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Symmetry species conversion in rotational tunneling systems observed by hole burning: high resolution spectroscopy of dimethyl-s-tetrazine in n-octane

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We present a summary of our results on methyl group spectroscopy and relaxation measurements of the dye molecule dimethyl-s-tetrazine and its CD_3- and CDH_2-substituted derivatives in a n-octane host. In the CH_3- and CD_3-substituted derivatives, two hole burning mechanisms occur: one is based on nuclear spin-transformation, the other is a structural transformation. The mechanism based on spin transformation leads to sharp antiholes, spaced by 37 and 20 GHz from the burning laser frequency for CH_3 and CD_3, respectively. The structural burning mechanism leads to side holes. Surprisingly, the splitting of the side holes is different from that of the antiholes. This phenomenon is interpreted in terms of two different dye species, which are distinguished through their local environment. Both species have very different yields for the structural and the nuclear spin phototransformation process. From the recovery of the central hole, the relaxation of the rotational tunneling states was measured as a function of temperature. The data support a Raman-type phonon scattering process. Deuteration does not slow down the relaxation but, instead, increases it by almost two orders of magnitude. According to our knowledge these are the first measurements of symmetry species conversion times of isotopic derivatives of methyl groups. Within the assumption of a Raman-type conversion mechanism we estimate a rather low hindering potential barrier for the rotors.

1. Introduction

Methyl groups attached to aromatic, heterocyclic or organic dye molecules did not gain much interest in optical spectroscopy in the past. They were used as substituents for lowering the symmetry of an electronic system and for breaking optical selection rules. Or they served as sources of structural disorder to inhibit crystallization and to induce transitions into the amorphous phase. However, recently it was shown that methyl groups can lead to specific optical features which are a result of fundamental quantum laws involving permutation symmetry [1]. The identity of the three hydrogen nuclei in a methyl rotor leads to a strict correlation between the symmetry of the rotor states and the symmetry of the associated nuclear spin states of the protons (or deuterons) involved. Operators causing transitions between states of different rotor symmetries necessarily have to depend on the nuclear spins. Phonons, for example, cannot induce such transitions directly and therefore remarkable long relaxation times have been obtained theoretically [3–6] and experimentally [7–13]. The situation is similar to the ortho- and para-hydrogen problem [14].

However, two important properties distinguish rotational tunneling molecular groups like CH_3 from H_2: firstly, the rotational constant B, which fixes the energy scale for quantum effects to be

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significant, is an order of magnitude smaller in CH_3 ($B_{CH_3} = 650\ \mu eV = 5.24\ cm^{-1} = 157\ GHz$) compared to H_2 and secondly, in contrast to H_2, purely intramolecular interactions can cause conversion relaxation transitions. It is especially the inelastic neutron scattering techniques which were used because the spin of the neutron can induce transitions among the nuclear spin states of the rotors. In addition, field-cycling NMR-techniques and specific heat methods were employed to elucidate the relaxation mechanisms of the rotational tunneling states. The specific relaxation features also induce optical hole burning [1,15,16,17]. This enables one to use optical techniques to study relaxation phenomena of rotational tunneling states of methyl groups.

The methylated dye probes of our study are protonated, perdeuterated and monomethyl-deuterated dimethyl-s-tetrazine. The host material is n-octane (Fig. 1(a)). The paper is aimed at presenting an overview of our studies on methyl groups in n-octane. It specifically addresses the relaxation of the rotational tunneling states, the influence of deuteration on these processes, localization by symmetry breaking and peculiar aspects of anti-holes and side holes.

2. Principle of optical pumping of ground state tunneling states in methyl groups

A big advantage of optical hole burning techniques in measuring rotational tunneling relaxation is their high sensitivity, the easy way to prepare a non-stationary state and the large dynamic range. In addition, they are easy to handle. Fig. 1(b) shows a simplified level scheme, from which the principles of optical pumping of rotational tunneling states and spectral hole burning in these systems is immediately obvious. It should be stressed that this simplified level scheme pertains to the CH_3 derivative.

