Roton-Rotation Coupling of Acetylene in ^{4}He

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Rotational absorption spectra of acetylene in superfluid ^{4}He calculated using a path-integral correlation function approach are seen to result in an anomalously large distortion constant in addition to a reduced rotational constant, with values in excellent agreement with recent experiments. Semianalytic treatment of the dynamics with a combined correlated basis function-diffusion Monte Carlo method reveals that this anomalous behavior is due to strong coupling of the higher rotational states of the molecule with the roton and maxon excitations of ^{4}He, and the associated divergence of the ^{4}He density of states in this region.

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Helium nanodroplets have become a useful matrix for isolation spectroscopy [1]. Unlike in classical liquids, the spectra of embedded molecules may be rotationally resolved in the superfluid environment of ^{4}He, which has led to numerous investigations of rotational constants of molecules in ^{4}He droplets (see Table I in Ref. [2]). For all but the lightest rotors, a significant reduction of the rotational constants with respect to their gas phase values has been found, with identical symmetry, which has been explained by the adiabatic following of a molecular-interaction induced nonsuperfluid fraction of the solvation shell [3]. In contrast, the lightest molecules exhibit relatively small reduction of their rotational constants in ^{4}He droplets [2]. Calculations have shown that the assumption of adiabatic following breaks down for light molecules [4] and that instead of coupling to localized helium solvation density, there is appreciable coupling to delocalized collective helium modes [5].

Acetylene (HCCH) is one such light molecule whose rovibrational spectrum has been obtained by infrared spectroscopy in ^{4}He droplets [6]. The effective rotational constant B_{eff} was found to be reduced to 88% of its gas phase value (1.1766 cm^{-1}) and a very large effective distortion constant D_{eff} was measured, showing a relative enhancement of D_{eff}/B an order of magnitude larger than that seen for heavier molecules such as OCS, SF$_6$ and (HCN)$_2$. It was speculated that the excessive broadening of the IR spectral lines might indicate coupling to excitations of the helium, but in the absence of theoretical understanding of such a coupling, no conclusions could be drawn. The calculations of the rotational absorption spectra of HCCH presented here show how coupling between the molecular rotation and the roton excitations of ^{4}He results in an anomalously large distortion constant as well as a reduced rotational constant, with predicted values in good agreement with experimental measurements. They also reveal that the higher rotational excitations display a secondary peak as well as a weak maxon-roton band between them that both result from this coupling. We discuss how these additional spectral features might be observed in order to stimulate experiments to measure this unique signature of rotation-roton coupling.

We calculate the rotational excitations using a path-integral correlation function (PICF) approach that provides a quantum simulation free from systematic approximations. We first evaluate the imaginary-time orientational correlation functions

$$S_J(t) = \frac{1}{Z}\sum_m \mathrm{Tr}\{Y^+_{Jm}(\Omega(t))Y_{Jm}(\Omega(0))e^{-H/kT}\} \qquad (1)$$

(Ω is the molecular orientation), sampled by path-integral Monte Carlo (PIMC) calculations from the full molecule-helium Hamiltonian H (with interaction potentials from Refs. [7,8]) that includes molecular rotation and all translational degrees of freedom as well as the exchange symmetry of helium [9,10]. $S_J(t)$ is numerically inverted to real frequencies to obtain the rotational absorption spectrum for dipole ($J = 1$), quadrupole ($J = 2$), and higher order transitions. The required inverse Laplace transform is made with the maximum entropy method [11]. Line shapes and broad spectral features cannot be obtained from inverting an imaginary-time correlation function, but the positions and relative strength of isolated peaks are reliable [9,11]. The PICF calculations are made using multilevel metropolis sampling [12], with the molecule treated as a translating rigid rotor [13]. Full methodological details will be presented elsewhere [9]. The dynamical origin of the PICF excitations are analyzed by a combination of correlated basis function (CBF) theory and diffusion Monte Carlo (DMC) that derives zero temperature excitation energies and absorption spectra from linear response theory [14] and then evaluates these with numerically exact DMC calculations for the required input ground state properties [5]. The CBF-DMC approach, while relying on approximate excited wave functions, allows a microscopic analysis of the spectrum and is essential for interpretation and explanation of the PICF spectra.

