Superfluid response of $^4\text{He}_N$–$\text{N}_2\text{O}$ clusters probed by path integral Monte Carlo simulations

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\textbf{Abstract}

Using an improved path integral Monte Carlo method, finite-temperature structural and dynamical properties of $^4\text{He}_N$–$\text{N}_2\text{O}$ clusters ($N \leq 40$) are investigated. The simulations employed a newly developed He–$\text{N}_2\text{O}$ 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 $N \approx 6$ for the effective rotational constant $B_{\text{eff}}$ is attributed to filling of the “donut” ring structure around the equator of the linear impurity molecule, and a second extremum in $B_{\text{eff}}$ for cluster sizes near $N \approx 10$ is associated with the emergence of superfluidity of the quantum solvent. A careful comparison with properties of $^4\text{He}$–$\text{CO}_2$ 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.

\section{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 $^4\text{He}$ nanodroplets ($N \sim 10^4$), but it undergoes hindered rotation in $^3\text{He}$ droplets around the same temperature [2]. This striking observation was taken as evidence for a microscopic manifestation of superfluidity in $^4\text{He}$ 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 ($\text{OCS}$, $\text{CO}_2$, and $\text{N}_2\text{O}$) embedded in relatively small $^4\text{He}$ 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 $^4\text{He}$ atoms.

A remarkable observation was made by Nauta and Miller [14], who found that in $^4\text{He}$ nanodroplets the rotational constant of $\text{N}_2\text{O}$ was just half of $\text{CO}_2$, even though the gas phase constants of the two are similar. The drastically different behavior of the two chromophores in $^4\text{He}$ 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–$\text{CO}_2$ PESs have been reported by several groups [15,16], of those for He–$\text{N}_2\text{O}$ [17–19], only one [20] incorporates explicit dependence on the $\text{N}_2\text{O}$ internal modes. Such dependence is essential for simulating the IR spectra of the $\text{N}_2\text{O}$ chromophore in such clusters.

With an accurate He–$\text{N}_2\text{O}$ PES, the spectroscopy of a $\text{N}_2\text{O}$ molecule embedded in $^4\text{He}$ 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 $^4\text{He}$ clusters, yielding rich insights [22,33]. In particular, the $^4\text{He}_N$–$\text{N}_2\text{O}$ 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.
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 \textit{ab initio} calculation of the He–N$_2$O 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 $^4$He$_n$–N$_2$O and $^4$He$_n$–CO$_2$ clusters. Finally, brief conclusions are presented in Section 5.

2. He–N$_2$O dimer potential energy surface

Following our earlier work [20], we treated He–N$_2$O as a three dimensional system whose coordinates were the distance $R$ between He and the center of mass of N$_2$O, the associated Jacobi angle $\theta$, and the N$_2$O monomer antisymmetric stretch coordinate $Q_3$. (The normal coordinates $Q_1$ and $Q_2$ 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 \textit{ab initio} calculations were based on a direct-product coordinate grid. Specifically, the following 22 point grid was used: $R = 3.6, 4.0, 4.5, 5.0, 5.2, 5.4, 5.6, 5.8, 6.1, 6.4, 6.8, 7.2, 7.6, 7.8, 8.0, 8.3, 8.6, 9.0, 10.0, 11.0, 15.0,$ 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 $\theta$ coordinate, twelve points were evenly distributed between 0$^\circ$ and 180$^\circ$, 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 calculation of the He–N$_2$O PES, and of \textit{ab initio} 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 (3s3p2d1f1g) for 3s and 3p, $\alpha = 0.9, 0.3, 0.1; 2d, \alpha = 0.6, 0.2; f, \alpha = 0.3$) [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$_2$O PES for the N$_2$O ground-state $\nu_1$ level. This was done by averaging the 3D \textit{ab initio} PES with appropriate vibrational wavefunctions:

$$V^{\nu_1}(R, \theta) = \langle \varphi_{\nu_1}(Q_3)|V(R, \theta, Q_3)|\varphi_{\nu_1}(Q_3)\rangle,$$

(1)

where $\varphi_{\nu_1}$ is the $\nu_1$ vibrational wavefunction for an isolated N$_2$O molecule. To take account of contributions from the symmetric stretching mode ($\nu_2$) which might be significant, as discussed in a previous work on the He–CO$_2$ system [33], we have calculated $\varphi_{\nu_2}$ using the average $Q_2$ value for ground state N$_2$O. In particular, for the $\nu_2 = 0$ wavefunction, $Q_2$ was fixed at a value determined by the average N–N and N–O bond lengths of 1.2872 Å and 1.18792 Å, respectively.

