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Methane clathrate: CH_4 quantum rotor state dependent rattling potential

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In methane hydrate the dominant peak in the density of states above 3 meV represents a rattling mode of the guest molecule CH_4 in the large ice cages. This mode shifts from 6.7 meV at $T=4.5$ K to $T=30$ K to 7.14 meV with conversion of CH_4 guest molecules into the tunneling ground state. The less symmetric angular density distribution $\Psi\Psi^*$ in the excited rotational state compared to the ground state allows the methane to fit better in the orientation dependent cage potential surface. This leads to a larger average distance to the cage-forming molecules with a weaker potential and a reduced rattling energy. A two state single particle model with characteristic rattling energies of 5.20 meV for pure T-methane and 7.3 meV for pure A-methane weighted by the population factors can fit the data. © *2006 American Institute of Physics*.
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I. INTRODUCTION

The discovery of methane hydrates as one of the largest energy reservoirs on Earth[1] has brought back inclusion compounds and supramolecular chemistry into the focus of public and scientific interest.[2–4] Methane clathrate crystallizes in the cubic type I structure with space group *Pm*3*n* and a unit cell formed by six large and two small ice cages.[5,6] The local dynamics of guest molecules in inclusion compounds and disorder in filling the cages are assumed to be the reason for their very low thermal conductivities.[7] Methane in the natural clathrate shows a dynamics which is fundamentally interesting.[8] The cages allow for anharmonic low energy translational oscillations (rattling) and almost free rotation. At the lowest temperature the molecular motion was quantitatively described as single particle quantum rotation[9] in weak rotational potentials. Different arrangements of the hydrogen bonds of the water cages lead to disorder with potentials, which differ weakly from cage to cage.[10] Modes of the CH_4 quantum rotor determine the low temperature spectrum up to energy transfers of about 3.5 meV. In the energy regime between 4 and 12 meV the large amplitude translational modes of the guest molecules take over in importance and dominate the density of states, but overlap with modes of the ice framework structure in the same energy range.[11] Rattling in the large cages is split into two bands due to the tetragonal cage symmetry and are calculated to appear at energies of roughly 3.5 and 6 meV.[12] The stronger hindering in the small cages leads to a higher rattling energy. Due to the average cubic symmetry of the small cages, all translational oscillations are degenerate and all scattered intensities are concentrated in a single band at a calculated energy of 10 meV.[13–15] Xe guest molecules display a similar pattern of rattling modes at lower energies, with the anharmonicity visible at higher temperature.[16] The molecular dynamics calculations which led to a quantitative understanding of the lattice dynamics of methane and other[15] clathrates were performed for temperatures between 66 and 145 K,[13] where quantum effects, if at all, play a minor role. Since lattice dynamics calculation is a classical technique, it cannot take care of effects due to the quantum nature of methane rotors,[11] resulting in anomalous rotation-translation coupling.

Below the vibrational density of states of methane clathrate is presented for temperatures below 20 K, where the properties of the CH_4 guest molecules change with the population of the two lowest rotational quantum states and influence the energy spectrum.

II. THEORY: SINGLE PARTICLE ROTATION AND RATTLING

A. Quantum rotation

The standard description of rotational tunneling and quasielastic scattering is the single particle model (SPM). In such a model the environment of a molecule is represented by a rotational potential $A(\omega_E)$, which is usually expanded into symmetry adapted functions. In the case of CH_4 these are cubic rotator functions. ω_E represents the Eulerian angles. At low temperatures when the classical rotational jump dynamics transforms to quantum modes, this potential determines the excitations of the hindered quantum rotor, which are the eigenvalues E_i of the stationary single particle Schrödinger equation[9]

$$\{-B\nabla^2 + A(\omega_E)\}\Psi_i = E_i\Psi_i. \qquad (1)$$

Here $B=\hbar^2/2\Theta=0.655$ meV is the rotational constant of the methane molecule with the moment of inertia Θ. ∇ is the nabla operator and Ψ_i are the eigenfunctions. Splittings within the lowest librational multiplet are generally called tunnel splittings $\hbar\omega_t$. With decreasing potential strength, transitions between the three lowest levels approach the values of a free quantum rotor with $E_{01}=2B$, $E_{12}=4B$, and $E_{02}=6B$.

