

Rotational Level Structure of SF₆-Doped ⁴He_N Clusters

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We present diffusion Monte Carlo calculations of low-lying rotational states of ⁴He_NSF₆ which confirm recent experiments suggesting that dopant molecules trapped inside ⁴He clusters behave as free rotors. Analysis of the rotational wave functions leads to a clear physical explanation for this effect based on angular momentum coupling arguments; a fraction of the helium density is found to follow the rotation of the SF₆ molecule adiabatically. This leads to a free-rotor spectrum and to a reduction in the effective rotational constant that is in excellent quantitative agreement with experiment.

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The rotational dynamics of a solute molecule in a classical liquid are rather complicated: collisions scramble the molecule's angular momentum and, as a result, it is rarely possible to observe sharp rotational lines. In recent experiments, however, rotationally resolved spectra of single molecules in a quantum liquid have been obtained: the "dopant" molecules are introduced into droplets of superfluid ⁴He using pickup techniques in a molecular beam which are then studied by laser spectroscopy [1–8]. The rotational spectra so obtained can be fit rather well by assuming a free rotor Hamiltonian, usually of the same symmetry as the gas phase molecule, but with a reduced rotational constant. By contrast, rotationally resolved spectra are not observed in fermionic ³He clusters which, at the temperatures achieved in the experiments ($T \sim 0.15$ – 0.4 K), lie above the corresponding superfluid transition temperature. These experimental findings have been taken to imply that free rotation of the dopant molecules is a consequence of the superfluidity of the bosonic ⁴He clusters [3].

SF₆ was the first molecule to be studied using high resolution spectroscopy in a ⁴He_N droplet [1]; accordingly, this Letter provides a molecular explanation for the experimental observation of a free rotor energy level pattern in SF₆-doped ⁴He clusters. We also provide a physical description of the *reduction* in the effective rotational constant, B . This is accomplished through explicit quantum calculations of the low-lying cluster rotational energy level structure for ⁴He_NSF₆, with $1 \leq N \leq 20$, which spans the first solvation shell of the molecule [9]. These calculations elucidate the generality of the phenomenon of apparent free rotation in ⁴He_N by demonstrating that the spectroscopically relevant excited states correspond to $J \sim j$, where J and j denote the total cluster and dopant angular momentum quantum numbers, respectively. Despite the anisotropy introduced by the dopant, these excitations distribute almost no angular momentum among the ⁴He atoms and j becomes a quasi-good quantum number. This is a consequence of the boson statistics of ⁴He, and would not be true for ³He_N clusters, in which the ³He atoms would carry some angular momentum, even in an isotropic

(central field) potential, due to fermion statistics. SF₆ is a prototype for molecules that are relatively strongly bound to He, and which have small rotational constants ($< 10^{-1}$ cm⁻¹). Our quantum calculations show that in this case the experimentally observed reduction in rotational constant is already achieved with $N \sim 8$ helium atoms. Analysis of the helium density around the rotating molecule reveals the underlying physics, namely, that a fraction of the helium density in the first solvation shell is able to follow the molecular rotation adiabatically. Our analysis demonstrates the interplay of two factors, namely (i) the strength of the anisotropic molecule-helium binding, and (ii) the magnitude of B_0 , the gas phase rotational constant, in determining the *extent* of the reduction in the effective rotational constant, B .

Calculation of the low-lying rotational energy level spectrum is accomplished here using a diffusion Monte Carlo algorithm. Quantum Monte Carlo methods are the only viable option for performing accurate calculations for clusters containing a large number of helium atoms. Alternatives such as coupled channel methods or basis set calculations are very difficult to extend beyond the simplest case of $N = 1$. This is true even if, as is done here, the Born-Oppenheimer approximation is used to uncouple the vibrations from rotations, i.e., the molecule is treated as a rigid body. Application of diffusion Monte Carlo methods to the rotation of rigid molecules was first made by Buch [10]. We introduce here a new approach, referred to as *fixed-frame* diffusion Monte Carlo (FFDMC), which is tailored to treat both overall and internal rotations of van der Waals clusters when the interactions are weak and exhibit pronounced anisotropy.

