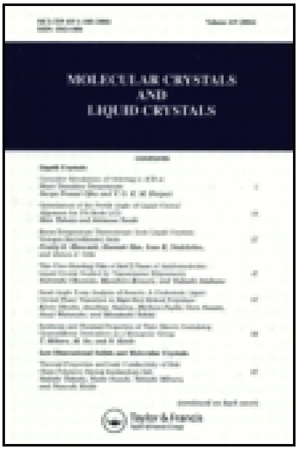

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Hole Burning Spectroscopy and Quantum Phenomena in Methyl Groups

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HOLE BURNING SPECTROSCOPY AND QUANTUM PHENOMENA IN METHYL GROUPS

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Abstract The rotational tunneling states of methyl groups are subject to severe symmetry restrictions which result, at sufficiently low temperatures, in extremely long lifetimes. Hence, these states can be used to store population and to do hole burning experiments. From the recovery of the holes the relaxation of the rotational tunneling levels can be measured. We performed experiments of this type with the probe molecule dimethyl-s-tetrazine in a series of n-alkane host materials. The methyl group turns out to be an extreme sensitive probe for the host lattice. *Direct-, Raman- and Orbach-type rotational tunneling processes* could be identified, with surprising details for the d-substituted rotor.

INTRODUCTION

In a series of experiments we focused on the rotational tunneling dynamics of the methyl groups of the dye dimethyl-s-tetrazine (DMST, Fig. 1) in several n-alkane host materials[1-6]. The methyl rotors have a threefold rotation axis. Hence, the respective potential (Fig. 1) has at least a threefold symmetry. We consider the lowest levels only. The respective wavefunctions overlap, hence, they split. This splitting is called the rotational tunneling splitting. A rotation by 120° corresponds to an even permutation of the methyl hydrogens. It is this correspondence which implies severe symmetry restrictions onto the rotational tunneling states: Pauli's principle requires the wavefunction of the methyl rotor to be totally symmetric. For the CH_3-group this requirement implies a strict correlation between the total nuclear spin of the protons ($\frac{1}{2}$, $\frac{3}{2}$) and the symmetry of the wavefunction of the rotor (A, E). In this case, it is immediately obvious that a transition between the rotational tunneling states involves the flipping of the proton spin and, hence, requires an interaction containing the nuclear spin operators[7, 8]. As a consequence, rotational tunneling relaxation processes in CH_3-groups are called nuclear-spin conversion processes[9, 10].

However, also rotational tunneling in the CD_3-group needs an interaction which breaks the C_3-symmetry and, hence, the correlation with the even permutations[11]. All

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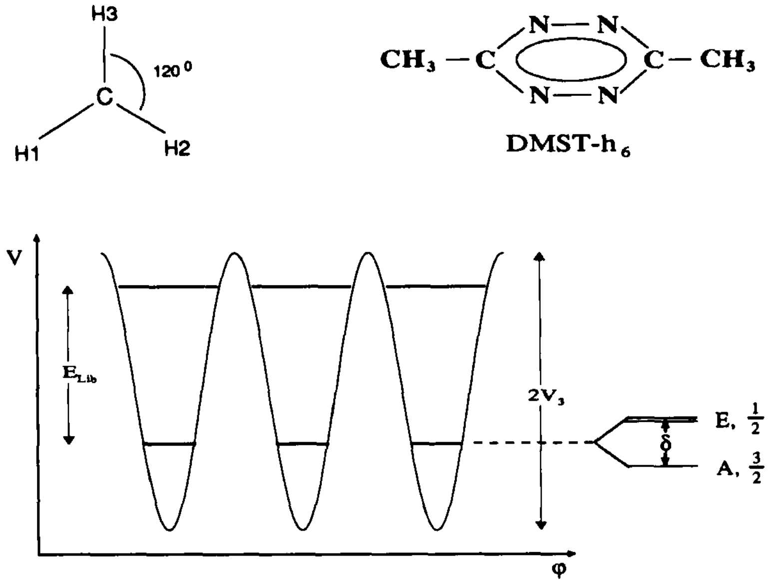