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High resolution neutron spectroscopy is an especially successful technique to observe the low energy transitions of weakly hindered rotors. For finite potential size with the ground state tunnel splitting $\hbar\omega_t \ll kT$ at experimental temperatures $T \leq 10$ K, equal population of all tunneling sublevels leads to a simple scattering function $S(Q,\omega)$.[9,17] For temperatures kT of the order of the tunnel splitting $\hbar\omega_t$, a factor $p_0(T)$ representing the population of the various tunneling sublevels has to be introduced into the scattering function. Only if spin conversion is fast, $p_0(T)$ is given by a Boltzmann factor; otherwise, the spin temperature can be significantly larger than the lattice temperature. With this modification and restricting ourselves to the two lowest rotational levels, we write

$$S(Q,\omega) = A_0(Qd)\delta(\omega) + (1 - A_0(Qd)) \times\{(1 - p_0(T))\delta(\omega + \omega_t) + p_0(T)\delta(\omega - \omega_t)\} \quad (2)$$

with momentum transfer Q and proton-proton distance d. $A_0(Q)$ is called the elastic incoherent structure factor of the motion.

Based on data from phase II of methane, it has been shown[18] that the Q dependence of the scattering of a free rotor is rather similar to that of a hindered tunneling species.

B. Rattling

The energies of lattice modes of methane hydrate are found in the meV regime. The neutron scattering function of a polycrystalline material in this energy regime is determined by the so-called weighted vibrational phonon density of states $g(\omega)$, which is the sum of all eigenmodes of the material weighted by the scattering cross sections of the atoms displaced by the respective modes. $g(\omega)$ represents an integral information on the dynamics. In case of inclusion compounds like the clathrates, it is convenient to split the lattice modes and the corresponding density of states into two subsystems containing on the one side modes mainly due to the framework structure as the acoustic phonons and another one mainly determined by the motion of guest molecules. Rotational tunneling of the methane guests represents such a "local" mode. Translational oscillations in the cages, called rattling modes, are another characteristic vibration of guest molecules. Depending on the cage symmetry, the motions along the main symmetry axes may be degenerate or not.

III. EXPERIMENT AND RESULTS

A fully protonated methane hydrate sample was prepared at the Institut of Crystallography, University of Göttingen, and stored in liquid nitrogen. For the experiment the sample was transferred at low temperature into a liquid He Orange cryostat. Cooling below the temperature of liquid He was achieved by pumping off the evaporating He with a 40 m^3/h pump.

All spectroscopic data were obtained by neutron scattering at the hybrid thermal time-of-flight spectrometer SV29 of Forschungszentrum Jülich.[19] Using a single Fermi chopper we could measure the spectra in the two relevant energy regimes *simultaneously*. At a setup with the first order wavelength $\lambda_1 = 3.52$ Å, the energy resolution was good enough to resolve well the tunneling transitions in the energy range of the rotor modes, while the characteristic part of the phonon density of states (below 20 meV) was well observable by inelastic scattering from the second order neutrons with $\lambda_2 = 1.76$ Å. All spectra were normalized and corrected for background in the usual way to make them directly comparable.

