Optical Measurements of Methyl-Group Tunneling and Nuclear-Spin Conversion

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We report a novel approach to measure rotational tunneling in condensed phases. High-resolution optical spectroscopic methods are used to unravel the tunneling level structure and to measure the rate of the nuclear-spin conversion. The method is demonstrated in experiments on the rotational motion of methyl groups in a crystal of durene doped with di-methyl-s-tetrazine, but it can readily be transposed to other tunneling systems.

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In condensed phases the potential hindering of the rotation of a methyl group has intramolecular contributions. This potential reduces the rotational motion of the methyl group to librations around the equilibrium positions. Because of the identity of the three protons the potential has a threefold symmetry and there are three strictly equivalent minima separated by energy barriers. The energy levels associated with the torsional motion show small splittings which arise because of the rotational tunneling of the $-CH_3$ group between the three-energy minima. Rotational tunneling is a very sensitive probe of the potential and has, in recent years, been investigated by inelastic neutron scattering (INS), nuclear magnetic resonance (NMR), electron-spin resonance (ESR), as well as calorimetric measurements.[1,2] Nearly all these studies have been confined to molecules in the electronic ground state, and in one case only the comparison of measurements by different techniques has demonstrated a large change of the tunneling splitting between the ground and an excited electronic state of the same molecule.[3]

The wave functions of the methyl group can be described in terms of combinations of pocket states in which the system is localized in one of the three wells of the potential: These yield a totally symmetric combination having A symmetry and two degenerate wave functions of E_a and E_b symmetry. The total wave functions are products of these spatial wave functions and nuclear-spin wave functions. They must be symmetric under a rotation by 120° as this is equivalent to an even permutation of the protons. The wave functions of A and E spatial symmetry are thus associated with nuclear spins of $\frac{3}{2}$ and $\frac{1}{2}$, respectively, and represent different spin isomers. Relaxation between the two is called spin conversion and is a very slow process. The determination of the interconversion rate has come into the focus of recent experimental and theoretical work.[4-6] Experimental determinations, based on neutron transmission measurements,[4] monitor the relaxation after a temperature jump, a method well suited for systems with large tunneling splittings (weakly hindered rotors). Recently, a new NMR method has been introduced, capable of also measuring the spin conversion of strongly hindered rotors.[5]

Optical measurements of rotational tunneling, demonstrated here, are based on the same approach that has successfully been used in the study of translational tunneling.[7] These measurements rely on the fact that the potential-energy surface of the methyl group is modified when the chromophore to which it is coupled is excited to a different electronic state. As the nuclear spin is not changed in the electronic excitation process, electric dipole transitions are allowed only between levels of the same spatial symmetry. At low temperatures only the two lowest-energy states of the methyl rotor are populated and the electronic transition is split into a pair of lines, the frequency difference of which measures the difference in tunneling splitting, $\delta-\delta'$, in the ground and excited electronic states of the chromophore. In the condensed phase these splittings have never been uncovered because of the inhomogeneous broadening of electronic transitions. In the experiment discussed here, optical hole burning, as a line-narrowing technique, resolves the line splittings. In this process the population of the nuclear-spin isomers is unbalanced and the relaxation dynamics (the rate of spin conversion) can be measured. An additional advantage of the optical probing is its great sensitivity, which allows measurements in very dilute samples where the methyl rotors are effectively isolated from each other.

Photochemical hole burning is the selective photolysis (photochemical destruction or "burning") of molecules within an inhomogeneous distribution of electronic transition energies. After burning, the absorption line shows a decrease (a dip or spectral "hole") in optical density at the frequency of the burning laser. The width of this hole is limited by the homogeneous linewidth and is, in low-temperature crystals, several orders of magnitude smaller than the inhomogeneous width.[8]

