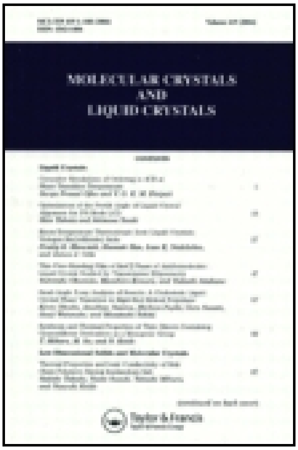

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ROTATIONAL AND TRANSLATIONAL PROTON TUNNELING AND RELAXATION IN CONDENSED MOLECULAR SYSTEMS

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Abstract Quantum motions of protons in organic crystalline solids are monitored via the optical transitions of suitable dye molecules coupled to the potential governing the proton motion. Tunneling splittings are determined using line-narrowing techniques and the relaxation dynamics is measured on timescales extending from picoseconds to hours. The relevance of these properties for material uses is discussed.

INTRODUCTION

Numerous applications (all-optical data handling and processing, image processing, optical data storage, etc.) require materials which change their properties under irradiation. While the electronic response, when off-resonant, can be quasi-instantaneous, other changes of the material, involving for example atomic displacements, occur on longer timescales and can become near-permanent when metastable states are reached. Hydrogen, being the lightest atom, plays a special role in this regard, as it does also in leading, because of its small radius, to the formation of hydrogen bonds.[1] Hydrogen or proton displacements can occur on a sub-picosecond timescale when, subsequent to an electronic excitation process, the new position of the potential minimum is reached in a barrierless process, so that the relaxation of the environment limits the speed of the material response. When, on the other hand, large barriers separate different tautomeric configurations, the establishment of new equilibria can be an extremely slow process, especially at low temperatures.[2] In this case tunneling of the proton across the barrier becomes the dominant relaxation process; it ultimately limits the lifetime of metastable proton states and makes materials "age" even at 0 K. Because the proton potential is dependent on the electronic state, situations can be envisioned where rapid switching may be achieved in an excited electronic state, while the new proton configuration, even though it is metastable in the ground electronic state, is longlived. Hydrogen transfer systems are therefore thought to hold promise for applications such as optical data storage.[3] The characterization of the tunneling effect in such systems is an important issue in this regard, as it is in nearly all biological systems and in numerous chemical reactions. We have developed a novel approach to the study of tunneling in condensed phases. This new method uses the optical transitions of a chromophore as a probe of proton structures and motions of the environment.[4-8]

TUNNELING

The so-called tunneling effect is a purely quantum mechanical effect: the delocalization of the wavefunction allows a particle to escape from a potential well, in which it would remain forever in a classical description. It was first invoked to explain the (irreversible) escape of a particle from a potential well (α-decay)[9] and to rationalize the inversion doubling of the ground state of ammonia:[10] A particle, initially localized on one side of a symmetric double well potential (reversible) oscillates between the two wells. The oscillation period, ν, or the splitting, $J = h\nu$, is a measure of the transparency of the energy barrier separating the two wells. For one dimensional potentials an approximate calculation of J yields:[11]

$$J = (E_o/\pi)\exp[-(\sigma d/h)\sqrt{(2mV_o)}] \qquad (1)$$

E_o is the zero point energy of the particle (mass m) in one of the wells, V_o and d are the height (w.r. to E_o) and width of the barrier, and σ a parameter close to 1 describing its shape ($\sigma = \pi/4$ for a parabola). While E_o measures the curvature of the potential near its minimum, J is a measure of the classically forbidden region of the potential. The tunneling matrix element, J, also determines the rate of escape, k, from a metastable well as k is proportional to J^2.

While tunneling is common for electrons, it is more rarely observed for heavier particles in condensed phases. Due to the strong mass dependence, the value of J becomes very small and perturbations by the environment dominate. Even at low temperatures when thermal fluctuations are eliminated, only few examples of an experimental determination of J exist. An exception are rotational motions, which lead to a permutation of identical particles.[12] The environment cannot distinguish these configurations while it distinguishes translational positions of a particle. As a consequence, rotational and translational tunneling represent two extremes in terms of the timescales of the relaxation processes that are involved, and examples of both will be given below.

METHYL GROUP TUNNELING

In condensed phases, the potential hindering the free rotation of a methyl group has intra- and inter-molecular contributions. Because a rotation by 120° around an axis perpendicular to the plane formed by the three H atoms leads to the same result as an even permutation, the potential is strictly threefold symmetric and the wavefunction of the methyl rotor must be unchanged under a rotation by 120°. The spatial wavefunctions are conveniently described by symmetric (A) and antisymmetric (E) combinations of so-called pocket states in which the system is localized in one of the three potential minima. The total wavefunction is - to a very good degree of approximation - a product of spatial and spin wavefunctions. Tunneling lifts the energy degeneracy of states of A and E spatial symmetry, which are associated with spin 3/2 and 1/2 respectively since the total wavefunction must remain unchanged. Transitions between the two levels require a change of nuclear spin and are most easily induced by neutron scattering.[12] Relaxation between them is an extremely slow process and is induced by small spin dependent terms of the Hamiltonian.[13] Optical transitions between different rotational tunneling levels are unobservable.

