Resonant Coupling of Free Quantum Rotors in Inclusion Compounds

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NH_3 groups in certain Hofmann clathrates form almost free one-dimensional quantum rotors with energy levels $E_n = n^2B$ and angular momentum $n\hbar$, where $n = 0, \pm 1, \pm 2, \ldots$. Recent neutron scattering experiments revealed a surprising temperature dependence for the linewidths of the $n = 0 \leftrightarrow 1$, $0 \leftrightarrow 2$, and $1 \leftrightarrow 2$ transitions. We propose a novel line broadening mechanism based on rotor-rotor coupling and obtain a simple analytic expression for the widths that depends on the rotor level occupation and on the 3-proton spin degeneracies of initial and final states. Our model provides, without adjustable parameters, a good fit both to the temperature dependence of the observed widths and to their relative magnitude.

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Molecular rotors in inclusion compounds have attracted much attention recently. Natural gas hydrates are of considerable environmental interest. About half of the combustible carbon on earth ($\sim 10^{16}$ kg) occurs as methane hydrate, to a large extent at the bottom of the ocean [1]. Depending on their stability, they represent a huge fossil energy resource or a serious climate risk, methane being a much more efficient greenhouse gas than carbon dioxide. A microscopic understanding of these systems requires both structural and dynamical information. At high pressure, these hydrates form H_2O crystals of cubic or hexagonal symmetry with voids that are filled by methane or carbon dioxide molecules [2,3]. Regarding the dynamics of the inclusion molecules, inelastic neutron scattering (INS) studies indicate almost free rotational motion where the four protons turn round the central carbon atom of the CH_4 molecule, with a quantum energy of the order of 1 meV [4]. At temperatures between 5 and 20 K, INS spectra show rather sharp lines for the transitions between the first three rotor levels of CH_4. (It has been known for a while that in the β phase of solid methane, one molecule out of four is a 3D almost free rotor [5].) The linewidth of methane in clathrates comprises a thermal contribution and inhomogeneous broadening due to the dipolar fields of the water molecules [4].

The ammonia groups of certain Hofmann clathrates $M(NH_3)_2M'(CN)_4$-G show free rotations of the three protons of NH_3, very similar to those of methane clathrates. Here, M and M' are divalent metal ions and G is a guest molecule. INS spectra for $M' = \mathrm{Ni}$, $M = \mathrm{Ni}$, Co, Fe, Mn, and phenyl or biphenyl as guest molecules, are very well described by a free rotor model [6–9]. The results for the transition $0 \leftrightarrow 1$ of $Ni(NH_3)_2(CN)_4$-$2C_6D_6$ suggest that the line broadening cannot be understood in terms of resonant phonon coupling but depends on the occupation of the rotor levels [7]. Very recently, Rogalsky *et al.* studied the transitions $0 \leftrightarrow 1$, $0 \leftrightarrow 2$, $1 \leftrightarrow 2$ between the levels $n = 0, 1, 2$ of the system $M' = \mathrm{Ni}$, $M = \mathrm{Ni}$, and $G = 2C_{12}H_{10}$ (biphenyl) over a wide range of temperatures $T = 2$–80 K and observed a most surprising variation of the linewidths [9]. The broadening increases exponentially at low T; the widths of the transitions $0 \leftrightarrow 2$ and $1 \leftrightarrow 2$ are equal and much larger than that of $0 \leftrightarrow 1$. At high temperatures the widths would seem to become constant. The numerical simulations of Ref. [9] indicate the relevance of thermal fluctuations of the environment on the rotor dynamics.

The present work was stimulated by the linewidths reported in [9] and shown in Fig. 1; we propose a novel mechanism for line broadening of almost free quantum rotors that is based on rotor-rotor coupling. The outline of the paper is as follows. We start with a brief summary of the quantum mechanics of 3-proton rotors and derive the leading term of the pair potential of nearby molecules. Then we calculate relevant two-time correlation functions that provide, in particular, the linewidths of the neutron scattering law, and finally discuss our results in view of the experimental data. (Line broadening due to rotor-rotor coupling has been evoked in a study on methyl rotation in manganese acetate [10].)