In the laboratory frame the Hamiltonian for N helium atoms interacting with a rigid SF₆ molecule via an anisotropic potential $V(r, \Theta, \Phi)$ is given by

$$H = -\frac{\hbar^2}{2m_I} \nabla_I^2 - \frac{\hbar^2}{2m_{\text{He}}} \sum_{i=1}^N \nabla_i^2 + \sum_{i < j}^N V_{\text{He}}^{\text{He}}(r_{ij}) + \sum_{i=1}^N V_I^{\text{He}}(r_{iI}, \Theta_{iI}, \Phi_{iI}) + H_{\text{rot}}^{\text{lab}}. \quad (1)$$

Here r_{ij} and r_{iI} denote He-He and He-molecule separations, respectively, Θ_{iI} and Φ_{iI} are the spherical polar angles specifying the helium position in a molecule-fixed frame, and m_I and m_{He} refer to the masses of the impurity (dopant) molecule and the He atom, respectively. $V_{\text{He}}^{\text{He}}(r_{ij})$ and $V_I^{\text{He}}(r_{iI}, \Theta_{iI}, \Phi_{iI})$ denote the He-He [11] and He-molecule [12] two-body potentials, respectively. For a spherical top molecule, the rotational part of the Hamiltonian is simply given by

$$H_{\text{rot}}^{\text{lab}} = B_0(j_x^2 + j_y^2 + j_z^2). \quad (2)$$

The essence of FFDMC is to recognize that the Monte Carlo translational and rotational moves can be made in the same frame of reference. Doing this avoids the problem of inadvertently averaging over the projections of the molecular angular momentum \mathbf{j} (or equivalently, over the potential anisotropy), which may happen if the translational and rotational moves are made in different frames of reference. This is a particularly acute problem for $^4\text{He-SF}_6$ because the ground state, although localized at the threefold sites, is somewhat “fragile” in that it lies *above* all of the saddle points in the potential. For a spherical top molecule such as SF_6 , both rotational and translational kinetic energy operators are quadratic forms that can be simultaneously diagonalized in any frame, so the rotational moves can be made around laboratory fixed axes, just like translational moves. For nonspherical tops, however, both rotations and translations must be performed in the molecule-fixed frame, i.e., with reference to the molecular principal axes.

The short-time Green’s function is factorized into the usual translational part, and a product of three one-dimensional rotational terms which are derived from $H_{\text{rot}}^{\text{lab}}$. For small rotations, each of these terms is of the form

$$\langle \phi_q | e^{-B_0 \tau j_q^2} | \phi'_q \rangle = (4\pi B_0 \hbar^2 \tau)^{-1/2} \exp\left[-\frac{(\phi_q - \phi'_q)^2}{4B_0 \hbar^2 \tau}\right], \quad (3)$$

where $q \equiv (x, y, z)$ are the laboratory frame Cartesian coordinates and ϕ_q denotes an angle of rotation about the q axis [13]. In an “unbiased” calculation, this short-time Green’s function is sampled together with the translational Green’s function to propagate the ground state wave function Φ [14]. For $N = 1$, i.e., the $^4\text{He-SF}_6$ “dimer,” when all moves are made consistently in the laboratory-fixed frame, the correct anisotropic ground state energy, $E_0^{\text{ani}} = -37.1(0.23)$ K (confirmed by close coupling calculations made with the method of Ref. [15]), is obtained with unbiased sampling. Unbiased sampling becomes inefficient as N increases however, and importance sampling is then essential for both ground and excited state calculations. Sampling from a distribution $f = \Psi_T \Phi$ which is “biased” by a physically motivated trial function Ψ_T increases efficiency and eliminates numerical instabilities (e.g., due to dissociation). For excited state calculations, it also allows

one to impose the necessary nodal constraints. This is done for the first time for rotational degrees of freedom here, implementing the importance sampling for rotations by using a trial function, $\Psi_T(\mathbf{R}_{N+1}, \alpha, \beta, \gamma)$, where α, β, γ are the Euler angles, which can be related to ϕ_x, ϕ_y, ϕ_z . This function is dependent on *both* translational and rotational coordinates. The angular degrees of freedom in the biased distribution $f = \Psi_T \Phi$ are then sampled by replacing $(\phi_q - \phi'_q)$ in Eq. (3) by $(\phi_q - \phi'_q - B_0 \tau F_q^{\text{rot}})$, where $F_q^{\text{rot}} = 2 \frac{\partial}{\partial \phi_q} \ln \Psi_T(\mathbf{R}_{N+1}, \alpha, \beta, \gamma)$, for each q [13]. Thus, rotations are treated on exactly the same footing as translations, at both the importance sampled and nonimportance sampled levels of calculation.