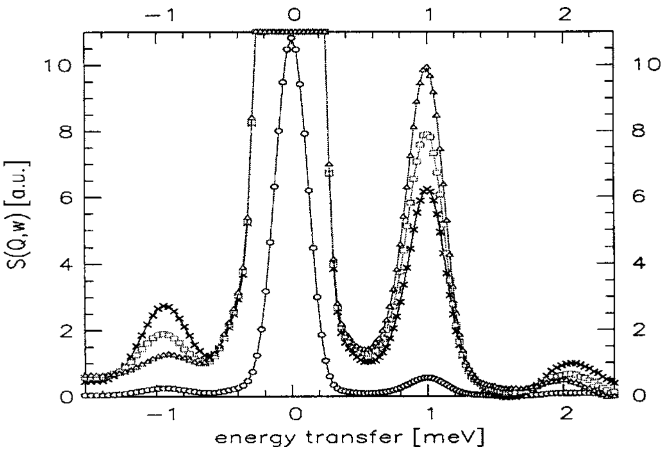

FIG. 1. Ions of the almost free CH_4 quantum rotor in methane clathrate. The time-of-flight spectrometer SV29 at DIDO reactor of Forschungszentrum Jülich is used with $\lambda = 3.52$ Å. Summed over all scattering angles, average momentum transfer $Q = 2.4$ Å^{-1}. Sample temperatures $T = 2.1$ K. Spin temperatures are $T_S = 4.3$ K (△), 6.8 K (□), and 11.3 K (x). The downscaled spectrum for $T_{\text{spin}} = 4.3$ K (○) shows a perfectly centered elastic line.

Two series of measurements were performed. At first the sample temperature was reduced step by step from 25 to 4.5 K. Due to equilibration of the quantum rotor system with the lattice temperature, the excited rotational levels of the methane guest molecules became depopulated. Corresponding changes of the density of states (DOS) were registered. In a second series of measurements the sample was quenched from various higher temperatures to 2.1 K. In this series of measurements all spectra were registered at the same low temperature of the phonon bath. The temperature reading showed the low temperature of $T = 2.1$ K a few minutes after the start of the cooling process. Due to long nuclear spin conversion times between states of different spins of the tunneling system, the lattice temperature and the nuclear spin temperature of the rotor system were no longer in equilibrium. A comparison of the two data sets allows to distinguish pure temperature effects from effects due to methane conversion. Differences of the densities of states of the two samples can only be due to different populations of excited quantum rotor states.

In agreement with earlier results[20] our spectra confirm extremely long spin conversion times at temperatures below 4.5 K. These long spin conversion times prevent further cooling of the rotor spin system. The equilibrium time reaches the order of days to weeks and is thus much longer than the typical time needed to obtain a neutron scattering spectrum. Therefore one can consider the spin system as frozen.

Figure 1 shows spectra of the sample at various stages of conversion into the tunneling ground state. The background

TABLE I. Relative population $r=I^-/I^+$ of the two lowest rotor levels of methane of all measured spectra of methane clathrate as obtained by a Gaussian fit of the transition bands. Corresponding spin temperatures T_S of the methane rotor system, energies of the gain (E_t^+) and loss (E_t^-) tunneling bands, and rattling mode $\bar{E}_r$ found in the DOS are shown.

$r=I_-/I_+$	T_S (K)	E_t^+ (meV)	E_t^- (meV)	$\bar{E}_r$ (meV)
0.423	13.2±0.3	0.995±0.010	0.950±0.010	6.69±0.02
0.366	11.3±0.3			6.76±0.02
0.283	9.0±0.3			6.86±0.02
0.186	6.8±0.3			6.99±0.02
0.118	5.3±0.2			7.08±0.02
0.100	4.9±0.2	0.995±0.010	0.935±0.010	7.12±0.02
0.091	4.7±0.3			7.15±0.02
0.079	4.5±0.3			7.15±0.02
0.070	4.3±0.4			7.14±0.02

on the left hand side of the spectrum comes from the overlap with the second diffraction order. For a quantitative analysis the tunneling bands are fitted by Gaussians. The transition energies obtained in this experiment are consistent with earlier results.[10] With depopulation of the excited rotational state the band at energy transfer of −0.99 meV weakens. Simultaneously the intensity of the band at 2 meV is reduced. The third and higher rotational levels do not have to be taken into account since they are not populated at the experimental temperatures. Thus a spin temperature can be attributed to the two lowest rotor states from the intensities of the energy gain and loss lines. The values are shown in Table I.

The mathematical description of the main part of the spectrum by an elastic resolution function and the dominant energy loss and energy gain rotor transitions by Gaussians convoluted with the resolution function shows that the energy of the loss line is independent of spin temperature within 10 μeV ($\cong 1\%$). The energy gain line, on the other hand, is located at an energy which is $\sim(45\pm15)$ μeV lower than the value on the loss side. Both energies are measured relative to the elastic line exactly at zero energy. The analysis of the temperature dependence shows that the energy gain line shifts little to lower energies with decreasing spin temperature. It was also ruled out that the difference of energy gain and loss transition is be due to an error in calibrating the wavelength.

