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Superfluid response of ^4He_N–N_2O clusters probed by path integral Monte Carlo simulations

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ABSTRACT

Using an improved path integral Monte Carlo method, finite-temperature structural and dynamical properties of ^4He_N–N_2O clusters ($N \leqslant 40$) are investigated. The simulations employed a newly developed He–N_2O interaction potential obtained at the CCSD(T) level. Good agreement with experimental observations was obtained for the evolution of the effective rotational constant as a function of cluster size. In particular, the experimentally observed turnaround at $N = 6$ for the effective rotational constant B_{eff} is attributed to filling of the "donut" ring structure around the equator of the linear impurity molecule, and a second extremum in B_{eff} for cluster sizes near $N = 10$ is associated with the emergence of superfluidity of the quantum solvent. A careful comparison with properties of He_N–CO_2 clusters suggests that the difference between the renormalized rotational constants of the two impurity molecules is due to the anisotropy of the solute–solvent interaction potential.

1. Introduction

Spectroscopic studies of impurity molecules embedded in low-temperature He clusters have revealed fascinating structural and dynamical behaviors of the micro-solvation environment [1]. For example, a linear impurity molecule (OCS) was found to have microwave spectra resembling a free rotor (albeit with a significantly smaller rotational constant) in low-temperature ^4He nanodroplets ($N \sim 10^4$), but it undergoes hindered rotation in ^3He droplets around the same temperature [2]. This striking observation was taken as evidence for a microscopic manifestation of superfluidity in ^4He droplets, apparently due to the exchange of the identical bosonic solvent atoms. This is a unique quantum mechanical phenomenon that has no classical counterpart.

A key question is concerned with the onset of microscopic superfluidity in such clusters. To this end, several infrared and microwave studies have been carried out to probe the micro-solvation environment for linear molecules (OCS, CO_2, and N_2O) embedded in relatively small ^4He clusters ($N < 100$) [3–13]. The variation of spectroscopic properties with the size of the cluster provided valuable information on the transition from a simple van der Waals complex to a quantum solution. Most interestingly, strong evidence has been presented for the emergence of superfluidity with only a few ^4He atoms.

A remarkable observation was made by Nauta and Miller [14], who found that in ^4He nanodroplets the rotational constant of N_2O was just half of CO_2, even though the gas phase constants of the two are similar. The drastically different behaviors of the two chromophores in ^4He clusters reflect the sensitivity of spectroscopy to the nature of the interaction between the solvent and impurity. Thus, an accurate dimer potential energy surface (PES) is particularly desirable for understanding the differences in solvation behavior. While elaborate He–CO_2 PESs have been reported by several groups [15,16], of those for He–N_2O [17–19], only one [20] incorporates explicit dependence on the N_2O internal modes. Such dependence is essential for simulating the IR spectra of the N_2O chromophore in such clusters.

With an accurate He–N_2O PES, the spectroscopy of a N_2O molecule embedded in ^4He clusters of various sizes can be simulated. To this end, an efficient quantum simulation method is needed to describe quantum fluctuation in these relatively large systems at finite temperatures. An ideal approach is the path integral Monte Carlo (PIMC) method [21], which has been extensively used to investigate doped ^4He clusters, yielding rich insights [22,33]. In particular, the ^4He_N–N_2O system has been studied by PIMC [9,25], as well as by other quantum methods [25,34,35]. This work uses the PIMC method developed by Blinov and Roy, which explicitly considers the rotational degree of freedom of the chromophore

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impurity [26,27,36]. The Bose identical-particle exchange was handled using the efficient worm algorithm [37,38].

The paper is organized as follows. Section 2 presents a brief description of the *ab initio* calculation of the He–N_2O PES, and of how it is fitted to an analytic function. Section 3 outlines the PIMC approach for doped ^{4}He clusters, and describes the framework of the superfluidity simulations. Section 4 then presents tests of the PES and the results of our PIMC simulations, together with an analysis of the evolution of the cluster structure and superfluid behavior with cluster size, and a comparison between the properties of ^4He_N–N_2O and ^4He_N–CO_2 clusters. Finally, brief conclusions are presented in Section 5.