Figure 1: View of the methyl group along the 4th carbon bond, the dye probe dimethyl-s-tetrazine (DMST-h_6) and the rotational potential $V = V_3 \cos(3\varphi)$ of the methyl group with the tunneling splitting δ and the librational energy E_{lib} indicated. E and A refer to the symmetry representation of the rotor wavefunction, $1/2$ and $3/2$ are associated nuclear spins.

these interactions must necessarily contain the nuclear spin operators, because it is their nuclear spin by which the protons or deuterons can be distinguished after a rotation by $2\pi/3$. In the CH_3-case the respective interaction is the nuclear spin-spin-coupling, in the CD_3-case it is the coupling of the deuteron quadrupole moment with the electric field gradient along the C-D-bonds. Both interactions are extremely small and, hence, at sufficiently low temperatures, the lifetime of the tunneling states can get as long as months.

Hole burning is a sensitive method with a large dynamic range (6-7 orders of magnitude) to measure the rotational tunneling dynamics. From the respective temperature dependence one is in many cases able to determine precisely the nature of the respective processes. In the following we present experimental results on the dynamics of the methyl groups of dimethyl-s-tetrazine in a series of n-alkanes, reaching from n-hexane to n-nonane. Although the host lattices seem to be similar, the dynamics can drastically change by going from one lattice to another.

SOME EXPERIMENTAL DETAILS

There are three reasons why hole burning can be exploited to investigate rotational tunneling relaxation: the long lifetime of the states involved, an efficient light-induced population redistribution via spin-conversion in the excited triplet state and a difference in the tunneling splitting δ and δ^* of the groundstate and the first excited singlet state, respectively[12]. This latter point is responsible that molecules converted from A to E (or vice versa) experience a frequency shift by $\pm|\delta - \delta^*|$, leading to a hole at the laser frequency and, symmetrically shifted, to three pairs of antiholes, if the two methyl groups feel different environments.

Instead of antiholes, sideholes can appear. This happens when the phototransformation is photochemical in nature. The phototransformation disturbs the equilibrium population of the tunneling states. Rotational tunneling relaxation reestablishes equilibrium by converting molecules from A to E and vice versa. Thereby sideholes appear. The respective relaxation processes can be measured by following the temporal changes of the central hole, the antiholes or the sideholes[2,13]. The concentration of DMST was on the order of 10^{-3}-10^{-4} mole/mole. Burning was performed with a ring dye laser. Typical power levels and burning times were on the order of 100 μW and 60 s, respectively.

RESULTS AND DISCUSSIONS

Figs. 2 and 3 show the ΔOD-spectra as inserts and the thermal behavior of the rotational tunneling relaxation for some selected examples of DMST-h_6 and DMST-d_6 in protonated and deuterated n-alkane host lattices. The total number of systems we investigated was about 20: DMST-h_6, DMST-d_6 in 8 different host materials (protonated and perdeuterated) as well as partially deuterated DMST in some of these host materials.

1. Thermal behaviour of the rotational tunneling relaxation

Fig. 2a shows DMST-h_6 in n-hexane[5]. The ΔOD-spectrum shows two antiholes separated by $|\delta - \delta^*| = 2.3\,\text{GHz}$. The fact that just 2 antiholes are observed supports the idea that the two CH_3-groups in DMST are identical. Further support comes from Stark-effect-experiments which show that DMST does not lose its inversion symmetry in the n-hexane-lattice. The hole recovery rate which is identical with the decay rate of the antiholes and which, therefore, directly reflects the rotational tunneling relaxation rate, shows two regimes: A low temperature regime, where the rate increases linearly with temperature and, above 6K, a clear turn-over to an activated regime. The linear regime corresponds with a so-called *direct process*, characterized by resonant phonon absorption and emission. The activated regime corresponds with a so-called *Orbach-process* characterized by two-phonon scattering processes to the first librational state of the torsional motion of the methyl group. The respective activation energy is 57 cm^{-1}. Together with results on DMST-d_6 in n-hexane (not shown) and some simplifying assumptions (no higher Fourier-components in the potential) we could solve the Mathieu-equation and determine the librational energies as well as the tunneling splitting. Knowing δ and the eigenenergies, the relaxation behavior as a function of temperature can be determined with no fit parameter (apart from scaling). Fig. 2a shows such a curve. The agreement with the experiment is quite satisfactory.