The corresponding spectra in the regime of lattice excitations are shown in Fig. 2. There are clear changes with conversion of the methane guest molecules into their rotational ground state. Primarily the main band at 6.7 meV shifts to higher energies (Table I). Secondly, the weak peak at 3.3 meV sharpens with lowering the temperature, and finally, a bump at 12.1 meV which is almost invisible at high spin temperature develops into a well-defined shoulder.

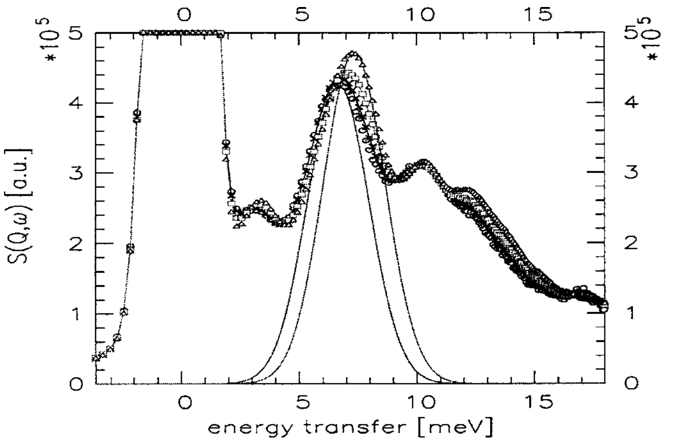

FIG. 2. Neutron scattering spectra taken in the regime of lattice modes and summed over all scattering angles. Spectrometer; SV29 of Forschungszentrum Jülich. Wavelength λ=1.76 Å. Sample temperature T=2.1 K for all spectra. Average momentum transfer Q=4.9 Å^{-1}. Spin temperatures are T_S =4.3 K (△), 6.8 K (□), 11.3 K (x), and 13.2 K (○). The two fit curves are discussed in the text. The maximum of the elastic line is perfectly centered.

A quantitative relation of the shift of the dominant peak of the density of states is based on the population c_T of the excited rotor state. The concentration c_T of excited rotors is deduced from the relative line intensities (Table I) by $c_T = I^-/(I^-+I^+)=r/(1+r)$. A linear dependence of the rattling energy from the concentration is found in Fig. 3, while c_T changes by almost an order of magnitude. $C_T=0$ represents a system in the ground state with $T_S=0$ K. Equal population, $c_T=\frac{1}{2}$, corresponds to infinite temperature. Population inversion characterizing a pure T-state system in a two-state model cannot be prepared in the experiment, but its characteristic rattling energy can be estimated from an extrapolation of the fit to $c_T=1$.

The tetragonal symmetry of the large cage requires a second rattling mode, which was placed at lower energies when modeling the lattice dynamics.[11] Uncertainties in the intermolecular interaction potentials could allow to assign the 7 meV mode to the lower rattling mode, which shows more intensity in the calculation since it represents the doubly degenerate mode. If we scale the energy of the fundamental rattling band at 7 meV according to Ref. 11, we expect this mode at about 12 meV. The shoulder observed at this energy transfer shows, indeed, the same temperature dependence as the fundamental rattling band. Because of the overlap with the stronger peak around 10 meV, its shift cannot be followed quantitatively. The weakening of the shoulder while moving into the neighboring band is obvious, however.

On the other hand, if we trust the phonon energies of the model calculations,[11] the mode at 12 meV must be attributed to rattling in the small ice cages. Qualitatively the behavior

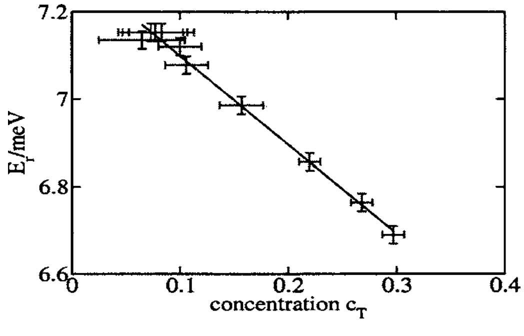

FIG. 3. Shift of the maximum of the DOS of methane clathrate with increasing population c of the excited tunneling level. A linear dependence is shown by the fitted straight line.