The magnitude of the tunneling splitting depends on the electronic state so that the excitation of a chromophore can alter this splitting for an attached or nearby methyl group. Such changes of tunneling splitting have been identified in one case by a combination of different experimental techniques[14] and more recently in isolated molecules by high resolution spectroscopy.[15] For a free methyl rotor the splitting of the lowest energy levels is 5.4 cm^{-1} so that this value represents the largest change that can be observed if the rotor is strongly hindered in one and nearly free in the other electronic state. Even at cryogenic temperatures the two lowest tunneling levels are thermally populated and so that all optical transitions between different electronic states involving a material containing methyl groups should be split. In general this splitting will be hidden by inhomogeneous broadening and no such observation has been reported as yet. We have recently reported the first direct measure in the condensed phase using holeburning as a linenarrowing technique.[8] This measurement requires that population relaxation occurs between the tunneling levels so that the population changes, induced by the laser for a frequency selected class of molecules in a given tunneling level, are transferred to other tunneling levels. Population relaxation, which requires the change of nuclear spin, is accelerated by interactions with paramagnetic centers. Relaxation of the optically excited chromophore to a triplet state provides, in an optical pumping cycle, one mechanism of population transfer from the tunneling levels involved in the selective excitation process to the ones that are not resonant with the laser. This population change leads to a spectral hole at the laser frequency and to antiholes at frequency intervals corresponding to the difference of tunneling splitting in the two electronic states (see Fig. 1a). This pattern disappears with the rate of relaxation between

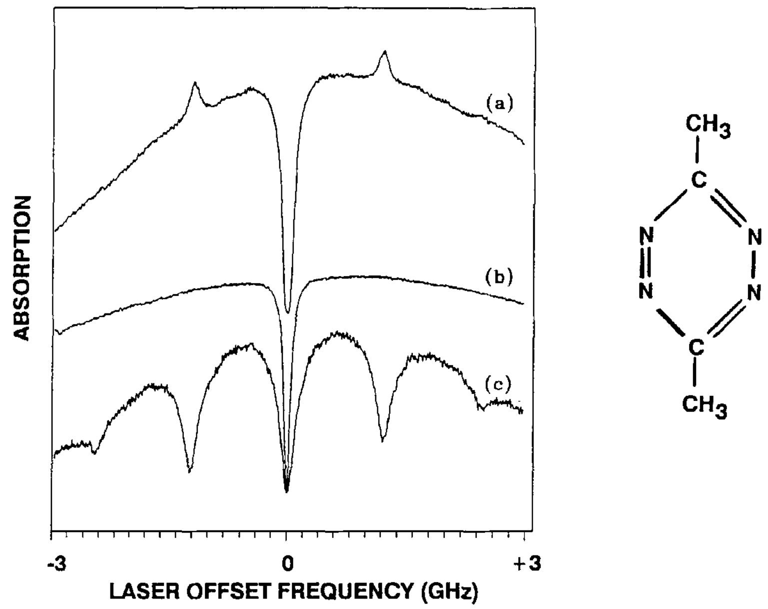

Figure 1 Measure of the difference of rotational tunneling in two electronic states in di-methyl-s-tetrazine (right) in durene (see text).

tunneling levels in the ground electronic state.At low temperatures this rate is very small, but increases rapidly with temperature. The rate depends strongly on the value of the tunneling splitting[13] and increases from $2 \cdot 10^{-5}$ sec^{-1} at 2.7 K to $5 \cdot 10^{-2}$ sec^{-1} at 12 K in the system shown in Fig. 1. Most organic glasses and polymers contain methyl groups and the corresponding tunneling splittings cover a wide range of values in these disordered media. Antiholes would therefore be smeared out over a frequency range of about 5 cm^{-1}, and the holes would show a range of temperature dependent recovery times. Clearly rotational tunneling provides one mechanism which explains the so-called photophysical holeburning in glasses.[3,16]

When the optical center is destroyed by the laser excitation, as is the case, under high laser power, for the system shown in Fig. 1, than the population deficit at the laser frequency is not compensated by a population surplus (Fig. 1b) and the relaxation distributes this deficit among the tunneling levels and leads to the formation of sideholes at the same frequency intervals as were observed the antiholes (see Fig. 1c).