Following the previous study on the potential fitting of He–N$_2$O [17], the 2D PESs were fitted to the analytical form:

$$V_{\text{He-N}_2\text{O}}(R, \theta) = V_{\text{ab}}(R, \theta) + V_{\text{sh}}(R, \theta),$$

(2)

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

$$V_{\text{ab}} = G(R, \theta) e^{\mu(R, \theta) - \eta(R, \theta)},$$

(3)

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

$$G(R, \theta) = R^{-2} \sum_{i=0}^{N} \sum_{l=0}^{L_i} \sum_{j=0}^{L_j} C_i^j \frac{P_i(\cos \theta)}{\sqrt{2l + 1}},$$

(4)

$$D(\theta) = \sum_{i=0}^{L} \frac{D_i}{\sqrt{2l + 1}},$$

(5)

$$B(\theta) = \sum_{i=0}^{L} \frac{B_i}{\sqrt{2l + 1}}.$$

(6)

with expansion lengths $L = 4, L_c = 5, and N = 4$.

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

$$V_{\text{ab}} = \sum_{i=0}^{12} \left( \frac{|f_i|}{R} \right)^i \sum_{i=0}^{4} C_i^j \frac{P_i(\cos \theta)}{\sqrt{2l + 1}},$$

(7)

with $f_i(x) = 1 - e^{-\sum_{i=0}^{10} x^i}/x!$. 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$_2$O cluster may be written as:

$$\hat{H} = \hat{H}_{\text{He}} + \hat{H}_{N_2O} + \hat{V}_{\text{He-N}_2\text{O}},$$

(8)

where

$$\hat{H}_{\text{He}} = \sum_{i=1}^{N} \left( \frac{\mathbf{P}_i^2}{2m_{\text{He}}} + \sum_{i<j} u(|\mathbf{r}_i - \mathbf{r}_j|) \right),$$

(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:

$$\hat{H}_{N_2O} = \frac{\mathbf{P}_0^2}{2m_{N_2O}} + \mathbf{B}_{N_2O} \mathbf{L}^2,$$

(10)

where $\mathbf{p}_0$ and $\mathbf{L}$, respectively, denote the linear and rotational angular momentum of N$_2$O. The rotational constant for N$_2$O is $B_{N_2O} = 0.4190110$ cm$^{-1}$ [49]. Finally, the interaction potential between He atoms and N$_2$O is also assumed to be a pairwise sum:

$$\hat{V}_{\text{He-N}_2\text{O}} = \sum_{i=1}^{N} V_{\text{He-N}_2\text{O}}(R_i, \theta_i),$$

(11)

where $R_i$ and $\theta_i$ are the Jacobi coordinates of the $i$th helium atom with respect to the molecular dopant.

3.2. Path integral Monte Carlo

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

$$\langle \hat{O} \rangle_{\beta} = \frac{1}{Z} \text{Tr}(\hat{O} \hat{\rho}(\beta)) = \frac{1}{Z} \int dq dq^i dq'^i d\Omega |\mathbf{q}\rangle \langle \mathbf{q}'| \hat{\rho}(\beta) |\mathbf{q}'\rangle \langle \mathbf{q}|,$$

(12)

where $Z = \text{Tr}(\hat{\rho}(\beta))$ is the partition function and $\beta = 1/k_B T$. The above integration is performed over the translational coordinates...
of both N₂O and He moieties, denoted as \( q = (r_{\Omega}, r_{p}) \), and the orientation of N₂O in the space-fixed frame, denoted as \( \Omega \).