Two features are essential for hole burning to occur: feature one is the strict correlation between nuclear spin states and rotor states. As phonons cannot change the symmetry of the nuclear spin state, transitions between the tunneling states are strongly hindered and excess populations in these states can be stored over long times. The second feature is based on the fact that the tunneling splitting in the electronic excited state δ^* is different from that in the ground state δ [1,18]. As a consequence, the AA* and EE* transitions can be spectroscopically distinguished. Hole burning occurs in the following way: suppose the methyl rotors of a given dimethyl-s-tetrazine molecule are in the rotational A-symmetric state. This symmetry state cannot be altered directly through a photon, but the electronic transition energy depends on the rotor state. Now the electronic excitation has a certain probability to relax into a relatively long living intermediate triplet state being associated with a large electronic magnetic moment. The induced magnetic field is inhomogeneously distributed over the range of the methyl rotors and allows for rapid symmetry changing conversion transitions from the A state to the E state. After the decay of the electronic excitation to the ground state, the rotor populates now the E species. The corresponding electronic excitation energy EE*, then, is no longer in resonance with the laser. As a consequence a hole appears at the burning frequency and two anti-holes, shifted by $\pm |\delta - \delta^*|$ pile up in the spectrum. Tunneling relaxation is measured by observing

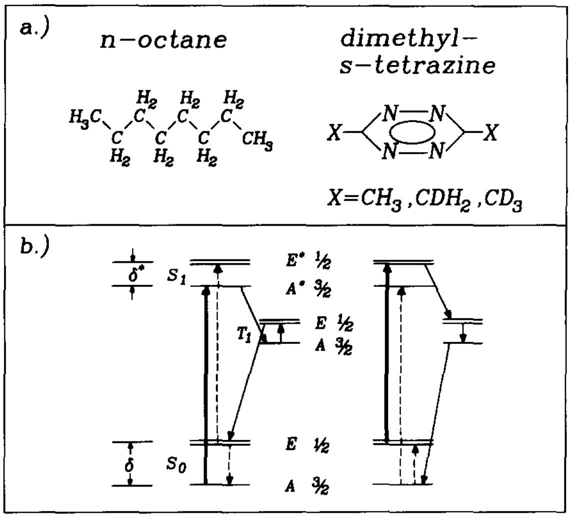

Fig. 1. (a) The host material n-octane and the guest molecules. (b) Optical pumping scheme of rotational tunneling states. δ, δ^* is the tunneling splitting in the electronic ground and excited state, respectively.

how the central hole recovers as a function of temperature or how the antiholes decay. The actual situation for dimethyl-s-tetrazine in n-octane is more complicated and is addressed below.

3. Experimental

All hole burning experiments were performed with an argon ion laser pumped dye ring laser. Typical burning powers and times were on the order of 100 nW/cm^2 and 1 min, respectively. The holes were burnt to relative depths of about 20%. At these depths they were strongly saturation broadened. Their width was of the order of 200 MHz. Holes and antiholes were detected in transmission. To this purpose, the laser beam was reduced by two orders of magnitude. The temperature was accurate within 0.02 K. We used a home-built He-bath cryostat below 4.2 K and a He-flow cryostat above 3.5 K. The hole recovery rates were determined by measuring the hole area. Above about 6 K, we took the hole depth as a measure for its area thereby increasing our time resolution to about 0.2 s. We stress that the hole showed no tendency for spectral diffusion broadening, at least not below 4.2 K where we could verify this experimentally. The concentration of the sample was about 2×10^{-4} mol/l. Its optical density was about 0.6. We used 0.2 mm glass cuvettes. No special procedure was maintained during cooling. There was no obvious indication that the cooling procedure affected the results. We measured the inhomogeneous absorption spectra (Fig. 2) with a monochromator whose resolution was set to about 1 cm^{-1}.

Dimethyl-s-tetrazine, its mono-methyldeuterated and perdeuterated derivatives were synthesized from hydrazine and acetaldehyde, acetaldehyde-2-d$_1$ and acetaldehyde-d$_4$, respectively [19]. Acetaldehyde-d$_4$ (isotopic purity 99%) was obtained from Aldrich. Acetaldehyde-2-d$_1$ was prepared by hydrolysis of vinylacetate with 20% D_3PO_4 in D_2O [20]. The isotopic purity of mono-methyl- and perdeuterated dimethyl-s-tetrazine were determined with a Bruker 500 MHz NMR spectrometer. The isotopic purity was found to be 98% for perdeuterated dimethyl-s-tetrazine and 90% for dimonodeutero-methyl-s-tetrazine with the main contamination being 3-di-deuteromethyl-6-mono-deuteromethyl-s-tetrazine. The structures of host and guest molecules are shown in Fig. 1(a).