Figure 1 shows the rotational excitations obtained from PICF for HCCH in a cluster of 64 ^{4}He atoms (approximately two solvation layers) at $T = 0.625$ K, and com-

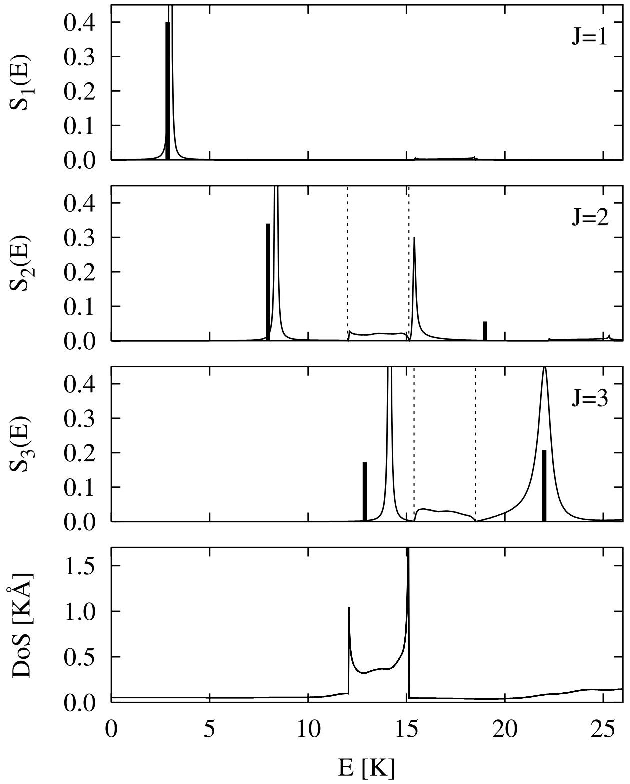

FIG. 1. PICF rotational excitations for HCCH in a cluster of 64 ^{4}He (broad solid lines, height proportional to the spectral weight). Thin solid lines: corresponding CBF-DMC absorption spectra $S_J(\omega)$, $J = 1, 2, 3$, for HCCH in bulk ^{4}He, lines broadened by 10 mK. Bottom panel: density of states $\varepsilon'(p) + \hbar^2 p/M$. Dotted lines: edges of the roton-maxon bands coupling the $J = 2, 3$ states to $\ell = 0, 1$ states, respectively.

pares these with the corresponding CBF-DMC ground state absorption spectra of HCCH in bulk helium for $J = 1, 2, 3$. The latter were calculated with the methods of Ref. [5] (see below). The PICF excitations are shown as broad solid lines with height proportional to their spectral weight. The peak positions and weights of both PICF and CBF-DMC excitations are given in Table I. The good agreement of the PICF spectra in $^4\text{He}_{64}$ clusters, which are free of systematic approximations, with the CBF-DMC spectra in bulk ^{4}He provides the validation of the CBF-DMC approach that allows it to be used for the microscopic analysis below of the rotational excitations. The agreement between the cluster and bulk calculations furthermore implies that the peak positions and strengths of the relevant ^{4}He excitations are already converged at this cluster size and that the rotational coupling to these modes is not sensitive to temperature variations below $T \sim 0.6$ K. We expect that size dependence of the excitations will be seen in smaller clusters (e.g., less than one solvation shell, $N \sim 20$) while other features such as the linewidth may be sensitive to cluster size over a broader range.

TABLE I. Rotational excitation energies of HCCH in ^{4}He calculated with PICF ($^4\text{He}_{64}$) and CBF-DMC (bulk ^{4}He). Experimental values from Ref. [6]. J' denotes the secondary (higher energy) peaks and w the respective spectral weights.