Our trial wave functions $\Psi_T(\mathbf{R}_{N+1}, \alpha, \beta, \gamma)$ are based on pairwise contributions in the ground state, multiplied by the appropriate rotational wave functions (Wigner rotation matrices) which are used to impose angular nodal structure in the laboratory frame for rotational excited states. The factorization of dopant angular terms and translation terms in Ψ_T ensures the correct limiting behavior when the dopant-helium interaction potential is isotropic. For N ^4He atoms, the laboratory frame trial wave function used is

$$\Psi_T = \left\{ \prod_{i=1}^N \Xi(r_{iI}, \Theta_{iI}, \Phi_{iI}) \right\} \left\{ \prod_{i < j}^N e^{t(r_{ij})} \right\} \varphi(\alpha, \beta, \gamma). \quad (4)$$

The He-He two-body wave function $e^{t(r_{ij})}$ is the same as used in earlier studies [9] and $\Xi(r, \Theta, \Phi)$ is the ground state $^4\text{He-SF}_6$ dimer trial function. For the latter we used both (i) the static ($B_0 = 0$, no SF_6 rotation) VMC wave function of Ref. [9], and (ii) a numerically constructed trial wave function obtained by nonlinearly fitting unbiased FFDMC distributions to the expansion:

$$\Xi(r, \Theta, \Phi) = \sum_{n_\ell, \ell, m} \chi_{n_\ell}^\ell(r) Y_\ell^m(\Theta, \Phi). \quad (5)$$

Similar excitation energies are obtained from both forms. Evaluation of the very small energy differences between ground and excited rotational states is done in the fixed node approximation, employing correlated sampling according to the algorithm of Wells [16].

For excited states we use trial wave functions corresponding to a rotational excitation localized primarily on the molecule, i.e., $J = j$. $\varphi(\alpha, \beta, \gamma)$ in Eq. (4) is then simply the rotation matrix appropriate to the state in question, e.g., for $J = 1$, $|j, k, m\rangle = |1, 0, 0\rangle$, where k and m are the projections of j on the molecule-fixed and space-fixed z axes, respectively. The separable trial function Ψ_T therefore represents an excited state in which the angular momentum is entirely localized on the dopant molecule, with zero angular momentum in the helium fraction. For an anisotropic potential, where j is no longer conserved, this is only an approximation to the true situation. However, for $N = 1$, comparison of ground and excited state energies derived from these trial functions with the results

of coupled channel calculations [15] show agreement to better than 99%, and also show that the $J = j$ components provide the dominant contributions to the low-lying eigenstates. Thus, a restriction to states with $J \sim j$, which correlate in the isotropic limit with trial functions having $J = j$, captures the correct nodal structure of the He-SF₆ dimer. The accuracy of the free rotor nodal structure for excitations in larger clusters has been demonstrated recently with the use of the projector Monte Carlo approach known as POITSE, which is free of nodal constraints [17].

Figure 1 shows the energy levels corresponding to $j = 0, 1, 2$, and 3 (relative to the ground state) as a function of the number of ⁴He atoms, N , in the cluster. There is a clear and systematic decrease in the level spacings with N . For all N the levels are well fit by the spherical top expression $BJ(J + 1)$. The value of rotational constant B in each case is shown at the top of the corresponding stack of levels. There is a rapid monotonic decrease in B from its starting value $B_0 = 0.091 \text{ cm}^{-1}$ at $N = 0$, to a saturation value of 0.034 cm^{-1} which is reached at $N \sim 8$. The asymptotic value achieved by B is in remarkable agreement with the experimental value $B = 0.033 \text{ cm}^{-1}$ obtained for clusters with $N \geq 10^3$ at $T = 0.3\text{--}0.4 \text{ K}$ [1,2].