At low temperatures (1.5 K) the rate of spin conversion is slow on the time scale of the optical experiment (ca. 1 min) and the spin isomers are virtually isolated from each other. Under these conditions a single spectral hole at the frequency ν_L of the burning laser is produced [Fig. 1(a), top]. This hole results from the photolysis of two classes of molecules: (a) molecules in the spin-$\frac{3}{2}$ state, whose $|0,A\rangle$-$|1,A\rangle$ transition frequency matches the laser frequency and (b) spin-$\frac{1}{2}$ isomers with the corresponding resonance condition for the $|0,E\rangle$-$|1,E\rangle$ transition (we introduce the obvious notation $|i,\alpha\rangle$ for the electronic-tunneling states, where $i=0,1$ labels the molecular electronic state and $\alpha=A,E$ the methyl-group tunneling level). Spin conversion equilibrates the population deficit produced by the selective photolysis among the tunneling levels and additional holes appear in the spectrum, symmetric about and separated from the central hole by the frequency difference of the $|0,A\rangle$-$|1,A\rangle$ and $|0,E\rangle$-$|1,E\rangle$ transitions [Fig. 1(a), bottom]. This difference equals the difference in tunneling splitting, $\delta-\delta'$, in the two electronic states $|0\rangle$ and $|1\rangle$.

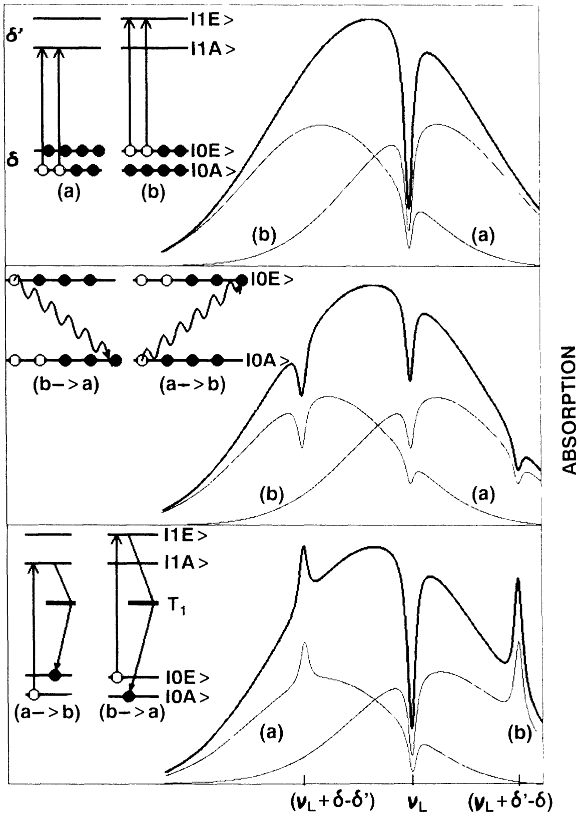

FIG. 1. Scheme of the measure of tunneling splittings in different electronic states and of the rate of spin conversion. Via permanent hole burning: Simulated spectra before (top) and after (middle) spin conversion. Via spin conversion in an excited state T_1 (bottom). For better visibility, the value of the frequency difference $\delta-\delta'$ with respect to the inhomogeneous broadening has been exaggerated in these simulations.

The rate of spin conversion at different temperatures is measured in these experiments by monitoring the temporal increase in depth of the side holes relative to the central hole.

A second way in which the same information can be obtained does not require the photolysis of the selectively excited molecules but operates if rapid spin conversion occurs in an excited state.[9] Relaxation from the excited singlet to a paramagnetic triplet state is common for most organic molecules. In the metastable triplet state, hyperfine coupling of nuclear and electronic spin accelerates the spin-conversion process, so that it can occur during the lifetime of this state. The optical pumping and relaxation cycle therefore leads to a spin interconversion of the selectively excited molecules. This produces a population deficit and a hole for molecules resonant with the burning laser, while a population surplus, leading to "antiholes" (i.e., an increase of optical density) is observed at the frequency intervals $\delta'-\delta$ and $\delta-\delta'$ (Fig. 1, bottom). Such photoinduced population redistribution has been called "population hole burning."[9] Spin conversion in the ground state leads to a disappearance of this pattern so that again its rate can be measured. In addition, the growth of the antiholes can be measured at different temperatures and contains information about the spin conversion in the triplet state.