To compute the density matrix, we adopt the path integral approach [50], in which the integral is discretized in imaginary time:

\[
\langle q| \Omega | e^{-\beta \hat{H}} | q, \Omega \rangle = \int \cdots \int \prod_{k=2}^{K'} d\Omega_k \prod_{k=2}^{K'} dq_k \\
\times \prod_{k=1}^{K'} \left\langle \Omega_k | e^{\beta \omega_{q} | \Omega_{k+1}} \right| q_0, \Omega_1 \rangle \\
\times \left\langle \Omega_{k+1} | e^{-\beta \hat{H}_n} | q_{k+1} \right\rangle (13)
\]

where \( \hat{T}_{\text{rot}} \) represents the rotational kinetic energy operator of N₂O, and \( \hat{H}_n \) stands for the remainder of the Hamiltonian in Eq.(8). Note that the Trotter time slices are defined separately for transitional and rotational degrees of freedom: \( \tau = \beta / K \) and \( \tau = \beta / K' \) [26]. In addition, boundary conditions are defined as \( (q, \Omega_1) = (q, \Omega) \) and \( (q_0, \Omega_{1-n}) = (q, \Omega) \). In the PIMC simulation, a closed form [51] was used for the rotational density matrix, while the primitive approximation was employed for the translational density matrix. The sampling for the rotational degree of freedom was carried out using a multilevel Metropolis algorithm [51,52], while that for the translational degrees of freedom was carried out using a multilevel Metropolis algorithm [21]. The Bose exchange was included in PIMC by the efficient worm algorithm [37,38]. The details of the implementation will be presented separately in the near future [53].

3.3. Superfluidity

The Feynman path integral provides a useful framework for the investigation of superfluidity in a bosonic system. In the so-called two-fluid model [9,23,29,54], the solvent density is separated into two components, the superfluid and normal-fluid densities. Linear response theory allows the calculation of the superfluid fraction for rotation parallel (||) or perpendicular (\perp) to the molecular axis of the impurity [55]:

\[
\mathbf{f}_{||} = \frac{4m_{\text{imp}}(\mathbf{A} \cdot \mathbf{n}_{||})^2}{\hbar^2 \mathbf{f}_{||}} 
\]

where \( \mathbf{f}_{||} \) is the classical moment of inertia. The unit vector parallel (||) or perpendicular (\perp) to the molecular axis of the impurity, \( \mathbf{n}_{||,\perp} \), is defined at the time slice \( \tau = 0 \). The path area

\[
\mathbf{A} = \frac{1}{2} \sum_{k} \sum_{k+1} [r_k \times r_{k+1} ] (20)
\]

is related to the positions of the \( i \)-th solvent atom at the imaginary time slices \( k \) and \( k+1 \).

Within the two-fluid model, the renormalization of the rotational constant is considered as the drag of the normal component of solvent atoms by a rotating impurity molecule, and the remaining atoms at superfluid state do not contribute to the moment of inertia. Thus, the expression for the moment of inertia contributed by the solvent atoms in the normal state \( f_{||}^{L} \) is:

\[
f_{||}^{L} = f_{||}^{L} (1 - f_{||}^{L}) (21)
\]

Denoting the moment of inertia of the impurity molecule as \( I_{\text{imp}} \), the total moment of inertia of the solvent–molecule complex can be expressed as \( I_{L} = I_{\text{imp}} + f_{||}^{L} I_{||} \). It is clear that in the superfluid limit \( f_{||}^{L} = 1 \) the perpendicular moment of inertia is dominated by that of the impurity. The effective rotational constant \( B_{\text{eff}} \) is related to \( I_{L} \), and it can be compared with that obtained by directly fitting the canonical orientational correlation function to the PIMC data [26].

4. Results and discussion

4.1. He–N₂O potential energy surface

The 63 fitting parameters defined in Eqs. (2)–(7) for the \( v_3 \) ground state of N₂O are listed in Tables 1 and 2. The good quality of fit is demonstrated by the very small (\( \leq 0.004 \text{ cm}^{-1} \)) root-mean-square (RMS) deviation from the \( v_3 \) initial points at energies below 100 cm⁻¹.

Fig. 1 displays a contour plot of the fitted He–N₂O PES for \( v_3 = 0 \). A T-shaped global minimum with an energy of \(-62.27 \text{ cm}^{-1}\) is located at \( R = 2.983 \text{ Å} \) and \( \theta = 87.02^\circ \), and a collinear minimum with an energy of \(-32.81 \text{ cm}^{-1}\) is located at \( R = 4.13 \text{ Å} \) with the He atom attached to the O end of the molecule. The energy minima are close to those reported in our earlier work (\(-62.34 \text{ and } -32.88 \text{ cm}^{-1}\)), which used the same CCSD(T) level of theory with smaller AVTZ basis set [20].