We have also calculated the excitation energies of the angular momentum states of the ⁴He atoms, i.e., $j = 0$ combined with the ladder of $\ell = 0, 1, 2, \dots$ states in Eq. (5), which give rise to cluster excitations having $J - j > 0$. These states are significantly higher in energy than the $J - j \sim 0$ states shown in Fig. 1. This suggests that there will not be an efficient transfer of angular momentum

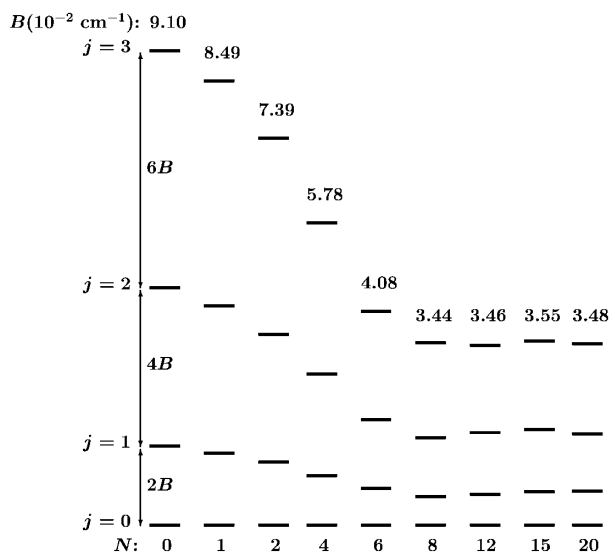


FIG. 1. Cluster rotational excitation energies corresponding to $J = j$, with $j = 0, 1, 2$, and 3, for ${}^4\text{He}_N\text{SF}_6$ with $N = 1\text{--}20$. The empirical value of the rotational constant B yielded by each stack of levels for given N is shown at the top of each stack. Both error bars in the excitation energies, and the resulting error in B obtained from the fit to a free rotor pattern are in all cases $O(10^{-4} \text{ cm}^{-1})$.

from the molecule to the ${}^4\text{He}_N$ matrix, so that the spectrum will be dominated by the low energy, free-rotor states.

In the experimental analysis of Ref. [1], the reduced rotational constant for SF₆ in ${}^4\text{He}_N$ was phenomenologically explained by making the simple classical assumption that a “supermolecule” is formed, consisting of SF₆ together with eight ⁴He atoms rigidly attached at the eight three-fold minima in the molecule-helium potential. These ⁴He atoms were regarded as blockers whose presence reduces the anisotropy of the interaction of the “dressed SF₆” supermolecule with the rest of the cluster, leading to essentially free rotation of the supermolecule. While attractively simple, this model does not account for the quantum nature of the ${}^4\text{He}_N$ environment and also ignores exchange effects with other helium atoms, particularly those in the first solvation shell which number considerably more than eight [9]. Moreover, such a supermolecule model cannot explain the behavior of lighter dopant molecules which are less strongly bound, have larger B_0 values, and which show considerably less reduction in rotational constant in ${}^4\text{He}_N$ [4–6,8].

Analysis of the FFDMC wave functions shows that the fundamental physics determining the magnitude of B is the extent of *adiabatic following* of the molecular rotation by the ⁴He atoms in its vicinity. This is illustrated in Fig. 2, which shows the ground state ⁴He wave function for $N = 8$, projected onto a sphere of fixed radius located at the maximum in the radial probability density from the SF₆ center-of-mass. When the true gas phase value $B_0 = 0.091 \text{ cm}^{-1}$ is employed, the amplitude is concentrated at the eight threefold sites of the SF₆ molecule (Fig. 2, left panel), but when a tenfold larger value of B_0 is used, the wave function is noticeably more delocalized (Fig. 2, right panel). Figure 2 (left panel) therefore reveals that