Fig. 2b shows DMST-h_6 in n-heptane-h_{16} and -d_{16}[6]. The development of the ΔOD spectrum (in n-heptane-d_{16}) as a function of time is shown in the insert. It nicely reflects

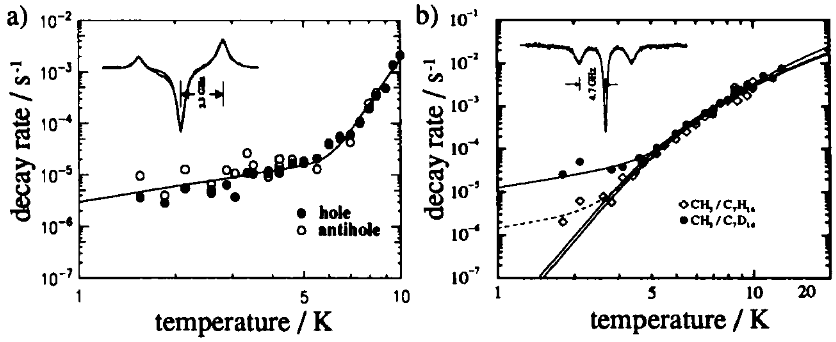

Figure 2: a) The decay rate of the central hole and the antiholes of DMST-h$_6$ in n-hexane-h$_{14}$ as a function of temperature. Insert: ΔOD-spectrum after hole burning at 3.5K.
b) The decay rate of the central hole of DMST-h$_6$ in n-heptane-h$_{16}$ and n-heptane-d$_{16}$. Insert: ΔOD-spectrum after hole burning at 4.5K and after a waiting time of 420min.

how a pair of sideholes grows in as a function of waiting time. Why we observe just one pair in this case, too, is an unresolved problem, because we know from Stark-spectroscopy that the two methyl groups are inequivalent. The relaxation dynamics differs drastically from the hexane case: Between 3 and 14K, it follows a *Raman-process*. Below about 3K, the two curves for protonated and deuterated heptane bend over to a weaker temperature dependence, most probably to a regime where *direct processes* prevail. The data also reflect quite an interesting behaviour, upon isotopic substitution, which we discuss below.

In Fig. 3a we compare the behavior of DMST-h$_6$ with DMST-d$_6$ in an n-octane-h$_{18}$ lattice[2,3,4]. There are two outstanding and surprising features: The ΔOD-spectrum of DMST-h$_6$ shows a huge hole-antihole-splitting of about 37 GHz[1]. Upon deuteration of the probe this splitting is reduced by almost a factor of 2, as it is expected for a nearly free methyl rotor. The second surprising feature concerns the isotope effect in the relaxation dynamics: Perdeuteration of the methyl groups does not slow down the tunneling dynamics but, instead, increases it by two orders of magnitude. The tunneling dynamics itself is governed by a *Raman-type process* for DMST-h$_6$ as well as DMST-d$_6$, resulting in an exact T^7 power-law for very low temperatures and a slight flattening for higher temperatures (above 4K). This flattening indicates a very low "Debye-temperature". It is about 30K, for both DMST-h$_6$ and -d$_6$. Experimentally, it is impossible to investigate the relaxation dynamics for temperatures beyond 8K, because part of the phototransformation involves local structural changes in the lattice, and the phototransformed species has a relaxation dynamics of its own (steep branch in Fig. 3a) which masks the tunneling dynamics.

Fig. 3b shows DMST-d$_6$ in n-nonane-h$_{20}$ and -d$_{20}$ /14/. The insert shows the hole burned ΔOD spectrum with two pairs of sideholes. One pair is characterized by a rather small, the other by a comparatively large $|\delta - \delta^*|$-splitting. We stated above that two different CH$_3$-groups require three pairs of sideholes. The relative spacing of these three pairs follows a strict rule: The spacing between the first sidehole and the central hole equals the spacing between the third and the second sidehole. According to this rule the missing third sidehole is so close to the second hole that it is congested in the respective broad envelope.