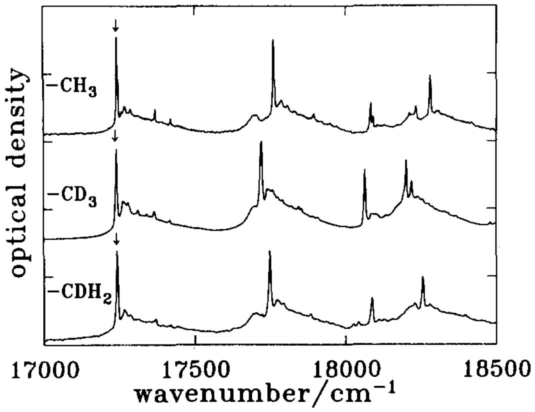

Fig. 2. Absorption spectrum of dimethyl-s-tetrazine in n-octane. Resolution: 1 cm^{-1}. Temperature: 4.2 K. Hole burning was performed at the red edge origin (arrows).

4. Results

Fig. 2 shows the three absorption spectra of dimethyl-s-tetrazine and its deuterated derivatives. The arrows indicate the frequency where the present hole burning experiments were performed. Note that the structure of the phonon wing in the neighborhood of the zero-phonon line is sensitive to deuteration indicating that some low frequency modes of the methyl groups, most probably librational modes, show up there.

In Fig. 3, we present part of the inhomogeneous profile of the zero-phonon line with the central hole at the laser frequency and two symmetrically spaced antiholes or side holes, respectively. The distance of the antihole is given by the difference in the tunneling splittings in the ground and excited state $|\delta - \delta^*|$. For the protonated dimethyl-s-tetrazine, this splitting is 37 GHz. In the perdeuterated derivative, it is 20 GHz. Note that at 4.2 K, it is difficult to measure antiholes in the perdeuterated case because the decay is faster by 2 orders of magnitude as compared to the parent compound (see below).

Fig. 4 shows the zero-phonon lines, where hole burning was performed, on an expanded scale. The CH_3 and the CD_3 derivatives are single lines, although with a somewhat asymmetric shape. For the CDH_2-derivative, the zero-phonon line has a double peak structure. The relative intensity of the two peaks depends strongly on temperature. However, for fixed temperatures, we do not observe any variations in the line shapes with time, indicating that the states involved are in thermal equilibrium.

Fig. 5 is a summary of the hole recovery rates as a function of temperature. These data show some noteworthy features: first, there are clearly two relaxation regimes which differ remarkably in their temperature dependencies. The high temperature regime is activated with an activation energy of 115 cm^{-1}. Note that all three probe molecules have this relaxation regime in common. However, the low temperature relaxation regime pertains only to the fully symmetric CH_3 and CD_3 rotors, respectively. The data of the symmetry-distorted rotor (CDH_2) does not bend over into the low temperature relaxation regime but, instead, continues to

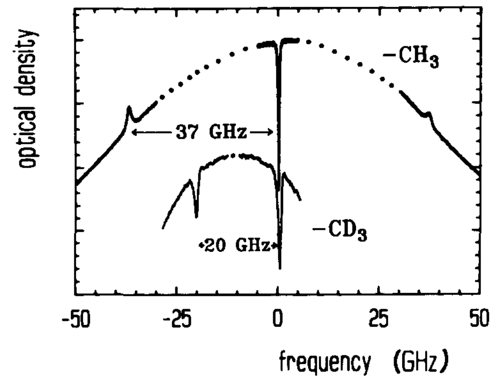

Fig. 3. Hole–antihole (side hole) splitting for dimethyl-s-tetrazine and its perdeuterated analogue in n-octane at 4.2 K.