2. He–N_2O dimer potential energy surface

Following our earlier work [20], we treated He–N_2O as a three dimensional system whose coordinates were the distance R between He and the center of mass of N_2O, the associated Jacobi angle θ, and the N_2O monomer antisymmetric stretch coordinate Q_3. (The normal coordinates Q_1 and Q_3 are determined by diagonalizing the vibrational Hamiltonian.) The explicit inclusion of Q_3 is designed to allow for realistic simulations of IR spectra of the clusters; however, the present work focuses on their rotational dynamics.

The *ab initio* calculations were based on a direct-product coordinate grid. Specifically, the following 22 point R grid was used: R = 3.6, 4.0, 4.5, 5.0, 5.2, 5.4, 5.6, 5.8, 6.1, 6.4, 6.8, 7.2, 7.6, 7.8, 8.0, 8.3, 8.6, 9.0, 10.0, 13.0, 15.0, and 19.0 Bohr. The grid points at large R are necessary to define the long-range interaction potential that is important for large clusters. In the θ coordinate, twelve points were evenly distributed between 0° and 180°, while five points were employed to describe the antisymmetric stretch Q_3. With a few more points added in the potential well region, a total of 1640 *ab initio* grid points were generated. The electronic structure calculations were carried out with the MOLPRO package [39] at the coupled-cluster singles and doubles level with non-iterative inclusion of connected triples, CCSD(T) [40], with the augmented correlation-consistent quadruple-zeta (AVQZ) basis set [41] being used for all atoms, and this basis was supplemented with bond functions (3*s*3*p*2*d*1*f*1*g*) (for 3*s* and 3*p*, α = 0.9, 0.3, 0.1; for 2*d*, α = 0.6, 0.2; for *f*, α = 0.3) [42] located at the center of the van der Waals bond. A supermolecular approach was adopted, and the full counterpoise procedure [43] was used to correct for basis-set superposition errors.

Following our earlier work [44], we further constructed a two-dimensional (2D) He–N_2O PES for the N_2O ground-state υ_3 level. This was done by averaging the 3D *ab initio* PES with appropriate vibrational wavefunctions:

$$V^{\nu_3}(R,\theta)=\langle\varphi_{\nu_3}(Q_3)|V(R,\theta,Q_3)|\varphi_{\nu_3}(Q_3)\rangle, \tag{1}$$

where $\varphi_{\nu_3}(Q_3)$ is the υ_3 vibrational wavefunction for an isolated N_2O molecule. To take account of contributions from the symmetric stretching mode (υ_1) which might be significant, as discussed in a previous work on the He–CO_2 system [33], we have calculated $\varphi_{\nu_3}(Q_3)$ using the average Q_1 value for ground state N_2O. In particular, for the υ_3 = 0 wavefunction, Q_1 was fixed at a value determined by the average N–N and N–O bond lengths of 1.12872 Å and 1.18792 Å, respectively.

Following the previous study on the potential fitting of He–N_2O [17], the 2D PESs were fitted to the analytical form:

$$V_{\mathrm{He-N_2O}}(R,\theta)=V_{sh}(R,\theta)+V_{as}(R,\theta), \tag{2}$$

in which $V_{sh}(R,\theta)$ is the short-range part with the following form:

$$V_{sh}=G(R,\theta)e^{D(\theta)-B(\theta)R}. \tag{3}$$

The functions D, B and G were expanded in terms of Legendre polynomials $P_l(\cos\theta)$:

$$G(R,\theta)=R^{-2}\sum_{i=0}^{N}R^i\sum_{l=0}^{L_G}g_i^l\frac{P_l(\cos\theta)}{\sqrt{2l+1}}, \tag{4}$$

$$D(\theta)=\sum_{l=0}^{L}d^l\frac{P_l(\cos\theta)}{\sqrt{2l+1}}, \tag{5}$$

$$B(\theta)=\sum_{l=0}^{L}b^l\frac{P_l(\cos\theta)}{\sqrt{2l+1}}, \tag{6}$$

with expansion lengths L = 4, L_G = 5, and N = 4.

