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LETTER TO THE EDITOR

The temperature dependence of inelastic rotational tunnelling transitions

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Abstract. The temperature dependence of position and width of inelastic rotational tunnelling transitions is investigated. Special emphasis is put on the functional dependence on the ratio of splitting and resonance width of the excited librational multiplets, and an upper bound for the prefactor of the linewidth is derived.

In the absence of magnetic interactions, a methyl or amine group in a crystal environment is described by the Hamiltonian

$$H = H_S + H_B + H_{SB} \qquad H_S = -\partial^2/\partial\varphi^2 + V\cos(3\varphi)$$
$$H_B = \sum_k \omega_k(b_k^+ b_k + \tfrac{1}{2}) \qquad H_{SB} = \sum_k g\cos(3\varphi + \delta_k)(b_k^+ + b_k) \tag{1}$$

the potential energy of which contains the lowest order terms of the Fourier and power series in the collective proton angle, φ, and the oscillator coordinates of the heat bath, respectively (Hewson 1982, Würger 1989). The eigenstates of the system Hamiltonian H_S are labelled by a librational quantum number, m, and a symmetry index, σ, the latter characterising the behaviour under proton exchange of the spin and space part of the wavefunction (Press 1981).

In a previous paper (Würger 1989, hereafter referred to as I—to link up with the notation used there, put $g_k^c \equiv g\cos\delta_k$ and $g_k^s \equiv g\sin\delta_k$) we considered the librational excitations ($0\sigma \rightarrow 1\sigma'$) and the tunnelling spectrum, i.e. the elastic ($0\sigma \rightarrow 0\sigma$), the quasi-elastic ($0E^a \rightarrow 0E^b$) and the inelastic transitions ($0A \rightarrow 0E$). The width of the quasi-elastic transitions came out to be much smaller than the resonance width. For the inelastic lines, we restricted ourselves to the case where the range of phonons resonating with the librations of the symmetries A and E do not overlap.

The resonance width of the levels of the ground state multiplet is given by the expression

$$\sum_{m>0} \pi |M_{0m}|^2 D(E_m) \frac{1}{e^{E_m/T} - 1} \equiv \sum_{m>0} \frac{\gamma_{0m}}{2} n(E_m) \tag{2}$$

which is well known from perturbation theory. As in I, M_{0m} denotes the coupling matrix element, E_m the average energy of the mth multiplet and $D(\omega)$ the density of states of the heat bath. The principal contribution to the resonance width of the levels of the mth

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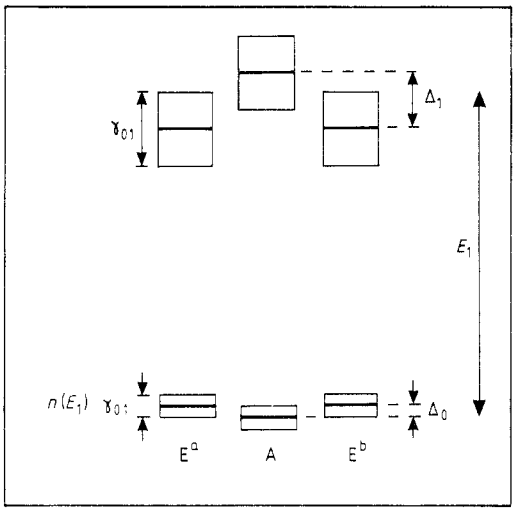

Figure 1. Level scheme showing the resonance widths for the two lowest multiplets. It does not represent the spectrum of the Hamiltonian (1), but illustrates rather the effects of the bath on the levels of H_S.

multiplet ($m > 0$) reads $\pi|M_{0m}|^2 D(E_m) \equiv \gamma_{0m}/2$; since the temperature-dependent terms are unimportant in the tunnelling regime, i.e. for $T < E_1$, they have for simplicity been discarded.

In this Letter we extend our previous treatment of the inelastic transitions to the case where the phonons resonating with the A and E librations are no longer distinct, as illustrated in figure 1.