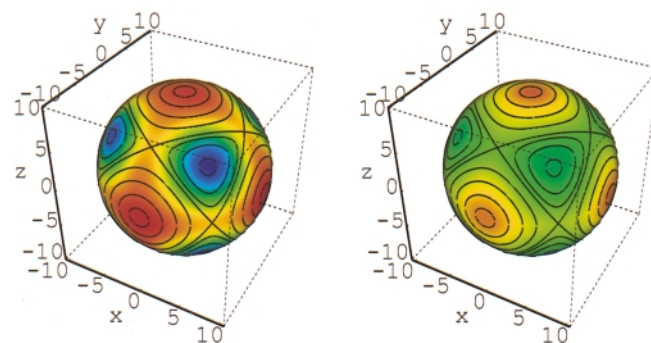


FIG. 2 (color). Ground state wave function for ${}^4\text{He}_8\text{SF}_6$, obtained from FFDMC without importance sampling, projected onto a sphere of radius $r = 8 \text{ a.u.}$ Results are shown for calculations with $B_0 = 0.091 \text{ cm}^{-1}$ [$B_0(\text{SF}_6)$], left panel, and $B_0 = 0.91 \text{ cm}^{-1}$ [$10 B_0(\text{SF}_6)$], right panel. The SF₆ molecule is located at the center of the sphere and the S-F bonds are aligned with the Cartesian axes. The amplitude is represented by a color scale, with blue denoting high values (on the C_3 axes) and red denoting low values (on the C_4 axes). The black lines superimposed show contour levels of the SF₆-He potential at this radius. All distances are given in a.u.

the eight ^4He atoms are able to follow the rotation of the SF_6 molecule adiabatically, i.e., they can adjust essentially instantaneously to the “slow” rotation of the SF_6 . With a larger value of B_0 , however, for a given potential anisotropy, the extent of adiabatic following decreases, which results in a more isotropic ^4He distribution in the molecule-fixed frame. The density also smears out as more ^4He atoms are added, implying that only a fraction of the first solvation shell (22-23 atoms in total) [9] can adiabatically follow [18].

The interplay between potential anisotropy and value of B_0 also controls the energetics, and hence the actual magnitude of B . This can be illustrated by raising the “rheostat” parameter B_0 beyond its natural value, whereupon the FFDMC excited state energies yield a much smaller reduction in B . For example, with $B = 0.91 \text{ cm}^{-1}$, a saturation value of $B = 0.85 \text{ cm}^{-1}$ is obtained for $N = 8$, representing a reduction to $\sim 93\%$ B_0 , which is far weaker than the reduction to $\sim 37\%$ B_0 seen in Fig. 1. The extent of reduction in B correlates with the extent of adiabatic following by the helium around the molecule. Conversely, the adiabatic following is dependent on the magnitude of the rotational kinetic energy (determined by the gas phase rotational constant B_0) relative to the anisotropy of the molecule-helium interaction potential. The ground state energies also increase with B_0 , until, in the limit of very large B_0 , the anisotropy is effectively averaged over and E_0^{iso} is obtained. For example, for $N = 1$ with $B_0 = 0.91 \text{ cm}^{-1}$, we obtain $E_0 = -34.1(0.19) \text{ K}$, which is now only $\sim 1 \text{ K}$ lower than E_0^{iso} [9]. Thus, for a given potential, the energetic effect of increasing B_0 is to move all energy levels to the isotropic limit.

To summarize, our FFDMC calculations for SF_6 rotating in $^4\text{He}_N$ demonstrate that there is a preservation of coherent rotational motion in a bosonic quantum fluid cluster. This occurs because only those rotational states in which the vast majority of the cluster angular momentum is carried by the dopant molecule are accessed. The existence of quantum rotational motion for a molecular dopant uncoupled with angular momentum states of $^4\text{He}_N$, is thus reflected in the appearance of a free rotor spectrum for small j . This behavior is consistent with the dominantly superfluid character of doped $^4\text{He}_N$ clusters at larger sizes N [18,19].

In this “molecular” quantum mechanical analysis, the essential difference between a bosonic ^4He cluster and a fermionic ^3He cluster appears in the trial function, Eq. (4). A qualitative analysis of the fermionic cluster at $T = 0$ may be made by replacing the first term by a determinantal wave function and neglecting He-He correlations. It is then apparent that for larger N , the ^3He atoms must carry some angular momentum, and the lowest energy excita-

tions will no longer have $J \sim j$. However the adiabatic following of helium identified above is independent of the isotope, so that whether the energy level structure is significantly different in $^3\text{He}_N$ is not evident in advance. The detailed rotational energy spectrum for doped ^3He clusters at $T = 0$ (or at finite temperatures below the corresponding superfluid transition) is thus a key open question for future study.

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