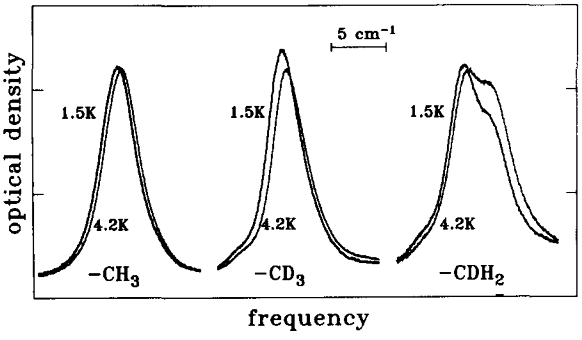

Fig. 4. The red edge zero-phonon origins of dimethyl-s-tetrazine and its deuterated derivative at 4.2 and 1.5 K.

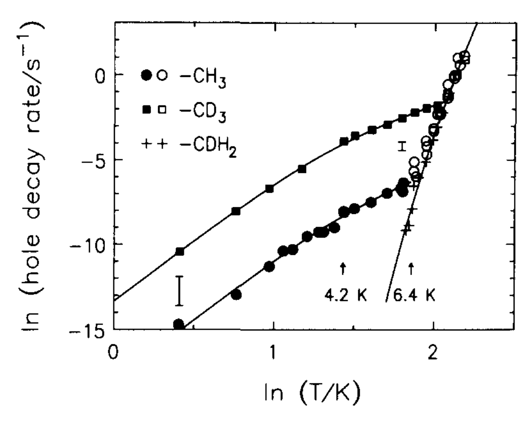

Fig. 5. Log–log plot of the hole recovery rate vs. temperature.

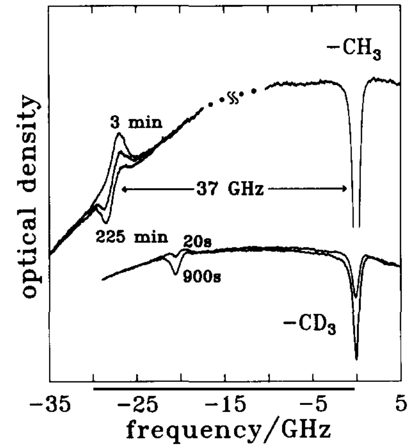

Fig. 6. Upper trace: the spectral range around the antihole in dimethyl-s-tetrazine at 4.2 K. Note that as the antihole decays, a side hole grows in, but the side hole is shifted. Lower trace: the same phenomenon as in the upper trace for the CD_3 derivative. The central hole is shown, too. The antihole is not as pronounced as in the upper trace, because at 4.2 K, relaxation in the CD_3-tunneling states is fast.

follow the activated branch. Second, an enhancement in the recovery rate of almost two orders of magnitude is found with deuteration, although the temperature dependence remains unchanged.

Fig. 6 (upper trace) shows how the antiholes decay when the central hole recovers. The surprising phenomenon is that the side hole, which grows in, is shifted significantly. The same phenomenon occurs for the CD_3-derivative (Fig. 6, lower trace). We stress that at the position of the side hole, there is no indication of an antihole and at the position of the antihole, no side hole appears.

5. Discussion

From a comparison of our results with the spectroscopic properties of dimethyl-s-tetrazine in durene [1], it is obvious that the influence of the host material is dramatic.

5.1. The host material: polycrystalline or nanostructured

N-octane is well known as a so-called Shpol'skii system. Shpol'skii systems are saturated hydrocarbons which give rise to quasiline spectra of guest molecules at low concentrations [21]. The lines have widths on the order of one wave number. Commonly several discrete origins can be found. As a rule, Shpol'skii systems are considered to be polycrystalline, sometimes they even have glass-like properties.

Recently, we investigated dimethyl-s-tetrazine in n-octane under isotropic pressure variations [22]. Surprisingly, these experiments showed that the material can be plastically deformed with no obvious low energy cut-off of the threshold energies. From these observations, we concluded that a large amount of the host material must be in the grain boundaries. We could even estimate the length scales of the ordered domains. They have dimensions of typically some tens to some hundreds of Å. These results lead us to conclude that n-octane is best characterized as a nanostructured material. This characterization may have severe implications on the properties of the acoustic phonons.