The calculation has been done within the framework of the Nakajima–Zwanzig theory (I, Haake 1973): after expanding the Liouville operator to the second order in the interaction, the time evolution operator is given by

$$\mathrm{i}\frac{\partial}{\partial t} V(t) = L_S V(t) + \int_0^t \mathrm{d}\tau\, K(\tau)\, V(t-\tau) \tag{3}$$

where use has been made of the definitions

$$\begin{aligned} &L_S \,.\, \equiv [H_{S'} \,.\,] \\ &K(t) \,.\, \equiv \mathrm{Tr}_B\{H_{SB'} \exp[-\mathrm{i}(H_S + H_B)t]\,[H_{SB'} \,.\, \exp(-\beta H_B)] \exp[\mathrm{i}(H_S + H_B)t]\}. \end{aligned} \tag{4}$$

The Fourier transform of (3) yields the scattering function which we want to calculate

$$S(z) \equiv \langle XV(z)X\rangle = \langle X[1/(z - L_S - K(z))]\, X\rangle. \tag{5}$$

The neutron scattering operator, X, causes spin flips between the A-symmetric ($I = \frac{3}{2}$) and E-symmetric ($I = \frac{1}{2}$) states of the three protons of a methyl group: hence (5) may be interpreted as a spin susceptibility.

The energies and widths of the tunnelling transitions are given by the lowest eigenvalue of the Liouvillian. As described in I, the operators L_S and K are represented by tetrads with respect to the eigenbasis of H_S. After expanding the determinant of the denominator of (5) in inverse powers of the higher diagonal elements, we obtain as the leading term for the linewidth

$$\Gamma(T) = \sum_{m>0} \gamma_{0m} \frac{\Delta_m^2}{\Delta_m^2 + \gamma_{0m}^2} \frac{1}{\mathrm{e}^{E_m/T} - 1} \equiv \sum_{m>0} \Gamma_m n(E_m). \tag{6}$$

The splitting of the mth multiplet is denoted by Δ_m. Since the ratio Δ_0/Δ_m is small for

$m > 0$, the ground state splitting has been omitted everywhere. There are two limits for the prefactor appearing in (6):

$$\gamma_{0m} \ll |\Delta_m|: \qquad \Gamma_m = \gamma_{0m} \tag{7a}$$

$$\gamma_{0m} \gg |\Delta_m|: \qquad \Gamma_m = \Delta_m^2/\gamma_{0m}. \tag{7b}$$

The result for large Δ_m, (7*a*), is equivalent to formula (3.14) of I. In the other limiting case, (7*b*), the contribution of the mth multiplet to the linewidth is given by twice the fraction $(\Delta_m/\gamma_{0m})^2$ of the corresponding contribution to the resonance width (2). In addition, (6) provides as an upper bound for the prefactor

$$\Gamma_m \leqslant |\Delta_m|/2. \tag{8}$$

Now we turn to the position of the A–E-tunnelling line, Θ. With the definition

$$\sigma_m(T) \equiv \sum_k \left(\frac{n(\omega_k)}{(E_m - \omega_k)^2} + \frac{1 + n(\omega_k)}{(E_m + \omega_k)^2} \right) \tag{9}$$

and τ_m being the same, but with the signs in the denominators interchanged, the energy transfer reads

$$\Theta(T) = \Delta_0 + \sum_{m>0} \Delta_m \left(\frac{\sigma_m}{1 + \tau_m} + \frac{\gamma_{0m}^2}{\gamma_{0m}^2 + \Delta_m^2} n(E_m) \right). \tag{10}$$

Again, for $\gamma_{0m} \ll |\Delta_m|$ the second term in the brackets is negligible and we recover formula (3.12) of I. For the inverse case, $\gamma_{0m} \gg |\Delta_m|$, the two contributions in (10) are of the same order of magnitude; with rising temperature the second term overtakes the first one.

At the origin of the above expressions is the decomposition of singular integrands of the type

$$\lim_{\eta \to 0} [1/(E - \omega \pm \mathrm{i}\eta)] \equiv P[1/(E - \omega)] \mp \mathrm{i}\pi\, \delta(E - \omega) \tag{11}$$

as they appear in formulae (3.10) of I. The Cauchy principal value accounts for the non-resonant, mainly acoustic, phonons and leads to the first term in brackets in (10), whereas the delta-function part describes the effects of resonant modes, $\omega \simeq E$, which are the linewidth and the second contribution to the temperature-dependent lineshift.

