128 (2008).
[d] H. Li, N. Blinov, P.-N. Roy and R.J. Le Roy, *J. Chem. Phys.* (2009, in press).