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used in actual calculations. Extensive convergence tests have thus been performed with respect to the number of time slices in both the rotational and translational degrees of freedom. It was found that 512 translational and 128 rotational time slices are sufficient to converge the results. The PIMC simulations were performed at $T = 0.37$ K. The number of Monte Carlo steps was of the order of $10^8$.

### 4.2.2. Structural properties

As shown in Fig. 1, the nearly T-shaped He–N$_2$O global minimum has a well depth of 62.27 cm$^{-1}$, which is eight times larger than that for the He–He pair (7.61 cm$^{-1}$). Moreover, at the collinear minimum and in the region connecting the two minima, this solvent–molecule interaction is still far stronger than the solvent–solvent interaction. As a result, the structures of small clusters will be mainly determined by the He–N$_2$O interactions. Only after the strongly attractive regions are occupied will the He–He interaction become significant.

As has been observed for other families of He-solvated chromophores (e.g., He–OCS [59–61] and He–CO$_2$ [27,33,62]), the first few He atoms form a “donut” structure, occupying equatorial positions around the linear impurity molecule, due to the deep T-shaped He–molecule potential minimum. Once that first ring of five solvent molecules is added, additional helium atoms start to form a second ring in the region near the terminal O atom of the N$_2$O impurity, supported by the collinear minimum. This is clearly shown in Fig. 2 by the distributions of the He atoms for $N = 5–8$. For $N > 9$, the ring at the collinear minimum is fully occupied, and the additional helium atoms start to build a ring about the N end of the molecule, and then caps are added and the density fills in. As discussed below, filling the first shell of helium atoms around the impurity molecule is a pre-requisite for superfluidity perpendicular to the molecular axis. As shown in Fig. 2, the impurity molecule becomes fully solvated near $N = 18$, and the second solvation shell starts to form after that. The distributions go zero at $\theta = 0$ and $\pi$ due to the angular normalization.

### 4.2.3. Energetics

The relative stability of the clusters can be characterized by the chemical potential, which is defined as

$$\mu(N) = E(N) - E(N - 1),$$

where $E(N)$ is the energy of the He$_N$–N$_2$O cluster. As shown in Fig. 3, the chemical potential is large and negative for the first few He atoms, indicating a large energy drop occurs when each additional He atom is added. An abrupt change occurs after the first “donut” ring is completed at $N = 5$. This can be understood by the fact that additional helium atoms only have access to less strongly attractive sites. The $\mu(N)$ curve increases slightly from $N = 6$ to 8, as helium atoms start to occupy the local minimal site at the oxygen side of the impurity, while for larger $N$ values $\mu(N)$ increases gradually as the helium atoms take positions in regions characterized by weaker solute–solvent interactions.

### 4.2.4. Rotational dynamics and superfluidity

The effective rotational constant of the solvated impurity can be computed using two approaches. In the conventional approach, it is obtained by fitting the rigid-rotor orientational correlation function directly to the PIMC data [26]. Alternatively, it can be computed using the two-fluid model discussed in Section 3.3. In Fig. 4, the calculated $B_{eff}$ values from both approaches are compared with experimental results for $^4$He$_N$–N$_2$O of different sizes [9,11]. Here, the calculated results are presented in the figure without error bars, since the statistical errors are very small, ranging from 0.0005 cm$^{-1}$ (large clusters) to 0.0027 cm$^{-1}$ (small clusters). The agreement between the calculated rotational constants and
the measured ones is quite satisfactory. In particular, the calculated rotational constants reproduce the first turnaround around \( N = 6 \), as well as the second minimum at \( N = 16 \). It has previously been suggested theoretically that the effective moment of inertia could increase from \( N = 20 \) to 30, due to “a new channel of exchanges in the second solvation shell” [25]. However, in agreement with the more recent experimental results [11], our theoretical results show no such increase. Furthermore, the agreement between the PIMC predictions and the experimental results remain excellent for the larger clusters.
It can be seen from Fig. 4 that the agreement with the experimental data is much better for $B_{\text{eff}}$ values calculated using the correlation function results than for those obtained from the two-fluid model, for which the results are comparable to those yielded by the earlier work of Xu et al. [9]. The differences between the predictions of the two PIMC-based methods could be taken as evidence that the correlation function approach provides a more realistic representation of the rotational dynamics. This may be expected because the two-fluid approach contains additional approximations inherent to linear response theory.