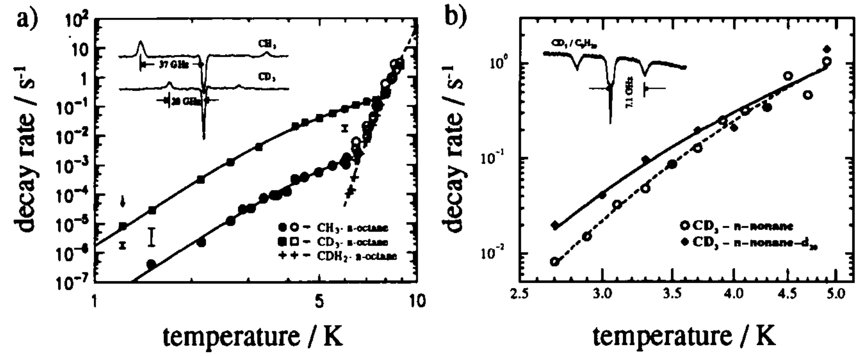

Figure 3: a) Decay rate of the central hole of DMST-h_6 and DMST-d_6 in n-octane-h_{18}. Insert: respective ΔOD-spectra after hole burning at 1.5K. The steep branch of the relaxation data has no relation to the methyl groups. It represents the hole recovery due to a structural hole burning process. Hence, the data of the symmetry broken rotor (-CDH_2) fall on this branch, too.

b) Decay rate of the central hole of DMST-d_6 in n-nonane-h_{20} and n-nonane-d_{20}. Insert: ΔOD-spectrum (n-nonane-h_{20}) after hole burning at 2.7K and after a waiting time of 385 min.

The rotational tunneling relaxation is activated in n-nonane-h_{20} as well as in n-nonane-d_{20}. The respective activation energies are 29 and 24K, respectively. This is in good agreement with the respective solutions of the Mathieu-equation.

2. Isotope effect in the rotational tunneling relaxation

Figs. 2 and 3 show interesting features upon deuterium substitution of the guest as well as of the host. Fig. 2b, for instance, deals with host deuteration[6]. In the temperature regime where the *Raman-type process* prevails (5-15K), host deuteration does not have any influence on the relaxation. This is surprising because host deuteration changes the potential and, hence, the tunneling matrix element. The reason for this specific behavior is due to the fact that the tunneling splitting cancels in a subtle way in the expression for the rate constant of the *Raman-process*, as was predicted by Würger[10]. In the regime of the *direct process* (< 4K), there is a pronounced host deuteration effect, as expected. However, the problem here is that it is the other way around as straightforward arguments would require. Deuteration reduces the tunneling splitting. Accordingly the direct process should be slowed down. Yet, the opposite occurs. This finding is not yet understood.

However, what is well understood, is the d-isotope effect of the DMST-probe in n-octane as shown in Fig. 3a[3,4]. Here, deuteration speeds up tunneling relaxation by two orders of magnitude. The reason is twofold, namely that, on the one hand, the rotor is almost free in n-octane and, on the other hand, that rotational tunneling is governed by the nuclear quadrupole interaction in the deuterated rotor instead of the magnetic dipole-dipole interaction which prevails in the protonated rotor. The coupling matrix element of the magnetic dipole-dipole interaction vanishes if the rotor gets free, hence, the respective d-isotope-effect diverges.

In Fig. 3b we only see a very small influence of host deuteration[14]. The solution of the Mathieu-equation with the parameters from DMST-h_6 and DMST-d_6 shows that the rotor is, like in n-octane, close to being free. Obviously, host deuteration does not change this situation severely in n-nonane, but it does so in n-octane. The reason for this might be seen in the larger size mismatch between host and guest in n-nonane. Host deuteration increases the density, hence, acts like external pressure. However, since the cavity is sufficiently large, the rotor is still free in the deuterated host.

SUMMARY

We presented some selected results of our investigations of the rotational tunneling dynamics of the methyl groups of the dye probe DMST in n-alkane-crystals. Methyl groups are quantum systems, hence, the basic laws of quantum mechanics (Pauli's principle, tunneling dynamics) can be tested in great detail. The results show a rich scenario of effects: We found all predicted processes in the rotational tunneling dynamics. Deuteration of guest as well as host leads to surprising results which provided deep insight into the quantum mechanics of methyl groups. Yet some mysteries concerning the spectral pattern as well as the associated dynamics are still to be solved.

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