5.2. Permutation symmetry and symmetry breaking

We discussed above how population can be stored in rotational tunneling states and how this population storage leads to hole burning (Fig. 3). It follows that a tunneling transition can occur only, if the symmetry of the nuclear spin function is changed simultaneously. The change of the nuclear spin symmetry is the bottleneck in the relaxation of rotational tunneling states. The slow relaxation not only enables hole burning, but also impairs thermal equilibration. That thermal equilibration is impaired follows from the fact that the influence of temperature on the red edge zero-phonon line is small for the CH_3 and for the CD_3 substituents (Fig. 4), although, at 4.2 K, the latter compound is close to equilibrium. Another indication of non-equilibrium is that in the CH_3 derivative the relative intensity of the two antiholes does not strongly depend on temperature.

If the rotational symmetry is broken by substituting one of the three hydrogen by a deuterium atom, the restrictive relation between nuclear spin and rotor states breaks down and relaxation becomes fast. A $2\pi/3$ rotation no longer corresponds to a permutation of identical particles and, therefore, the three possible orientations are no longer strictly equivalent. In general, this leads to 3 different low lying rotational states. More important is that transitions between these low lying states can now directly be accomplished by phonons. They occur on time scales many orders of magnitude shorter than conversion relaxation transitions times. The rotor levels cannot be brought into a non-equilibrium population for times longer than microseconds. The breakdown of the symmetry is immediately evident from the fact that the zero-phonon line(s) split. We had expected to see three lines instead of two, but the third transition may still be underneath the inhomogeneous envelope. The occurrence of thermal equilibration is obvious from the strong temperature dependence of the relative intensity of the two components (Fig. 4).

5.3. *Hole burning processes of dimethyl-s-tetrazine in n-octane*

It is an important aspect for the understanding of the temperature dependence of the dynamics of methyl groups in n-octane, that hole burning does occur in the CDH_2-substituted compound, despite the breakdown of the symmetry restrictions. The straightforward conclusion is that there must be a second phototransformation process which occurs in addition to the symmetry conversion process as it is observed in the symmetric, CH_3- and CD_3-substituted probe molecules. In the asymmetric probe molecule, there is just one hole burning process. As to the nature of this additional process, we state that it is thermally reversible, because the hole refills comparatively quickly for temperatures above 6 K (Fig. 5, activated branch, crosses). Hence, it cannot be due to an irreversible photodecomposition commonly observed for dimethyl-s-tetrazine in solid matrices at low temperatures. Our interpretation is that this additional hole burning process is based on a photoinduced structural transformation. For instance, non-radiative decay from the excited states of the probe molecules disposes a large amount of energy into the lattice degrees of freedom in the immediate neighborhood, which can lead to a change of the orientation of the probe molecule in the host lattice. In glasses, processes of this kind are referred to as non-photochemical or photophysical hole burning processes.

In n-octane, the barrier which stabilizes the structurally transformed species against the ground state is well defined. Its height is 115 cm^{-1}, and the temperature dependence of the associated hole recovery mechanism is Arrhenius-like (Fig. 5, high temperature branch).

5.4. *Spin-conversion relaxation in the methyl rotors*

We mentioned above that hole burning is an excellent technique for measuring relaxation of rotational tunneling states as a function of temperature. All one has to do is to burn a hole at different temperatures and observe how this hole refills. For dimethyl-s-tetrazine in n-octane the situation is a little bit more complicated due to the additional, nuclear spin independent hole burning mechanism mentioned above.

However, since this activated relaxation branch can be safely identified via the symmetry broken rotor and, in addition, can be easily separated because of its steep temperature dependence, things become simple again. For the deuterated compound both processes are well separated below 7.4 K, for the protonated compound separation occurs below 6 K. Hence, below these temperature boundaries, we can neglect contributions to the recovery of the central hole due to the structural transformation process. We safely attribute our data to processes involving the nuclear spin.

In order for the tunneling states to relax an interaction is needed which breaks the rotational symmetry. For the CH_3 rotor, this interaction is the magnetic dipolar interaction between the nuclear spins of the protons. For the CD_3 rotor, the nuclear quadrupole interaction is shown to dominate the mixing between different symmetries [7].