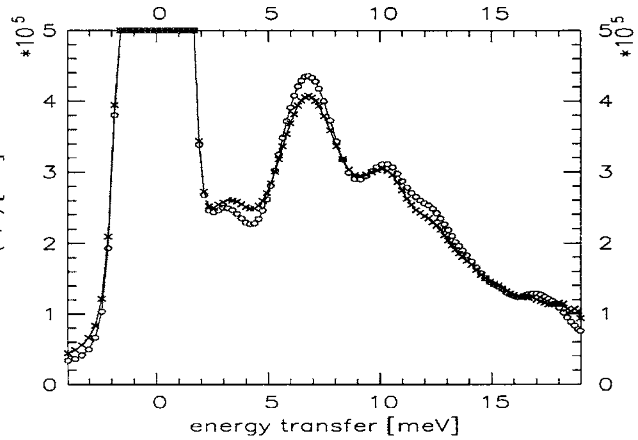

FIG. 4. Neutron scattering spectra taken in the regime of lattice modes and summed over all scattering angles. Spectrometer: SV29 of Forschungszentrum Jülich. Wavelength $\lambda = 1.76$ Å. Average momentum transfer $Q = 4.9$ Å^{-1}. Spin temperature $T_S = 13.2$ K for both spectra. Sample temperatures are $T = 2.1$ K (○) and $T = 13$ K (×××).

of methane guest molecules in the two cages must be similar since they feel very similar rotational potentials,[10] and the above explanation can be transferred.

With further increasing the sample temperature, a reversion of the observed softening of rattling modes has been found in other clathrates.[21] With increasing mean square displacement, the guest molecules explore more the steeper anharmonic part of the interaction potential with a corresponding new hardening of the rattling mode.

Because of fast spin conversion at higher temperatures,[20] a spectrum measured at a sample temperature of 13 K represents the rotational states of the guest molecules in thermal equilibrium with the lattice (Fig. 4, ×××). A comparison with a quenched low temperature spectrum measured at $T = 2.1$ K but at very similar spin temperature $T_S = 13.2$ K (Fig. 4, ○○○) shows that, up to 15 meV, all characteristic modes appear at exactly the same energies. The only difference is a general reduction of the intensity due to detailed balance. This observation confirms that the changes in Fig. 2 are entirely due to the different populations of the rotational states of the methane guest molecules.

IV. DISCUSSION

A. Rotor states

Three of the observed bands can be assigned to transitions between the three lowest rotor states of CH_4. Both, the fundamental $0 \rightarrow 1$ almost free rotor transition at 0.99 meV and the transitions to higher levels, $E(1 \rightarrow 2) = 2.3$ meV and $E(0 \rightarrow 2) = 3.3$ meV, are well known from earlier measurements.[13,10] The mean energy and inhomogeneous linewidth of the lowest rotor band were quantitatively explained with a distribution of rotational potentials due to the many possible configurations of the hydrogen bonds in the ice framework.[10] The three dimensional rotational potentials were calculated from established intermolecular interaction potentials and on many realizations of the crystal structure. The ground state splitting was obtained from the rotor eigenvalues of Eq. (1).[22]

A new observation concerns the unexpected 4% difference of tunneling transition energies in energy gain and loss. For a better understanding we consider two sample properties which may lead to the observed effect.