	PICF		CBF-DMC		Exp.
J	E [cm^{-1}]	w	E [cm^{-1}]	w	E [cm^{-1}]
1	1.99 ± 0.10	1.00	2.08 ± 0.04	0.98	2.01
2	5.54 ± 0.10	0.85	5.82 ± 0.24	0.82	5.55
$2'$	13.20 ± 0.90	0.14	10.70 ± 1.31	0.08	⋯
3	8.95 ± 0.41	0.43	9.82 ± 0.69	0.33	⋯
$3'$	15.28 ± 0.53	0.52	15.28 ± 0.70	0.49	⋯

The CBF-DMC spectra in Fig. 1 have sharp Lorentzian peaks associated with excitations of finite lifetime, as well as broad features between these peaks. We first compare with the corresponding rotational excitation energies derived from recent spectroscopic measurements for HCCH in ^{4}He droplets having $N = 10^3 - 10^4$ atoms. In Ref. [6], rotational transitions $J = 0 \leftrightarrow 1$ and $J = 1 \rightarrow 2$ were observed (accompanied by excitation of the C-H vibrational stretches), giving rise to the experimental values of $J = 1, 2$ excitation energies that are listed in Table I. The two excitations that were accessed by the spectroscopic measurements are seen to be in excellent agreement with the theoretical values for $J = 1$ and for the primary (lowest energy) peak of the $J = 2$ spectrum. Table II compares the spectroscopic constants B_{eff} and D_{eff} obtained by fitting these two excitations to the nonrigid linear rotor spectrum $B_{\text{eff}}J(J + 1) - D_{\text{eff}}[J(J + 1)]^2$, for both the PICF and CBF-DMC calculations. Particularly significant is the magnitude of the distortion constant relative to B, namely D_{eff}/B, which is extremely large compared to that measured for heavier molecules [2,6]. Until now, no quantitative explanation has been provided for this unusual feature of HCCH, which is also the only light linear molecule for which more than one rotational excitation and hence D_{eff} is experimentally accessible. We show below that the analytic insight by the CBF-DMC calculations reveal that this large value of distortion constant results from a strong coupling of the $J = 2$ excitation with the helium roton and maxon excitations. The anomalously large D_{eff} value for HCCH thereby constitutes the first demonstrable evidence of such *direct* coupling between rotations and rotons.

Reference [5] showed that coupling of collective excitations of the ^{4}He to the rotational motion of a molecule

TABLE II. Rotation constant B_{eff} and distortion constant D_{eff} of HCCH in ^{4}He. PICF and CBF-DMC results are compared with results of fit to $J = 0 \rightarrow 1$, $J = 1 \rightarrow 2$ ro-vibrational transitions in IR spectra [6] (units in cm^{-1}).

HCCH	PICF	CBF-DMC	Exp. [6]	Gas Phase [6]
B_{eff}	1.031	1.075	1.042	1.172
D_{eff}	0.0179	0.0175	0.0195	1.62×10^{-6}

renormalizes the rotational energy $\hbar\omega_J$ corresponding to total angular quantum number J for a linear molecule with bare mass M and gas phase rotational constant B by an energy-dependent, complex self energy $\Sigma_J(\omega_J)$ [15],

$$\hbar\omega_J = BJ(J+1) + \Sigma_J(\omega_J), \tag{2}$$

which is a functional of the ground state HCCH-^{4}He pair distribution function calculated by DMC calculations [5]. For a symmetric linear molecule like HCCH, one can show from angular momentum conservation [5] that the dominant effect of the superfluid ^{4}He environment on the molecular rotational excitations J is to couple molecular rotational states that differ by $|J - \ell| = 2$. When the momentum p is such that the input energy $\hbar\omega$ equals the sum of $B\ell(\ell + 1)$ (molecular rotation), $\epsilon(p)$ (phonon-roton excitation), and $\hbar^2 p^2/2M$ (kinetic energy of the recoiling HCCH), these states can be excited by decay of the rotational excitation $\hbar\omega = \hbar\omega_J$, leading to finite lifetimes.