TRANSLATIONAL PROTON TUNNELING

In contrast to the situation described in the preceding section all successive positions occupied by a proton in a translational motion are distinguishable. In a double well potential such as arising, for example, for a proton engaged in a hydrogen bond between two heavy atoms, the lowest levels can again be described as a combination of localized states. There arise no restrictions concerning the nuclear spin and transitions between tunneling levels are (IR or Raman) allowed. Even though for an isolated molecular system the potential may be symmetric it will become asymmetric in the condensed phase, and this asymmetry fluctuates as a function of motions of the environment. The frictional forces resulting from these fluctuations damp the free oscillation of the proton and tend to localize it in one or the other potential well. In a solid, the proton becomes localized since the static asymmetry, A, of the potential usually exceeds the tendency to delocalize (i.e. A>>J). The level splitting is $(A^2 + J^2)^{1/2}$, and the intensity of transitions between them decreases as $(J/A)^2$. It is only when the forces exerted by the environment accidentally cancel, that the tunneling splitting may become observable, and this explains the paucity of experimental measurements. The system shown in Fig. 2 is the only one for which both the value of J and the rate of relaxation at low temperatures have been determined. This was achieved by using the same optical techniques as described above. The approximate compensation of the environmental forces which distort the intrinsically symmetric dimer, was made possible by using a suitable dye, but this compensation is a function of the electronic state so that the protons are significantly delocalized only in one of the electronic states of the dye. As before, line narrowing techniques were required to resolve the small line splittings resulting from the proton tunneling.[5,7] Fig 2 shows the result of a holeburning measurement. In this case the appearance of the sideholes could not be time resolved as the relaxation rate is fast ($\approx 10^{-9}$ sec^{-1}) on the timescale of the experiment (≈min). These rates were however measured by a variety of techniques and as a function of the proton delocalisation and temperature [4,6] and were quantitatively analyzed within a simple model using only parameters which could be determined in independent measurements.[17] The proton relaxation rates determined in these optical experiments could also successfully explain the low temperature behavior of NMR and inelastic neutron scattering (INS) measurements made in the same carboxylic acid. Upon deuteration these rates decrease by about three orders of magnitude[4] which corresponds to a reduction of the tunneling matrix element by a factor of about 30. Recent NMR experiments are in excellent agreement with the optically determined rates.[18] The fact that the low temperature relaxation rates are of the same order of magnitude in a variety of carboxylic acids in which the geometry of the dimer ring is similar[18] indicates that these results are, beyond the specific example of benzoic acid, of general validity. There exist no other measurements of the tunneling matrix elements in intermolecular hydrogen bonds of organics, but for isolated formic acid dimers a cal

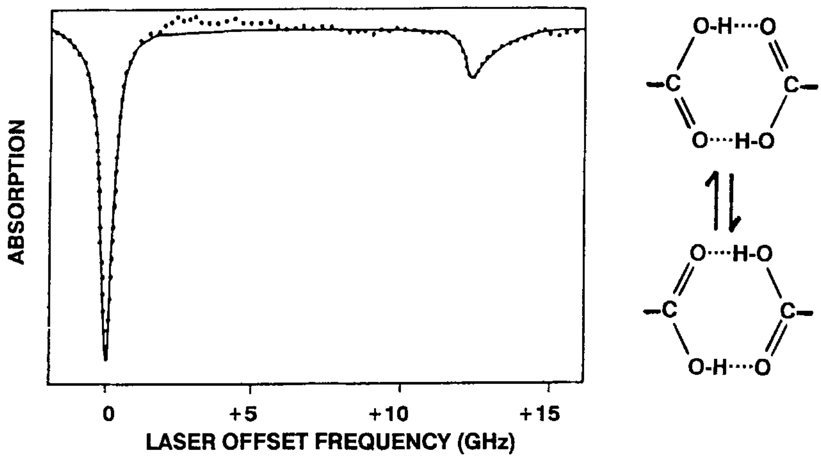

Figure 2 Resolution of the tunneling splitting corresponding to the tautomerization (right) in benzoic acid dimers (see text).

culation has been performed in which the potential energy surface was evaluated by ab initio calculations and the energy levels were determined in a potential surface reduced to three degrees of freedom thought to be essential in the description of the proton motion.[19] The calculated value in formic acid dimers is smaller by a factor of about 70 than the experimental value in benzoic acid crystals: The question of whether this difference is due to the difference in materials (solid state vs. free dimer) or results from an inadequate theoretical description of the relevant potential energy surface is, at present, unresolved.

An other interesting issue concerns the coupling of proton motions in different dimers. While the motions of the two protons within one dimer are very strongly correlated, the correlation between different dimers in the solid is not quantitatively known. In the optical experiments two equivalent dimers, which sandwich the chromophore, are monitored and the coupling of the two, across the dye, amounts to several cm^{-1}. The direct coupling is conceivably larger and could explain the increase of the asymmetry, A, in going from high to low temperatures as being linked to the increase of proton order. Sufficient coupling of the proton potentials is required if the proton motion in the material is to become collective. The determination and control of this parameter is obviously of importance in applications where it is desirable to stabilize the two states of the system by a collective response, as is the case on a macroscopic level in ferroelectrics, for example.

CONCLUSION

Optical methods are a powerful tool to monitor in low temperature solids the quantum behavior of a light atom such as hydrogen. We have shown here that relaxation processes extending from 10^{-5} to 10^{12} $\sec^{-1}$ can be measured. The use of single crystals allows to identify processes and to measure parameters which are distributed in disordered solids and are therefore less accessible. The determination of the tunneling matrix element in particular is important as it probes the classically inaccessible regions of the potential.

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