The average structure obtained from the diffraction experiment[6] shows well-defined long range order of the clathrate with equal population of the two possible proton sites in each hydrogen bond of the ice framework. On the other hand, the cage of an individual guest molecule represents a unique arrangement of H bonds with a characteristic rotational splitting. Disorder means that there are many different configurations which contribute with their characteristic splittings to the rotational band. This band is now assumed to be represented by a Gaussian with an average splitting ω_0 and the inhomogeneous linewidth Γ_{dis}. Weighting by the Boltzmann population factor with characteristic temperature T_S leads to the measured rotational bands which obviously change with changing the population of rotational states. The nuclear spin temperature T_S is used instead of the lattice temperature, since the rotor system is not in thermal equilibrium with the lattice. The main effect is observed at energy gain of the neutrons. The center ω_0 of the undistorted Gaussian, found for infinite temperature, shifts in first order smoothly towards a new lower effective energy $\bar{\omega}$ at temperature T_S

$$\bar{\omega} = \omega_0 - \frac{\Gamma_{\text{dis}}^2}{k_B T_S} \qquad (3)$$

until the line finally has zero intensity. For scattering from the ground state the spectra for zero and infinite temperature are both equal to the undistorted inhomogeneous distribution with identical centers of gravity. An inherent assumption of our model is that a common spin temperature describes the equilibrium in all different rotational potentials. This means that all slightly different rotor systems have a very similar spin conversion time. Since our energy resolution is not good enough to derive a precise value of Γ_{dis}, we use the inhomogeneous linewidth of 20% or $\Gamma_{\text{dis}} = 0.2$ meV as measured with high resolution in the earlier experiment.[8] With this value and a spin temperature $T_S = 10$ K, the apparent mean transition energy $\hbar\bar{\omega}$ of the downscattering line should be 40 μeV lower than the value $\hbar\omega_0$ of the energy loss line. This is very close to our observation (Table I).

Another aspect is worth discussing: It is rather likely that the local cage environment relaxes when the methane density changes during a rotational transition. Thus the rotational potential and levels would be different in the ground and excited states with the energy differences dissipated into the coupling degrees of freedom. Such a phenomenon is not contained in the single particle description of molecular rotation generally used. An important quantity is also the time scale on which this occurs. Can one rely on a Born-Oppenheimer type behavior with particles or is the relaxation much slower? At present we prefer to remain with the analysis given above.

B. Vibrational phonon density of states

The global features of the vibrational density of states are already well known. Molecular dynamics simulation with atom-atom interaction potentials developed especially for ice allow an assignment of the peaks of the DOS to characteristic eigenmodes. Calculations were performed for a methane clathrate sample at a temperature $T=145$ K.[13] On this basis the mode at 6.7 meV observed in later experiments[11,12] can be assigned to a translational motion of methane molecules in the large ice cages. The 10 meV line is proposed as the fingerprint of the rattling mode in the smaller cages. However, less clearly peaked modes of the host lattice are found at similar energies[11] and, of course, the lattice dynamics of the complete host-guest system is complicated.

1. Effect of thermal contraction

To estimate a possible effect of thermal contraction the observed shift of the rattling mode is tentatively related to a relative change $\delta r/r$ of intermolecular distances by the standard formula

$$\frac{\delta r}{r}=\frac{1}{3}\alpha\delta T. \tag{4}$$

Here δT is the temperature difference creating the expansion δr and the proportionality factor is the thermal volume expansion coefficient α. We further assume that the rattling potential is harmonic $V_r=a_r r^2$ and that its steepness increases $\sim r^{-n}$ like the repulsive part of atom-atom potentials. Then the energy levels E_r change with intermolecular distance as $\delta E_r/E_r=-n(\delta r/r)$. Therewith the observed energy shift δE_r can be related to an increased intermolecular distance $r+\delta r$. From Eq. (4) the corresponding change of temperature δT can be calculated. For molecular solids α is of the order of $10^{-5}\ \mathrm{K}^{-1}$. With this value a temperature change of $\delta T\sim 200$ K is needed to explain the observed line shift, while the sample was cooled by ~ 10 K only. Thus a classical explanation fails.

Finally, a shift of rattling energy with *time* is seen in the sequence of spectra taken at a constant low sample temperature. This fact, above all, excludes thermal contraction as reason of the hardening of the rattling mode.