The open square points in Fig. 4 correspond to PIMC correlation-function results obtained while neglecting identical particle bosonic exchange. It is clear that the quantum results start to deviate from this classical Boltzmann behavior for $N > 6$. This deviation of the quantum $B_{\text{eff}}$ values from their classical counterparts clearly suggests the emergence of superfluidity stemming from Bose identical-particle exchange. To further understand the superfluid response of the solvent, Fig. 5 shows plots of our calculations of the superfluid fraction in directions parallel and perpendicular to the N$_2$O axis (see Eq. (19)). The parallel fraction increases rapidly with $N$ and reaches 100% for very small clusters. This implies that for rotation parallel to the molecule axis, the normal moment of inertia vanishes for cluster sizes with $N > 6$, which is confirmed by the lack of a Q-branch in ro-vibrational spectra of doped clusters in this size range [2,9].

Fig. 5 also shows that the superfluid fraction perpendicular to the molecule axis behaves quite differently. Here, our calculated results may be compared with those extracted from experimental determinations of the effective moments of inertia of doped clusters. For cluster sizes $N = 4–6$ both simulation and experiment exhibit a steeper negative slope. This is understandable, as the first few helium atoms increase the effective reduced mass of the rotor. Near $N = 5$, an unambiguous turnaround occurs that suggests the onset of a decoupling between the N$_2$O rotation and the helium dynamics. As $N$ increases further, the superfluidity fraction rises and eventually approaches 100%. This picture is consistent with experimental results shown as solid round points in Fig. 5.

The turnaround shown in Fig. 4 can also be explained by the two-fluid model. In particular, the rise of perpendicular superfluid fraction shown in Fig. 5 leads to a depletion of the normal moment of inertia $I_n$ for $N > 5$. Consequently, the effective rotational constant of the chromophore stays at roughly the same level, as the superfluid helium atoms contribute negligibly to $B_{\text{eff}}$. Fig. 4 shows that the qualitative agreement between the rotational constants calculated from fitting orientational correlation functions and from the two-fluid model continues to hold for larger clusters, although significant quantitative differences are clearly evident.

### 4.2.5. Potential function dependence of superfluid behavior

It is interesting to compare the rotational dynamics of the impurity in $^4$He$_{N}$–N$_2$O and $^4$He$_{N}$–CO$_2$ clusters. As was pointed out earlier, the effective moments of inertia of these two impurity molecules are quite different in $^4$He clusters, despite the fact that the $B$ rotational constants are quite similar for the isolated molecules. Interestingly, as shown in the inset panel of Fig. 6, the classical Boltzmann rotational constants are quite similar for the two clusters, indicating that the difference in $B_{\text{eff}}$ behavior is due to quantum Bose exchange. In the upper panel of Fig. 6, the superfluid fraction in the perpendicular direction is plotted for the two clusters as a function of $N$. It is clear that the transition from normal fluid to superfluid is swift and complete for the $^4$He$_{N}$–CO$_2$ clusters with $N > 5$, while that for the $^4$He$_{N}$–N$_2$O clusters is much more sluggish. As discussed in Section 3.3, a large superfluid fraction corresponds to a reduced classical contribution of helium atoms to the effective moment of inertia, which explains the smaller $B_{\text{eff}}$ for the $^4$He$_{N}$–CO$_2$ clusters.
The differences in the variation of $B_{\text{eff}}$ with $N$ can be attributed to differences in the interaction potential between He and the impurity. Here two factors are particularly important. First, the orientation-dependent potential function wells for the He--N$_2$O complex are about 20% deeper than those for the He--CO$_2$ complex, as shown in the lower panel of Fig. 6. A strong solvent–solute interaction generally inhibits solvent exchange, and thus also superfluidity. Indeed, when the strength of the He--N$_2$O potential is artificially scaled to that of He--CO$_2$ (purple dotted curve in lower panel), the perpendicular superfluid fraction increases significantly (purple triangle points in upper panel of Fig. 6). However, this increase does not account fully for the differences between the two cases.