Small molecules with an exact symmetry due to the exchange of identical particles show quite particular dynamics. The best-known example is molecular hydrogen that occurs as para-H_2 or ortho-H_2, characterized by a total nuclear spin $S = 0$ and a symmetric spatial proton wave function ψ, or $S = 1$ and antisymmetric ψ, respectively. Similar but slightly more complicated symmetry properties arise from the cyclic exchange of the three protons of ammonia or methyl groups, with total nuclear spin $S = \frac{1}{2}, \frac{3}{2}$, or of the four protons of methane with $S = 0, 1, 2$ [5]. The different nuclear spin states impose particular selection rules for transitions between states of the same spin ($\Delta S = 0$) and transitions that involve a spin flip ($\Delta S = 1$). In the solid state the molecular motion is usually strongly hindered by crystal fields. Then the cyclic proton exchange can be viewed as rotational tunneling between two or three minima that are separated by an angle π for H_2 and $2\pi/3$ for ammonia and methyl groups; the splitting Δ of the ground state and the first rotor level is exponentially small in the barrier height. Because of the magnetic selection rules, the lifetime of these tunnel states may exceed several weeks, and they can be observed as sharp excitations

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at temperatures where the thermal energy $k_B T$ exceeds the tunnel splitting Δ by several orders of magnitude [5,11,12].

Besides the proton exchange symmetry, free rotors require an approximate continuous symmetry with respect to the corresponding rotational degree of freedom. We consider one-dimensional rotation of a molecular group such as NH_3 about its molecular axis. With the proton mass m and the distance from the axis d, the moment of inertia is given by $\Theta = 3md^2$, and the kinetic energy reads as

$$K = \frac{L_z^2}{2\Theta}. \tag{1}$$

The relevant variable $\varphi = \frac{1}{3}(\phi_1 + \phi_2 + \phi_3)$ is the average angle of the three protons. With the angular momentum $L_z = -i\hbar\partial_\varphi$ one finds immediately that the eigenfunctions are plane waves $\psi_n(\varphi) = e^{in\varphi}$ with $n = 0, \pm 1, \pm 2, \ldots$. The free rotor levels thus read

$$E_n = Bn^2, \tag{2}$$

with the rotational constant

$$B = \hbar^2/2\Theta. \tag{3}$$

For the three protons of an ammonia or methyl group we have $d \approx 1$ Å and hence $B \approx 0.7$ meV [5]. There is evidence that the proton rotation is coupled to a precession of the whole molecule; this is already taken into account by the above renormalized values of B [7].

The proton wave function satisfies the Pauli principle; spin and spatial parts are either symmetric or antisymmetric under proton exchange. The spin quantum number S of the three protons takes the values $\frac{1}{2}$ or $\frac{3}{2}$. The requirement of an antisymmetric wave function relates the free rotor level E_n to the spin functions according to

$$\begin{aligned} S = \tfrac{3}{2} &: n = 0, \pm 3, \pm 6, \ldots, \\ S = \tfrac{1}{2} &: n = \pm 1, \mp 2, \pm 4, \mp 5, \ldots. \end{aligned} \tag{4}$$

In group theoretical language, the levels $n = 3m$ (with entire m) correspond to the one-dimensional representation A of the group C_3, and the levels $n = 3m + 1$ and $n = 3m - 1$ to the complex conjugate representations E_a and E_b. (Explicit expressions for the spin functions can be found, e.g., in [5].)

Exchange of two protons is irrelevant since it would require breaking of atomic bonds. A cyclic exchange of three protons, however, roughly corresponds to a rotation by $2\pi/3$ of the NH_3 group about its axis and thus is relevant for the motional spectrum. The potential energy of N molecules $V(\varphi_1, \ldots, \varphi_N)$ is invariant under proton exchange and in particular under the cyclic operation $\varphi_i \to \varphi_i + 2\pi/3$. As a consequence, its Fourier series involves only terms of the form $v_{n_1 \ldots n_N} e^{i3n_1\varphi_1 + \ldots + i3n_N\varphi_N}$. (This constraint just reflects the fact that a static potential cannot induce transitions between free rotor levels that correspond to different spin states.) The kinetic energy (1) with a single-particle potential $v_1 \cos(3\varphi)$ leads to the Mathieu differential equation that describes neutron scattering and NMR spectroscopy data for many systems [5].