The long-range asymptotic term $V_{as}(R,\theta)$ was given in the Tang–Toennies form [45], which includes a damping term for small R:

$$V_{as}=\sum_{i=6}^{12}\left(\frac{f_i[B(\theta)R]}{R^i}\sum_{l=0}^{L_{\max}}C_i^l\frac{P_l(\cos\theta)}{\sqrt{2l+1}}\right), \tag{7}$$

with $f_i(x)=1-e^{-x}\sum_{k=0}^{i}x^k/k!$. This analytical potential form was suggested by Tang and Toennies, and modified by Bukowski and coworkers by introducing anisotropy [46]. The fitting was based on the Levenberg–Marquardt nonlinear fitting algorithm [47]. The parameters in the previous work [17] were used as initial guesses for our fit, and the expansion lengths were extended gradually.

3. Path integral Monte Carlo method

3.1. Hamiltonian

The Hamiltonian for the He_N–N_2O cluster may be written as:

$$\widehat{H}=\widehat{H}_{\mathrm{He}}+\widehat{H}_{\mathrm{N_2O}}+V_{\mathrm{He_NN_2O}}, \tag{8}$$

where

$$\widehat{H}_{\mathrm{He}}=\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m_{\mathrm{He}}}+\sum_{i<j}u(|\mathbf{r}_i-\mathbf{r}_j|) \tag{9}$$

denotes the Hamiltonian for He atoms with $\mathbf{p}_i$ and $\mathbf{r}_i$ ($i\neq 0$) being the momentum and position of a He atom, respectively. The He–He pair potential u is that of Aziz et al. [48].

The Hamiltonian for the impurity (i = 0) treats it as a translating rigid rotor:

$$\widehat{H}_{\mathrm{N_2O}}=\frac{\mathbf{p}_0^2}{2m_{\mathrm{N_2O}}}+B_{\mathrm{N_2O}}\mathbf{L}^2, \tag{10}$$

where $\mathbf{p}_0$ and $\mathbf{L}$, respectively, denote the linear and rotational angular momentum of N_2O. The rotational constant for N_2O is $B_{\mathrm{N_2O}}=0.4190110\ \mathrm{cm}^{-1}$ [49]. Finally, the interaction potential between He atoms and N_2O is also assumed to be a pairwise sum:

$$V_{\mathrm{He_NN_2O}}=\sum_i V_{\mathrm{He-N_2O}}(R_i,\theta_i), \tag{11}$$

where R_i and θ_i are the Jacobi coordinates of the ith helium atom with respect to the molecular dopant.

3.2. Path integral Monte Carlo

For any quantum mechanical operator ($\widehat{O}$), its canonical average can be calculated as follows [21]:

$$\begin{aligned}\langle\widehat{O}\rangle_\beta&=\frac{1}{Z}\mathrm{Tr}\{\widehat{O}\hat{\rho}(\beta)\}\\&=\frac{1}{Z}\int d\mathbf{q}d\mathbf{q}'d\mathbf{\Omega}d\mathbf{\Omega}'\langle\mathbf{q\Omega}|\widehat{O}|\mathbf{q}'\mathbf{\Omega}'\rangle\langle\mathbf{q}'\mathbf{\Omega}'|\hat{\rho}(\beta)|\mathbf{q\Omega}\rangle,\end{aligned} \tag{12}$$

where $Z=\mathrm{Tr}\{\hat{\rho}(\beta)\}$ is the partition function and $\beta=1/k_BT$. The above integration is performed over the translational coordinates