Most of the methyl rotors studied so far by INS and NMR are associated with molecules which absorb light in the blue of the spectrum (near UV or UV). While narrow-band lasers do become more readily available in these spectral regions we have preferred for our study the molecule of di-methyl-s-tetrazine (DMST, see Fig. 2). The optical spectra of this relatively simple molecule are well characterized.[10] It has a moderately strong ab-

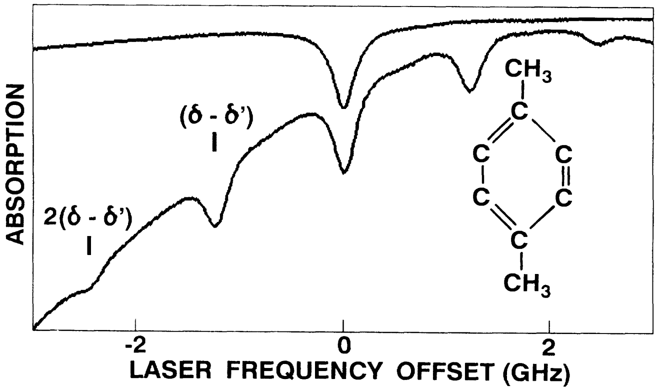

FIG. 2. Photochemical hole-burning spectrum of the $S_0 \rightarrow S_1$ transition of di-methyl-s-tetrazine in a durene host crystal. After burning at 1.4 K only the central hole at the laser frequency is visible (top spectrum). Pattern of side holes observed (at 1.4 K) after heating the sample to about 100 K for ca. 10 sec leading to thermal equilibration of the spin isomers (bottom spectrum).

sorption at around 588 nm (the peak of the R6G dye-laser region) involving a $n\pi^*$ excited state. DMST forms substitutional mixed crystals with durene (1,2,4, 5-tetra-methyl-benzene, TMB) and hole burning has been demonstrated for this system.[10] In condensed phases the photolysis of DMST is thought to be a stepwise two-photon process and is obtained under high laser intensity only.[11]

In the mixed crystal (typical DMST concentrations are 10^{-3} mol/mol), all methyl groups occur as equivalent pairs related by the molecular inversion center of DMST and the site symmetry of the crystal.[12] The description of the spectral changes due to hole burning given above for a single methyl group is readily extended to two equivalent methyl groups coupled to the chromophore. Side holes appear at frequencies of $\pm(\delta'-\delta)$ and $\pm 2(\delta'-\delta)$ from the central hole if the coupling of the two methyl rotors is negligible as is the case here.

In the region of the pure electronic transition of DMST in durene several lines are observed which have tentatively been assigned to different ^{13}C and ^{15}N isotopic species of DMST:[10] Our precise measure of their relative intensities confirm this assignment. The measurements of the tunneling splittings showed no isotope dependence and have mostly been done on the line at 5874.5 Å, the transition of the ^{15}N isotopic species. Figure 2 shows the observed pattern of holes after photolyzing with high laser intensity at the frequency marked 0 for a sample at 1.5 K. Initially, only the central hole at the frequency of the laser is observed, the weaker holes at higher and lower frequencies appear after a temperature cycle in which the sample is heated to ca. 100 K for 10 sec. This time is sufficient for full thermal equilibration of the spin isomers and the intensity ratio of the holes equals the ratio of 1:4:6:4:1 predicted for full thermal equilibration. The difference of tunneling splitting in the two electronic states is obtained as $|\delta-\delta'| = 1.24\pm0.04$ GHz. The width of the holes is due to power broadening: With low laser power holes as narrow as 50 MHz were observed, a value entirely determined by the excited-state lifetime of DMST.[10]

Figure 3 shows the holes and antiholes (measured at 1.5 K) which are observed due to spin conversion in the triplet state after irradiating the sample at 4.2 K with low laser power (minimizing photochemical destruction). The width of ca. 500 MHz of the features is due to the fact that at the burning temperature of 4.2 K dephasing makes a dominant contribution to the homogeneous optical linewidth and limits the effective resolution. Only the stronger antiholes at $\pm(\delta-\delta')$ are visible at the same frequency differences as observed in the experiment described above. The antiholes disappear with a time constant of about 30 min. With irradiation at 1.5 K no antiholes are observed, indicating that the spin conversion in the triplet state is slow compared to the average decay rate of this state (1.2×10^4 sec^{-1}).[13]