In this paper we consider almost free rotors with zero one-particle potential, $v_1 \approx 0$. Still, the molecules carry electric multipoles and cause elastic deformations of the host lattice. A nearby neighbor thus experiences a time-dependent electric or elastic perturbation that gives rise to a pair potential $V(\varphi_i, \varphi_j)$. Because of the threefold molecular symmetry the Fourier series of this potential is dominated by the third-order terms $n_i, n_j = \pm 1$. Replacing the corresponding Fourier coefficients by a constant and discarding phase factors, we obtain

$$V(\varphi_i, \varphi_j) = 2v_{ij} \cos(3\varphi_i) \cos(3\varphi_j). \tag{5}$$

[The most general form would involve terms as $\cos(3\varphi_i \pm 3\varphi_j + \delta_{ij})$. These modifications being irrelevant here, we discard them for the sake of simplicity.]

Time evolution is determined by the total Hamilton operator $H = \sum_i K + \frac{1}{2}\sum_{ij} V$ that contains the kinetic energy (1) and the pair potential (5) of all molecules. For almost free rotors, the neutron scattering law reads as

$$S(\mathbf{q}, t) = \sum_X f_X(\mathbf{q}) \langle X^\dagger U(t) X \rangle, \tag{6}$$

where the spatial part of the scattering operators X induce transitions between rotational states n and m, $\langle \cdots \rangle$ indicates thermal averaging, and the structure factors $f_X(\mathbf{q})$ depend on the momentum transfer $\mathbf{q}$. Time evolution $U(t) = e^{-iLt/\hbar}$ is most easily expressed in terms of the quantum Liouville operator L whose action on a variable A is given by the commutator $LA = [H, A]$. Here we evaluate $U(t)$ according to standard time-dependent perturbation theory for the Liouville operator $L = L_K + L_V$, where L_K arises from the kinetic energy and L_V from the pair potential [13]. As "relevant operators" we choose those of a given molecule. Performing a partial thermal average $\langle \cdots \rangle_N$ over all neighbors and resorting to a Markov approximation, we obtain the reduced time evolution operator for molecule i

$$u(t) = e^{-i\Omega t/\hbar - \Gamma t/\hbar}. \tag{7}$$

(u, Ω, and Γ are superoperators acting on the space of operators $X = |n\rangle\langle m|$ of molecule i.) The frequency matrix is given by the energy difference of free rotor levels,

$$\Omega_{nm} = \mathrm{Tr}\{X^\dagger [K, X]\} = E_n - E_m, \tag{8}$$

and the rate matrix by the long-time limit of the double commutator

$$\Gamma_{nm} = \frac{1}{2\hbar} \int_{-\infty}^{\infty} dt \langle X^\dagger L_V e^{-iL_K t} L_V X \rangle_N. \tag{9}$$

In principle the double commutator gives rise to four terms. Here, those with a negative sign vanish, and the remaining terms yield

$$\Gamma_{nm} = \gamma_n + \gamma_m, \tag{10}$$

where γ_n is the level width of the rotor state n of molecule i due to resonant rotor-rotor coupling,

$$\gamma_n^i = \pi v^2 \sum_{j,r} p_r^j \sum_{\{\pm\}} \delta(\Omega_{n,n\pm3}^i + \Omega_{r,r\pm3}^j). \tag{11}$$

(Here the signs $\pm$ are varied separately such that the sum $\{\pm\}$ contains four terms, and v is the average coupling strength.) The label r runs over all states of molecule j, with the thermal occupation factor

$$p_n = (1/Z) g_n e^{-E_n/k_B T}, \tag{12}$$

where $Z = \sum_n g_n e^{-E_n/k_B T}$ is the partition function. The spin degeneracy

$$g_n = 2S + 1 \tag{13}$$

takes the values $g_n = 4$ for states with $S = \frac{3}{2}$ and $g_n = 2$ for $S = \frac{1}{2}$. Accordingly, the A-symmetric rotor states $n = 0, \pm 3, \pm 6, \ldots$ with $S = \frac{3}{2}$ have the double weight in (12). (Yet there are two times more E-symmetric rotor states $n = \pm 1, \pm 2, \pm 4, \pm 5, \ldots$ with $S = \frac{1}{2}$.)