Details of the coupling between the rotational tunneling states and the lattice can be inferred from the temperature dependence of the relaxation rate: There are three possible processes:

i) The direct process determined by absorption and emission of phonons being resonant with the tunneling energy. Its temperature dependence is governed through the occupation number of resonant phonons.

ii) The Orbach process which involves the excited states of the rotor of the same symmetry (librational excitations) and which can easily be induced by phonons. For temperatures below the first librational level this process leads to a librationally activated temperature dependence.

iii) The Raman process where the transition energy δ is matched through inelastic phonon scattering. Its temperature dependence goes like T^7 for temperatures sufficiently small as compared to energies where deviations occur from a quadratic density of phonon states. For a Debye model the T^7 dependence slows down and eventually bends over to a quadratic temperature law above the Debye temperature.

What kind of process do our data support?

We discard the direct process, because the temperature dependence measured is too steep. The data also do not support an Orbach process. If an Orbach process governed the relaxation, there had to be a change in activation energy upon deuteration. This is definitely not the case. The slopes of the data for the deuterated and the protonated compound are identical. Along these lines of reasoning, it follows that relaxation of the tunneling states occurs via Raman-type scattering process. An observation which supports this conclusion is the fact that both data series follow a slope close to 7 below 4 K.

For Raman-type phonon scattering processes, the temperature dependence of the relaxation rate R_R is governed by an expression of the form

$$R_R \sim \left[\frac{T}{\theta_c}\right]^7 \int_0^{\theta_c/T} \frac{e^x x^6}{(e^x-1)^2}\,dx. \tag{1}$$

If $T \ll \theta_c$, the above mentioned relaxation regime $R_R \sim T^7$ is obtained. As T approaches θ_c, the temperature dependence slows gradually down to reach a quadratic regime for $T > \theta_c$. The slowing down is clearly seen in our results. For the data of the deuterated rotor, it is very pronounced. Fig. 5 shows fit curves to the above equation. The fit is based on just one parameter, namely θ_c, apart from a scaling factor. For both data series, it is very good. The magnitude of θ_c is in both cases 30 ± 3 K. The problem remains to interpret this low θ_c value.

Formula (1), which we used to fit our data, is based on a Debye model. We assume that, up to a temperature θ_c, the phonons are well described by this model. θ_c here rather describes the high frequency cut off for the rotor–phonon coupling and therefore cannot be compared to values obtained by specific heat measurements. This means that the higher energy phonons must be decoupled from the methyl groups and hence cannot induce tunneling relaxation. Why our data support a Raman-type tunneling relaxation mechanism even at temperatures as low as a few kelvin, is a question which has to be explored. One possible reason could be a negligibly weak linear coupling of the breathing type [23]. The low temperature conversion then becomes highly inefficient, and other processes can successfully compete. Nevertheless, at elevated temperatures, the linear coupling to shaking type modes [23] should lead to an Orbach-type conversion. In the considered compound, these processes may be hidden by the structural transformation process. For the temperature dependent shifting behavior of the tunneling frequency, a pronounced negative shifting would be predicted from this argument [5].

5.6. *Specific features of the perdeuterated rotor*

We report on measurements of conversion times of a fully deuterated methyl rotor system. To our knowledge, this is for the first time that isotope effects in conversion rates have been measured. Deuteration affects both, the side hole splitting and the conversion relaxation times. Let us first address the hole–antihole (side hole) splitting, which is given by $|\delta - \delta^*|$ (see Fig. 1(b)). Since the moment of inertia of the rotational tunneling motion influences the tunneling splitting in an exponential fashion, deuteration can lead to a reduction of the tunneling splitting of more than an order of magnitude. In our case $|\delta - \delta^*|$ changes by less than a factor of two (1.85) (see Fig. 3). What conclusions can we draw from this observation? Assuming a threefold potential $\sim V_3 \cos 3\varphi$ (φ being the angle coordinate of the rotor) for all cases of electronic excitation and isotopic species and assuming that V_3 remains unchanged with deuteration but is changed to V_3^* with electronic excitation, we can show:

$$\alpha^* > \frac{B - (37\,\text{GHz})}{B - \alpha(20\,\text{GHz})}\,\alpha \tag{2}$$