When $\Im m\Sigma_J$ is small, the real part of the solutions of Eq. (2) correspond to the positions of well-defined peaks in the dipole ($J = 1$), quadrupole ($J = 2$), ... absorption spectra of the molecule from its ground state, given by

$$S_J(\omega) = \frac{\Im m\Sigma_J(\omega)/\pi}{[\gamma_J(\omega) - \hbar\omega]^2 + [\Im m\Sigma_J(\omega)]^2}, \tag{3}$$

where we have defined $\gamma_J(\omega) = BJ(J+1) + \Re e\Sigma_J(\omega)$. In the opposite limit, when $\Im m\Sigma_J$ is large, Eq. (3) shows that the absorption $S_J(\omega)$ can become large regardless of whether or not ω is a solution of Eq. (2). In this case, CBF-DMC predicts a broad absorption band that cannot be uniquely associated with a single molecular rotation mode, but instead is due either to a simultaneous excitation of both the molecular rotation and ^{4}He modes, or of only ^{4}He modes [5].

The spectra of HCCH in Fig. 1 show both types of features. We discuss first the sharp peaks, which are obtained from both PIMC and CBF-DMC, and whose energies are used to extract the anomalously large D_{eff} value. Figure 1 shows that for $J = 1$, a single peak is obtained but that for both $J = 2$ and $J = 3$, *two* peaks appear in $S_J(\omega)$, in contrast to the expected pattern of excitations for a linear rotor which has only a single excitation at energy $BJ(J + 1)$. This surprising double peak feature is found both with the PICF and CBF-DMC methods. Thus, unlike heavier linear rotors such as OCS, the pure rotational spectrum of HCCH in ^{4}He for excitations higher than $J = 1$ does not conform with the simple pattern predicted for an effective linear rotor. A similar behavior was seen in Ref. [5] for HCN, but comparison with experiment was limited to the $J = 1$ excitation only in that case, and no measurement of D_{eff} was possible.

The locations $\hbar\omega'$ of peaks in the CBF-DMC spectrum $S_J(\omega)$ are found by solving the equation $\gamma_J(\omega) - \hbar\omega = 0$ [see Eq. (3)], which can have one or more solutions. Analysis of these solutions as in [5] shows that the reason for the occurrence of two peaks for absorptions to $J = 2$ and $J = 3$ is the nonmonotonic behavior of the collective excitation spectrum in ^{4}He, in particular, the divergent density of states at both the roton minimum and the maxon maximum of the helium excitation spectrum (see bottom panel of Fig. 1). This can split spectral peaks close to the roton and maxon into two, shifting the "primary" peak below the roton minimum and moving the "secondary" peak above the maxon maximum [5]. For HCCH the dipole spectrum, $J = 1$, has only a single peak, because the $J = 1$ excitation energy is much lower than the roton energy and consequently does not couple effectively, so that the secondary $J = 1$ absorption peak has negligible weight and is not observed. For $J = 2$, the weight of the secondary peak is small but non-negligible, while for $J = 3$, more than half of the spectral weight is actually carried by the secondary peak (see Table I).

The coupling between molecular rotation and helium rotons implied by this splitting is a sensitive function of the gas phase rotational constant B. This is seen in a calculation of the spectrum as a function of B, which allows the molecular rotational energy for $J = 2$ to be tuned across the roton-maxon energy regime and the coupling between molecule and helium to be thereby modulated. Figure 2 shows the quadrupole spectrum $S_J(\omega)$, $J = 2$, as B is artificially varied between $0.5 \times B$ and $1.5 \times B$ in Eq. (3) and in the expression for the self energy. For simplicity, the same molecule-helium pair distribution function is used for calculations with all B values. When the gas phase value of B is sufficiently small that the $J = 2$ excitation does not couple to the roton excitations, $S_2(\omega)$ has only a single peak, like $S_1(\omega)$ in Fig. 1. On increasing B to its actual gas phase value, 1.1766 cm^{-1}, the secondary peak emerges and simultaneously a weak roton-maxon band (see below) starts to grow between the two peaks. On increasing B beyond its actual value, the secondary peak continues to grow until it eventually accounts for the entire spectral weight and the primary peak vanishes. Figure 2 shows that the resonant coupling of the molecular $J = 2$ excitation with the roton and maxon excitations shifts the primary