Imagine we had diagonalised the Hamiltonian (1) and written its eigenstates in the standard basis as

$$\sum_{m,\{n_k\}} c_{m,\{n_k\}} |m\sigma, \{n_k\}\rangle. \tag{12}$$

As above, $m = 0, 1, \ldots$ denotes the librational levels of the molecule and $\{n_k\}$ gives the phonon occupancy: since the phonons mix librational states of the same symmetry, the symmetry label σ is the only 'good' quantum number. In the tunnelling regime the temperature is well below librational energies, thus the accessible states of type (12) are made up mainly of terms with $m = 0$.

First let us look at the quasi-elastic scattering. E^a- and E^b-symmetric states form time-reversed pairs: the relevant part of the scattering operator correspond approximately to time reversal, and the transitions are almost elastic. (Actually, the width calculated in I is proportional to the square of the amplitude which the scattering operator does not map on the time-reversed state.)

Now we turn to the inelastic case, where initial and final states differ—due to the multiplet splitting—in the absolute value of the expansion coefficients in (12); as a consequence, an A-symmetric state can be scattered in many E-symmetric ones with a certain distribution of energy. Because of the complicated level structure of H_S, there is no exact solution: in the present work the linewidth (6) characterising the final energy distribution about the average energy transfer (10) has been calculated by expanding the Liouville operator—not the Hamiltonian—in a power series. In this perturbative approach the broadening and the crossover between the limiting cases (7) is traced back to the destruction of coherent scattering of the probability amplitude in higher multiplets with increasing splitting.

The functional form of the prefactors in (6) fulfils the condition imposed by requiring the width to be an analytic function; as it cannot depend on the sign of the splitting, Γ_m must be an even function of Δ_m.

We have distinguished between the transition width (6) and the resonance widths (2) of initial and final states. In the limit (7*a*) the former is given by the sum of the latter; this result can also be obtained in the frame of time-dependent perturbation theory. Recently, the prefactor for the other limiting case (7*b*) has been derived using a different approach, by mapping the problem on an exactly soluble model consisting of a lattice of coupled harmonic oscillators (Hüller 1989).

The most striking feature seems to us to be the upper bound for the prefactors, because it relates the quantities describing the temperature dependence to the multiplet splittings, which are determining by the tunnelling energy at zero temperature. Δ_m being exponentially small in the potential, (8) provides quite a strong condition. Furthermore, the resonance width $\gamma_{01}/2$ is given by the width of the librational excitations at zero temperature. (In passing we note that the factor of 2 in the first term to Γ_{lib} in (3.22) of I is wrong; it should be omitted.)

The two contributions to the line shift in (10) are due to acoustic phonons and to those in resonance with the molecular libration; because of the many degrees of freedom connected with the latter type of motion in molecular crystals, one might expect the 'phonon' density of states to exhibit a strong peak at librational energies. Then the second term in the brackets in (10) would lead to an Arrhenius type of law for the line shift; for $|\Delta_1| \simeq \gamma_{01}$ the prefactor equals that for the broadening.

There is some experimental support for the inequality (8) holding: evidently, the most interesting systems are those with a high potential that give small multiplet splittings. It is sound to focus on the first triplet, because due to the Bose occupation factors the $m = 1$ term dominates in the tunnelling regime. For NH_2–CO–CH_3 (Heidemann *et al* 1989), CH_3I (Prager *et al* 1987) and C_6H_5–CH_3 (Cavagnat *et al* 1986) the values for the ratio $\Gamma_1/|\Delta_1|$ lie between 0.5 and 0.8. Given the uncertainty of, typically, 50%, these are still compatible with the theoretical upper bound of $\frac{1}{2}$. There are experimental data available for compounds with a still higher potential of about 25 meV, resulting in $\Delta_0 \simeq 1\ \mu$eV and $\Delta_1 \simeq 40\ \mu$eV; for MNAC (Heidemann *et al* 1987) no broadening could be detected, whereas for 2,4-hexadiyne (Cockbain *et al* 1982) it would seem to be due entirely to the second multiplet. These findings are explained by our formulae (6) and (8) as the suppression of the $m = 1$ contribution to the broadening below the experimental resolution.

In the framework of a previously developed approach to the temperature dependence of rotational tunnelling we have found the position and width of the inelastic lines to depend in an unexpected fashion on the ratio of multiplet splitting and resonance width; for the limits of that ratio being both small and large, our result is in accordance with both an oscillator model put forward recently and perturbation theory, respectively.

We have derived an upper bound for the linewidth that is independent of the quantities describing the bath. Further experimental work on this matter seems particularly desirable.

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