The δ function in (11) selects resonant terms such that the transition frequencies of molecules i and j cancel. In order to regularize the sum over j, we note that, due to the pair potential, the frequencies Ω_{nm} are not exactly the same for all molecules but rather show a narrow but continuous distribution $\rho(\Omega_{nm})$ about the value $(E_n - E_m)$. (The width of this distribution is of the order of the coupling parameter, thus $\rho \propto 1/v$ close to resonance.) Noting $p_n = p_{-n}$ and putting $\sum_j \delta(\cdots) = \rho$ at resonance, we finally obtain a simple result for the broadening of the rotor levels,

$$\gamma_n = 2\pi\rho v^2 (p_{n+3} + p_{n-3}). \tag{14}$$

According to (10), the widths of the transitions lines read

$$\Gamma_{nm} = 2\pi\rho v^2 (p_{n+3} + p_{n-3} + p_{m+3} + p_{m-3}). \tag{15}$$

This is the main result of the present paper. Note that the temperature dependence is entirely determined by the thermal occupation factors p_n.

In view of the data of [9] we discuss in some detail the widths involving the lowest levels $n = 0, 1, 2$. We start with the limit of low temperatures, $kT < B$. First consider the transitions $0 \leftrightarrow 1$. The occupation factors of the levels 3, 4 being much smaller than $p_2 \approx (1/2)e^{-4B/k_B T}$, we have in a good approximation

$$\Gamma_{01} \approx \pi\rho v^2 e^{-4B/k_B T} \text{ (low } T). \tag{16}$$

Regarding the transitions $0 \leftrightarrow 2$ and $1 \leftrightarrow 2$ and retaining the dominant term $p_1 \approx (1/2)e^{-B/k_B T}$ only, we find

$$\Gamma_{02} \approx \Gamma_{12} \approx \pi\rho v^2 e^{-B/k_B T} \text{ (low } T). \tag{17}$$

At low temperatures, the inequality $p_1 \gg p_2$ thus implies $\Gamma_{02} \approx \Gamma_{12} \gg \Gamma_{01}$. The widths increase exponentially with rising temperature, with apparent activation energies B and $4B$.

In the opposite case of high temperatures beyond 80 K, i.e., $kT > 10B$, the occupation factors of the lowest rotor levels are determined by the spin degeneracy g_n, resulting in the ratio,

$$\Gamma_{01} \approx \Gamma_{02} \approx \tfrac{3}{2}\Gamma_{12} \text{ (high } T). \tag{18}$$

In this range the linewidths depend very weakly on temperature; for thermal energies kT well beyond $25B$, i.e., $T > 200$ K, we expect a slight decrease. Finally we note that transitions involving the level $n = 3$ show a width which is finite at $T = 0$ and decreases with rising temperature. For example, regarding $2 \leftrightarrow 3$ we find $\Gamma_{23} = 2\pi\rho v^2$ at $T = 0$.

In Fig. 1 we compare the theoretical result (15) with the neutron scattering data reported in Ref. [9] and find a good agreement within the experimental error bars. In particular, all widths show the exponential increase (16),(17), and those of the transitions $0 \leftrightarrow 2$ and $1 \leftrightarrow 2$ are identical at low temperatures. Their relative magnitude in the intermediate range up to $kT = 4B$ is well described by our theory. At present the high-temperature ratio (18) cannot be verified, since in the range $kT > 4B$ data are available for $1 \leftrightarrow 2$ only. Both the temperature dependence of the three widths and their relative magnitude are determined by the free rotor spectrum (2). Accordingly, the prefactor ρv^2 is the only adjustable parameter; for the fits we have chosen $2\pi\rho v^2 = 2B$. (A similar fit can be obtained for the data of the transition $0 \leftrightarrow 1$ of [7].)