Another important factor is the symmetry of the anisotropy of the interaction potential, which is present for He--CO$_2$ and absent for He--N$_2$O. In He$_{24}$--CO$_2$, the population of helium atoms near both ends of the impurity grows approximately symmetrically after the donut ring is completed at $N = 5$. This effectively gives rise to a continuous density distribution around the impurity molecule which facilitates the exchange of $^4$He atoms [31]. As indicated in Eq. (19), the perpendicular superfluid fraction can be expressed as the ratio between the area estimator projected on the direction perpendicular to the impurity molecule axis and its classical counterpart. The area estimator is a sum of cross products between two vectors (Eq. (20)) defined from the impurity center of mass to two different He atoms. As a result, the perpendicular superfluid fraction is dominated by the exchange of helium atoms in the continuous shell around the impurity, and for the normal direction the corresponding area vector is perpendicular to the molecular axis. This can also be understood phenomenologically by the argument that the exchange of helium atoms at the two ends of the impurity is equivalent to rotation of the impurity itself.

For the non-symmetric N$_2$O, the distribution of helium atoms immediately after the filling of the donut ring at $N = 5$ is asymmetric, and concentrates on the $O$-atom side of the central donut ring, as shown in Fig. 2. This limits the possibility for the exchange of helium atoms along the length of the N$_2$O molecule. However, such exchange becomes increasingly possible for $N > 10$, as both the $O$ and $N$ sides of the central ring become populated with helium atoms. The green diamond-shaped points in the upper panel of Fig. 6 present values of the superfluid fraction calculated using a hypothetical He--N$_2$O potential function that has essentially the correct overall anisotropy, but was artificially symmetrized $(V(\theta) = [V(\theta) + V(\pi - \theta)]/2$; short-dash curve in the lower panel of Fig. 6). It is clear that the enforced artificial symmetry boosts the superfluid fraction values significantly for clusters with $N > 5$, moving them closer to the He$_{24}$--CO$_2$ results. The purple open-triangle points in the upper panel of Fig. 6 were obtained from another modified potential energy surface whose overall anisotropy strength was damped to make it closer to that for He--CO$_2$ (dotted curve in the lower panel of Fig. 6). It clearly shows a further enhancement in the superfluid fraction for larger $(N > 5)$ clusters. Finally, the open square points at the top of Fig. 6 show that a fully isotropic potential with the same overall strength as that of the T-shaped minimum of He$_{24}$--N$_2$O yields a maximum superfluid response regardless of clusters size. Since such a fully isotropic potential has no angular dependence, no corresponding curve is shown in the lower panel of Fig. 6.

The results shown in Fig. 6 confirm that it is indeed the anisotropy of the interaction potential that causes the inertial drag of the quantum solvent as far as the perpendicular superfluid response is concerned. Although Moroni and coworkers [8,63] had discussed the effect of anisotropy on the effective rotational constants, their ground state simulations could not be used to assess the superfluid response directly. The present analysis therefore complements their findings by making the additional connection to the superfluid response.

5. Conclusions

This work reports an accurate new He--N$_2$O dimer potential energy surface based on high-level ab initio calculations. A reduced-dimension 2D analytic potential energy function was fitted to these results to provide a convenient “working potential” for use in performing simulations. With this accurate potential energy surface, we have carried out finite temperature PIMC simulations of the rotational dynamics of the N$_2$O embedded in $^4$He clusters of various sizes. The simulation results are in reasonably good agreement with known experimental data.

A detailed analysis of the superfluid response as a function of cluster size has been performed. It is shown that the calculated effective rotational constant deviates from the classical Boltzmann limit around N--5, which indicates the onset of superfluidity in the cluster. This deviation results in a turnaround in the values of the effective rotational constant as a function of $N$, as has been observed experimentally. This turnaround can also be attributed to the rise of the perpendicular superfluid fraction of the helium atoms, due apparently to Bose exchange. In addition, it is shown that fitting to simulation results for the orientational correlation function gives better predictions of superfluid behavior (better agreement with experiment) than does the two-fluid method, particularly for larger clusters.

Finally, we have elucidated the difference in the nature of the rotational dynamics between a symmetric (CO$_2$) and asymmetric (N$_2$O) impurity in $^4$He clusters. It is shown that the difference in renormalization of the rotational constants of the two helium solvated impurity molecules can be attributed to the anisotropy of the He-impurity interaction potential, which resulted in different onsets of superfluid behavior perpendicular to the molecular axis.

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