(In this paper, an asterisk labels quantities in the electronically excited state.) $\alpha \equiv \delta_{(\mathrm{H})}/\delta_{(\mathrm{D})}$, is the (inverse) relative isotopic shift of the tunneling frequency, and $B = 157$ GHz, is the rotational constant of CH_3. $|\delta_{(\mathrm{H})} - \delta^*_{(\mathrm{H})}| = 37$ GHz and $|\delta_{(\mathrm{D})} - \delta^*_{(\mathrm{D})}| = 20$ GHz are the measured values for the side hole splittings. From expression (2), it follows that $\alpha^* > \alpha$ and therefore $V_3^* > V_3$. Furthermore, the change in the hindering potential for the electronically excited rotor should be enormous if the hindering potential is not too small. This suspicion is confirmed through the observed pronounced increase in conversion rates (see below).

As to the isotope effect in the rotational tunneling relaxation, the experiments show that it enhances the relaxation rate by almost two orders of magnitude (Fig. 5). For a Raman process, a change in the conversion rate τ^{-1} with deuteration of the methyl rotor is expected [7], as is shown in Fig. 7. The ratio $\tau_{(D)}^{-1}/\tau_{(H)}^{-1}$ is plotted versus $\delta_{(H)}/B$. An orientational potential $\sim V_3 \cos 3\varphi$ is assumed, where V_3 is independent of deuteration. Moreover, the Raman-type rotor–phonon coupling strength is supposed not to change with deuteration. At low temperatures ($kT \simeq \delta_{(H)}$), this ratio is only very weakly dependent on temperature. It is only for relatively weakly hindered rotors, that the conversion is expected to increase more than a factor of 10 with deuteration. According to Fig. 7, an observed factor of almost 100 can be explained by a tunneling splitting $\delta_{(H)} \simeq 122$ GHz corresponding to a barrier height $V_3 = 1.65$ meV. Here a realistic value for the ratio of the quadrupolar coupling energy for deuterons and the dipolar energy for protons $C_Q/(\gamma^2/r^3) = 1.0$ has been used. For the height of the hindering barrier V_3^* in the electronically excited molecule, a value $V_3^* \simeq 2.85$ meV can be concluded for both isotopic species. The obtained parameters for the potentials nicely fit to the observed change in the side hole splitting. The increase $V_3^* > V_3$ can be explained by the larger diameter of the dimethyl-s-tetrazine molecule when being electronically excited so that the hydrogen atoms of the methyl rotors come closer to the neighboring n-octane molecules.

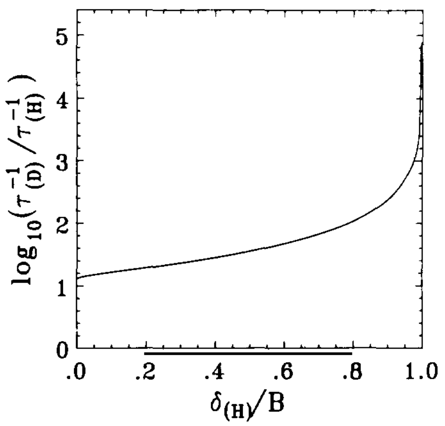

Fig. 7. Ratio of the conversion rates τ^{-1} for deuterated (D) and protonated (H) methyl species versus the tunneling frequency $\delta_{(H)}$ in units of the (protonated) rotational constant B of the protonated rotor, assuming a Raman process as conversion mechanism. This ratio is nearly temperature independent. It is assumed that the height V_3 of the orientational potential and the rotor–phonon coupling strength do not change with deuteration. For the ratio of the quadrupolar energy C_Q of a deuteron in the electric field gradient of a CD bond and the dipolar energy (γ^2/r^3) between two protons in a methyl group a value $C_Q/(\gamma^2/r^3) = 1.5$ is assumed here.