For quasielastic scattering our linewidth formula simplifies to

$$\Gamma_{n,-n} = 2\gamma_n. \tag{19}$$

As a caveat we note that quasielastic scattering corresponds to a damped zero-frequency pole of the time evolution operator. Its proper evaluation would require calculation of the whole rate matrix instead of the above diagonal elements (10). In principle, the nondiagonal parts could reduce the quasielastic linewidth. (Such an effect occurs

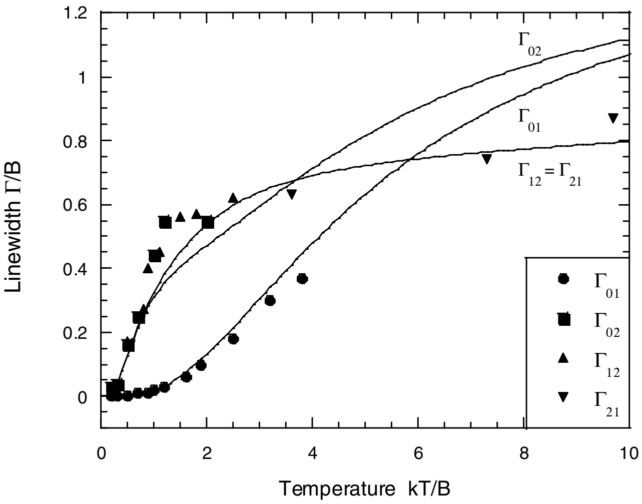

FIG. 1. Temperature dependence of the widths of the lowest transitions. The data points are from Ref. [9]; the solid lines are obtained from Eq. (15) with the parameter $\pi\rho v^2 = B$. Note the numerical value $B/k_B \approx 8$ K.

for the quasielastic scattering of strongly hindered rotors, where the line broadening by resonant phonons is rather ineffective between E_a and E_b states [12].)

Measuring the quasielastic width is not an easy matter, due to the presence of a huge elastic peak. Yet in view of (19) it would be interesting to compare the quasielastic width with the data reported in [9]. Note that the intensity of the transition $n \longrightarrow m$ carries the initial state population factor p_n. Thus one expects that the quasielastic intensity disappears at zero temperature. At small momentum transfer $\mathbf{q}$, it involves mainly the transitions $1 \leftrightarrow -1$; at low T the width reads as $\Gamma_{1,-1} \approx 2\Gamma_{01} \approx 2\pi\rho v^2 e^{-4B/k_BT}$, according to (19).

We briefly discuss the numerical value of the coupling constant in (5). With $\rho \sim M/v$ and M nearest neighbors, our fit parameter $\pi\rho v^2 = B$ requires a v of the order of B/M, i.e., a few tenths of meV. For comparison we note that both elastic and dipolar electric interactions of nearby cyanide or lithium impurities in alkali halides are of the order of 10 meV [14]. Since the electric and elastic multipole moments of ammonia molecules are significantly smaller and their minimum distance in Hofmann clathrates larger, our estimate $v \sim 0.1$ meV would seem a reasonable value.

The line broadening due to rotor-rotor coupling obtained in this paper may attain values of the order of the rotational constant B. This is by several orders of magnitude larger than comparable effects on rotational tunneling. For strongly hindered rotors, pair potentials similar to Eq. (5) have been extensively discussed in the literature. Both a mean-field calculation [15] and exact diagonalization of small clusters [16] have shown that rotor-rotor coupling is rather irrelevant for moderate or large rotational barriers.

With a few modifications, our findings for NH_3 rotors apply equally well to methane in hydrates. The width $0 \leftrightarrow 1$ reported in [4] increases significantly with temperature, whereas the transitions $0 \leftrightarrow 2$ and $1 \leftrightarrow 2$ broaden weakly between 5 and 20 K. Though these few data do not allow for a definite statement, they would seem to agree qualitatively with our results. We may conclude that there is strong evidence for the thermal line broadening in methane hydrate being due to rotor-rotor coupling.

In summary, we have proposed a line broadening mechanism for free quantum rotors that is based on resonant interaction of nearby molecules. The resulting width depends both on the 3-proton spin degeneracy g_n and on the thermal occupation of the rotor levels. With a single adjustable prefactor ρv^2, our model describes the temperature dependence and the magnitude of the linewidths observed for free ammonia rotation in Hofmann clathrates between 2 and 80 K. In particular, our linewidth formula accounts for the exponential increase with different activation energies at low T and the saturation at high T. Moreover, our theory predicts a spin dependent linewidth ratio (18) and a quasielastic linewidth (19), that await experimental verification.

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