2. Single particle model

Thus the mechanism causing the hardening of the cage with decreasing temperature must be related to a change of properties of the guest molecule when changing its rotational state. In the following qualitative argumentation the methane molecule is treated as a free rotor. For simplicity we argue in terms of a one dimensional model. Then the molecular ground state wave function $\Psi(\omega_E)=\mathrm{const}$ and the proton density $\Psi\Psi^*$ is isotropic and constant. In the first excited state the wave function becomes $\Psi\sim\sin\varphi$ with a corresponding elliptical density distribution. In this state the molecule can adjust to an angle dependent charge distribution of its local environment. Thus, molecules in the ground state need more space and explore more of the repulsive part of the atom-atom potential. Due to the rather stable water cage, this leads to an increased rattling energy. On the other hand, a molecule in the excited state can adjust orientationally to the nonspherical shape of the modulated potential surface of the cage towards a minimum energy orientation with larger average distance to cage atoms. The resulting softer potential reduces the rattling energy. The change follows, with temperature, the classically expected direction, its unusually large shift may be viewed as an anomalous rotation-translation coupling.

In the simplest quantitative model we introduce two different Einstein type rattling energies, E_A for the guest molecules in the rotational A ground state and E_T for those in the excited T state. The intensities of the two lines are determined by the population $c_T(T)$ and $1-c_T(T)$ of the two states, respectively. The spectral response is the weighted superposition of two peaks described by functions $R(E,\omega)$ at the rattling energies E_A and E_T,

$$S(T,\omega)=c_T(T)R(E_T,\omega)+(1-c_T(T))R(E_A,\omega). \tag{5}$$

E_A and E_T are the free parameters of the model. If the lines overlap, the change of concentration c_T with spin conversion or temperature will show up as a line shift only. Indeed, on lowering the spin temperature the normalized spectra reflect the loss of intensity on the low energy side of the peak and a simultaneous gain at high energy transfers. Almost pure A-state methane clathrate is obtained at the lowest spin temperature $T_S=4.3$ K. On the other hand, the experimentally accessible highest sample temperature is limited, since the quantum nature of rotation gets destroyed at high temperature by an increasing coupling to phonons. Despite this limitation of the experiment, E_T can be deduced by extrapolating the measured line shift for $c_T=1$. The model reproduces the measured shift of the rattling mode, but, due to the presence of just two different rattling energies fitted at $E_A=7.14$ meV and $E_T=5.20$ meV, the change with temperature is not as smooth and linear as observed.

It should be kept in mind that the neglect of any other inelastic intensity in the meV regime besides rattling represents a very rough approximation.

Furthermore, there must be secondary effects which smooth the more steplike temperature evolution obtained in the above bimodal description. Disorder due to different configurations of the hydrogen bonds of a cage is certainly a main source of energetically weakly different rattling modes. The presence of phonon dispersion also leads to a broadening of rattling bands and thus to a more continuous shift with lowering temperature.

Another simplification used so far is the limitation to a single cage. In reality, the monolayer water shell of the cage is shared with the neighboring cages, which also host methane guest molecules. The increase of the rattling energy with conversion shows that the methane guest molecule exerts a pressure onto the monolayer cage wall, which influences the rattling potential of the neighboring cage. Due to the larger number of neighbors, there are many small changes of the local rattling potential possible. Therefore the rattling mode can change more smoothly than in the single-cage model. For a more quantitative description we can adopt formally a model developed some time ago for the analysis of tunneling spectra of methane defects in rare gas matrices[18,23] as well as for the evolution of tunneling spectra at the lowest temperatures in phase II of pure methane.[24] The basic assumption of these models is that the mean energy and the width of a line are determined by the disorder of the environment with respect to either the kind[18,23] or the excitation state[24] of the neighboring molecule. In the model we take into account, for example, $N=6$ neighbors. Arbitrarily it is assumed that the rattling energies E_{rn} depend linearly on the number n of excited nearest methane neighbors. The probabilities of configurations are given by a binomial distribution with $N=6$, which is completely determined by c_T, the concentration of methane molecules in the excited tunneling state. We obtain a smooth shift of the mean rattling energy with c_T,

$$\bar{E}_r(T_S) = E_{rN} + (E_{r0} - E_{rN})(1 - c_T). \tag{6}$$

E_{r0} means the rattling energy if all methane neighbors are in the A rotational ground state and E_{rN} if all would be in the excited T state. Gaussian resolution function placed at the respective temperature dependent energies is shown as solid lines in Fig. 2 for the two extreme spin temperatures $T_S = 13.2$ and 4.3 K. The characteristic parameters of the model are $E_{r0}=7.30$ meV and $E_{r6}=5.25$ meV and are very similar to the parameters of the single-cage model. (The single cage model is identical to the multicage model with $N=1$.)