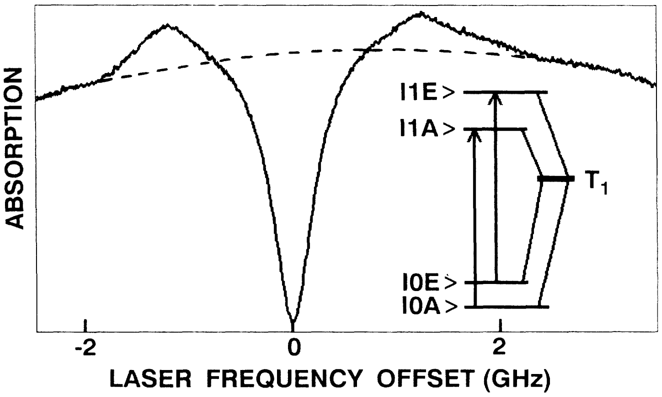

FIG. 3. Population hole burning observed (at 1.4 K) after irradiation at 4.2 K with low laser power, and resulting from spin conversion in an excited state. The dashed line indicates the line profile prior to laser irradiation and the marks at the top indicate the positions of the three strongest holes observed in the spectra of Fig. 2. The integrated absorption decrease at the burning laser frequency is larger than the total increase of absorption because even with the relative low laser power photochemical hole burning contributes to the central hole.

The rate of spin conversion in both the metastable triplet state and the ground electronic state varies strongly with temperature: At 1.5 K the conversion time in the ground electronic state is longer than 600 h; it decreases at 4.2 K to about 30 min and is in the range of seconds at 100 K. The great sensitivity of the optical measurements makes it possible to monitor spin-conversion processes with high precision on time scales ranging from seconds to hours or longer.

For the mixed-crystal system studied here no previous INS or NMR measurements are available and the absolute value of the tunneling splitting in the ground electronic state is not known. Also the methyl groups that are coupled to the DMST chromophore remain to be identified. Preliminary experiments with the same chromophore in different host crystals (including fully deuterated durene) suggest that it is possibly a pair of the durene methyl groups that is monitored in our experiments. In principle, both the absolute value of the tunneling splitting and the sign of the change upon electronic excitation can also be measured in hole-burning experiments. If the material has come to thermal equilibrium at very low temperatures, the side holes produced after burning and equilibration at high temperatures will show an intensity imbalance which reflects the Boltzmann distribution before burning. The intensity ratio is greater or smaller than unity depending upon the sign of the change in tunneling splitting. The low temperatures required and the very slow rate of spin conversion make this method not very practical for tunneling splittings smaller than the corresponding thermal energy.

This first successful demonstration of direct optical measurements opens the way for a host of new experiments to study rotational tunneling in condensed phases. The method is ideally complementary to existing INS and NMR techniques in being able to study very dilute samples and excited molecular species. A confrontation of these complementary techniques should be very fruitful and is possible for isotopically (proto-deutero) mixed crystals, for example, where the concentration can be continuously varied.

As long as the environment is not altered in the electronic excitation process, intramolecular and intermolecular contributions to the potential can be identified. Direct hole burning of singlet-triplet transitions should also be possible in the system studied here (as well as others): The pattern of side holes reflects in this case both the electronic spin and the tunneling splittings in the excited triplet state. The use of magnetic fields and combined microwave optical double-resonance experiments will provide further insight in the tunneling level structure as well as in the relaxation mechanisms.

The resolution of the optical techniques with current commercial lasers is in the range of about 1 MHz, but systems with smaller ground- (excited-) state splittings can be investigated provided that the change of tunneling splitting upon excitation is sufficiently large. For small splittings, level crossings in magnetic fields should become observable leading to a measure of the magnitude of the splittings. Finally, it should be emphasized that the application of the technique presented here is very general, due to the possibility of population hole burning, and can be used, in particular, for systems already studied by INS and NMR when narrow band near-UV and UV lasers are employed.

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