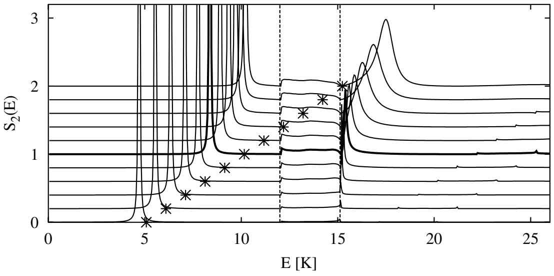

FIG. 2. Absorption spectrum $S_J(\omega)$ for the $J = 0 \rightarrow 2$ transition of HCCH in ^{4}He, where the gas phase rotational constant value is varied between $0.5 \times B$ (bottom curve) and $1.5 \times B$ (top curve), in steps of $0.1 \times B$. Asterisks mark the locations of the gas phase transition energies, $6B$.

peak to lower energy and is responsible for the large value of D_{eff}.

The second spectral feature that results from this rotation-roton coupling is the presence of broad, weak absorption bands between the two peaks in the higher excitations ($J = 2, 3$). Such broad features cannot be retrieved from analytic continuation of the PICF to real frequencies and hence are only evident in the CBF-DMC spectra of Fig. 1. Excitations in this region decay instantaneously, due to the high density of states between the roton and maxon excitations of ^{4}He. Although these roton-maxon bands appear small, they do possess non-negligible weights of 0.06 and 0.08 in the $J = 2$ and $J = 3$ spectra, respectively. The roton-maxon band for $J = 3$ is shifted in energy by $2B$ with respect to the corresponding band for $J = 2$, because for $J = 2$, the molecular rotation is coupled to a pure ^{4}He excitation with the molecule falling into its rotational ground state $\ell = 0$, while for $J = 3$, the rotation is coupled to $\ell = 1$. In both cases $J - \ell = 2$, which corresponds to the strongest contribution to the self energy $\Sigma_J(\omega)$, as noted above.

Experimental detection of these weak roton-maxon bands and of the secondary peaks is very challenging. The homogeneous linewidth of the absorption spectra in Figs. 1 and 2, $\Im m\Sigma_J(\omega)$, results from rotational relaxation only. The experimental IR linewidth for HCCH is believed to also have contributions from vibrational relaxation as well as inhomogeneous broadening due to finite size effects [6]. Vibrational relaxation may lead to a reduced lifetime of a secondary transition such that it is too short to be observed. Multiphonon excitations, which become prevalent in bulk ^{4}He for excitation energies around 20 K and higher and are not incorporated in the CBF analysis, may also broaden the peaks at higher energies. Another complication for comparison with the IR spectra is that the $J = 2$ state is accessed experimentally by the dipole transition $J = 1 \rightarrow 2$, while both the PICF and the CBF-DMC calculations yield the quadrupole transition $J = 0 \rightarrow 2$, with different transition matrix elements for the HCCH-^{4}He coupling. Measurement of the rotational Raman spectrum may allow a direct access to the $J = 0 \rightarrow 2$ transition. The primary experimental evidence for this unusual direct rotation-roton coupling today is therefore the anomalously large distortion constant D_{eff}.

In summary, calculations of the rotational excitations of HCCH in ^{4}He using a path-integral correlation function approach result in a distortion constant D_{eff}, in excellent agreement with experimental measurements that are anomalously large relative to values measured for heavier molecules in ^{4}He. Analysis of the excitation energies with the semianalytic CBF-DMC approach shows that this anomalous value of D_{eff} results from a strong direct coupling of the $J = 2$ and higher molecular rotation states to the roton and maxon excitations of helium. The excitation spectra for $J = 2$ and $J = 3$ show secondary peaks at higher energies as a result of this coupling, while a CBF-DMC analysis also reveals the presence of weak roton-maxon bands between the two peaks. We expect that these unique signatures of coupling between roton-maxon modes of helium and rotational modes of embedded molecules will be found in Raman spectra, as well as possibly in microwave and IR spectra for other light molecules.

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