C. Related systems

The above interpretation is supported by an observation for methane trapped in the similar rigid C_{60}.[25] For this material the largest ground state tunnel splitting is ~0.65 meV. A peak in the density of states at 10 meV is interpreted as a rattling band. It shifts by about 1 meV if the sample temperature is lowered from 4.5 to 1.5 K. The authors try an explanation by arguing with population changes of various sublevels contributing to the band. According to the cited paper the system is always in thermal equilibrium due to a fast spin conversion time $\tau_{1/2}=2.6$ h. In view of our results we attribute the shift to the change of the charge density distribution of methane molecules with conversion into the rotational ground state.

Contrary to methane clathrate, pure methane represents a system where the lattice can adapt to the change of molecular properties with conversion into the rotational ground state. In pure methane II the rotational potential is *reduced* with decreasing temperature.[24] The weak differences between the tunneling sublevels lead to an extended proton density $\Psi\Psi^*$ in the rotational ground state with a reduced octopole moment. The total energy of the crystal is minimized by following macroscopically the broadened angular probability distribution $\Psi\Psi^*$ of the converted molecules. This is the reason why pure methane expands below $T \sim 20$ K, with a maximum negative thermal volume expansion coefficient of -5×10^{-5} K^{-1}.[26] In methane clathrate we have competing effects. Expanding guest molecules have to work against a contracting rigid host lattice. The experiment[27] shows that the lattice parameter is stabilized by the ice host framework.

D. General implications

The outlined phenomenological models show that the changes of the rattling energies can be traced back to the variations of the guest molecule and environmental properties at low temperatures. Classical lattice dynamical calculations are based on invariable interaction potentials such as the universal force field[28] and therefore will miss the observed effect. Vice versa, refining atom-atom potentials (AAPs) from data sets acquired at two not too different low temperatures, for example, $T=5$ K and $T=20$ K, may lead to spurious differences of the intermolecular interaction parameters. Thus transferability of AAP, which makes this concept useful for a larger community, can be violated in systems where quantum effects become important.

V. CONCLUSION

The main band of the vibrational density of states of methane water clathrate at energy $E_r \sim 7$ meV is found as in earlier experiments to represent a CH_4 rattling mode in the large ice cages. Below $T=25$ K this band shifts to higher energies with lowering temperature. Assuming a typical thermal expansion coefficient of a molecular solid, this shift is about a factor of 10 too strong to be explainable classically by lattice contraction. This interpretation is confirmed by the fact that the same shift is found as a time dependent phenomenon at constant low temperature for a quenched sample.

The shift can be linearly correlated with the population of the first excited methane rotational state (Fig. 3). The origin of this behavior is found in the anisotropy of the proton density distribution in the excited rotational state compared to the more isotropic density in the ground state. The new degree of freedom obtained by the symmetry reduction allows the molecule to adopt orientationally and energetically better to the modulated potential surface of the cage. At the larger average distance to the cage walls, the repulsive branch of the intermolecular potential is less explored and the rattling potential weakens.

A single particle model which describes the rattling band as a concentration weighted superposition of two modes associated with CH_4 molecules in the ground and excited rotational states, respectively, can fit the data. The model parameters are the rattling energies in pure A-methane and in pure T-methane clathrate. They differ by about 25% or 2 meV. Disorder of hydrogen bonds, varying excitation states of methane guest molecules in neighboring cages, as well as dispersion of rattling phonon branches smooth the shift with temperature.

The observation has implications for molecular dynamics simulations. High precision molecular dynamics (MD) calculations are, in general, based on structural parameters as precise as $\sim 10^{-3}$ Å and transferable pair interaction potentials. The experiment shows that pair interaction parameters established for some temperature regime may not be valid globally since changes of the quantum state of a molecule with temperature can strongly modify the parameters.

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