5.7. *Side holes and antiholes: are there two different tunneling species?*

We stressed above that dimethyl-s-tetrazine in n-octane shows a series of surprising features. Fig. 6 adds another one. The upper trace shows the spectral region around the low energy antihole of the CH_3 rotor. At 4.2 K, where these experiments were performed the spin-conversion relaxation time is about 1 h. Clearly, as the antihole relaxes, a side hole grows in. What is puzzling is the fact that the in-growing side hole is shifted as compared to the antihole. For the CH_3 rotor, the shift is about 1.6 GHz, for the CD_3 rotor it is about 1.1 GHz (Fig. 6, lower trace). Note that in the latter case it is more difficult to measure the antihole because relaxation is much faster. Nevertheless, the antihole can be clearly identified, and the basic situation is the same as in the CH_3 case.

Where does the side hole come from? We stressed above that the hole burning properties of the symmetry distorted rotor require an additional hole burning mechanism, in addition to the nuclear spin-conversion process, which we classified as a photoinduced structural rearrangement of probe and lattice. It was pointed out by Borczyskowski et al. [1] that any kind of photochemical or structural hole burning process can induce nuclear spin conversion relaxation leading to the appearance of side holes. This comes from the fact that the hole burning process changes the equilibrium population of the tunneling states for the frequency selected ensemble considered. Equilibrium, however, is restored again through the spin-conversion processes. Hence, the hole at the laser frequency is partially filled as a consequence of spin-conversion relaxation, and the side holes grow in. Along these lines of reasoning, it is clear that the side holes correlate with the structural hole burning process whereas the antiholes correlate with the nuclear spin transformation process. From Fig. 5 it is clear that, at 4.2 K, the structural hole recovery processes are much slower as compared to the rotational tunneling hole recovery processes. Hence, the two processes can be considered as being completely decoupled.

The conclusion from the experiment is that the difference in the tunneling splitting $|\delta - \delta^*|$ is different for the structurally transformed molecules as compared to the spin-transformed molecules. This can be understood if the two sets of molecules are in two different sets of environments. We stress that these two different sets of environment pertain to the ordered domains. If, for example, one class of molecules would preferentially sit in the grain boundaries, the sharp quasiline spectra would be on top of a broad background which is not the case. There is an additional subtlety which concerns the respective quantum yields of the two phototransformations: The experiment definitely shows that there is no onset of an antihole right at the frequency of the side hole and no indication of a side hole at the frequency of the antihole. This observation implies that both categories of probe molecules undergo either one of the two hole burning processes. The two processes do not occur in parallel. For instance, the probability that a molecule which undergoes photoinduced spin transformation, can be simultaneously transformed structurally, is zero. This is peculiar, indeed.

However, these examples just demonstrate that in systems as simple as dimethyl-s-tetrazine in n-octane, unexpected phenomena do occur and there is still an open field for further work.

6. Summary

Hole burning is a simple technique with specific advantages in the investigation of symmetry breaking relaxation processes in methyl tunneling states. Such advantages are, for instance, its easy handling, its high sensitivity and its large dynamic range.

We have applied this method to investigate symmetry species conversion processes in dimethyl-s-tetrazine and to measure, for the first time, the influence of deuterium substitution. Deuterium substitution increases the relaxation rates by almost two orders of magnitude, yet does not alter the temperature dependence. This behavior was interpreted in terms of a Raman mechanism. The increase in the rates was mainly attributed to the quadrupolar interaction. The pronounced increase of the conversion rate with deuteration, assuming a Raman-type process, allowed for an estimation of the strength of the hindering barrier $V_3 \simeq 1.65$ meV, corresponding to a tunneling frequency of $\delta_{(H)} \simeq$ 122 GHz. Based on these results, we could estimate the orientational barrier height for the methyl rotor in the electronically excited state to be of the order of $V_3^* \simeq 2.85$ meV. This value fits nicely to the observed isotopic shift of the side hole splitting.

If just one proton in the methyl group is substituted, the rotor symmetry is broken and, consequently, the correlation between rotor and spin states is broken. Yet, hole burning still occurs demonstrating that an additional mechanism has to be present. We ascribed it to a structural transformation affecting the mutual orientation of guest and host molecules. This hole burning mechanism, although it has nothing to do with the nuclear spin, induces nevertheless nuclear spin relaxation processes which are reflected in slowly growing side holes. It was a surprising observation that side holes and antiholes have different frequencies. The conclusion was that there are two distinct probe species present, which undergo either one of the two burning process. The reason for this subtle behavior is still a matter of investigation.

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