Quantum effects in the dynamics of proton glasses

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The dynamics of proton and deuteron glasses has been studied via the NMR spin-lattice relaxation (T_1) of ^{87}Rb and O–D···O deuterons down to $T=1.6$ K in $Rb_{0.50}(NH_4)_{0.50}H_2PO_4$,$Rb_{0.58}(ND_4)_{0.42}D_2PO_4$, and $Rb_{0.68}(ND_4)_{0.32}D_2AsO_4$. In the glassy phase the relaxation rate was found to be anomalously short and temperature independent as $T\rightarrow 0$, whereas this effect is absent in pure ferroelectric RbH_2PO_4. The temperature independence of T_1 at low temperatures demonstrates the presence of phonon-assisted tunneling of the proton and the deuteron between the two potential minima in the H bond. The proton and deuteron glass phases are thus quantum rather than classical glasses. [S0163-1829(96)50634-X]

The microscopic nature and the low-temperature dynamics of the proton-glass phase in solid solutions of hydrogen-bonded ferroelectric and antiferroelectric crystals such as $Rb_{1-x}(NH_4)_xH_2PO_4$ (RADP-x) (Refs. 1–9) are one of the large open problems in the physics of orientational glasses. The O–H···O bonds in these systems are of the double minimum type and represent elementary two-position reversible electric dipoles.[1,2] It is usually assumed that the motion of the protons in the double well O–H···O potentials is randomly frozen out at low temperatures, implying a static quenched disorder characteristic of classical orientational glasses.[3,7]

Specific-heat measurements[4] indicate that the assumption of a static frozen glass disorder at low temperatures may be too restrictive and that the intra-H bond hydrogen motion still may persist in the form of quantum tunneling. The existence of a slow non-Arrhenius intrabond motion in the range 45–24 K has been reported also in a recent 2D NMR exchange study of acid deuterons in $Rb_{0.68}(ND_4)_{0.32}D_2AsO_4$ (Ref. 8). The apparent activation energy $E_a=12.8$ meV was found to be much smaller than $E_a=70$ meV, deduced from the deuteron spin-lattice relaxation data in the 290–90 K range.[9]

On the other hand, the question of the existence of proton tunneling in pure compounds of the KH_2PO_4 (KDP) family has been studied extensively in the past.[10–12] These systems show a large isotope effect in the ferroelectric transition temperature T_c on deuteration. No definite microscopic evidence for proton tunneling has been obtained so far. This is so as tunneling can be studied in a clear way only at low temperatures, whereas the para-to-ferroelectric transition in KDP crystals—where the long range order sets in at relatively high temperatures—prevents this observation. The conditions for the detection of tunneling are more favorable in proton glasses where the system remains macroscopically in the paraphase structure down to the lowest temperatures.

In this paper we report clear evidence for the existence of incoherent O–H···O hydrogen tunneling in proton and deuteron glasses at low temperatures. From the measurements of ^{87}Rb NMR spin-lattice relaxation in $Rb_{0.50}(NH_4)_{0.50}H_2PO_4$ (RADP-50), $Rb_{0.58}(ND_4)_{0.42}D_2PO_4$ (DRADP-42), and the O–D···O deuteron relaxation in $Rb_{0.68}(ND_4)_{0.32}D_2AsO_4$ (DRADA-32), we determined the intra-H-bond dynamics in a large-temperature interval from room temperature down to 1.6 K. The results are compared to those obtained in pure ferroelectric RbH_2PO_4 (RDP). We show that at high temperatures the dynamics is of the classical thermally activated hopping type. At low temperatures the intra-H bond motion in the glass phase persists in the form of phonon-assisted tunneling down to the lowest measured temperatures. This demonstrates that RADP and DRADP mixtures are not classical proton glasses[2]—where tunneling is absent—but represent a physical realization of a quantum pseudospin glass.[13,14]

The key physical quantity in the determination of the proton-glass dynamics is the autocorrelation time τ_c for the proton intrabond motion. The temperature dependence of τ_c should allow the discrimination between different microscopic proton transfer mechanisms. The uncorrelated thermally activated hopping over the barrier in an asymmetric double minimum potential obeys the Arrhenius form of the autocorrelation time[8]

$$\tau_{\mathrm{Ar}}=\tau_\infty\frac{\exp\{E_a/k_BT\}}{2\cosh(A/2k_BT)}, \tag{1}$$

and shows an exponential dependence on temperature. The activation energy E_a is a measure of the potential step size and A is the asymmetry of the double well O–H···O potential.

At low temperatures the thermally activated hopping becomes inefficient and the Arrhenius jump times become practically infinite. Here another transfer mechanism becomes dominant. This is the quantum tunneling through the barrier, which persists down to zero temperature. At nonzero temperatures the lattice thermal motion assists tunneling. The shear strain phonons couple to the electric dipole moment of the H bond and induce transitions between the protonic eigenstates. Within the Slater-Takagi model,[10] the proton transfer in the O–H···O bond results in the creation of

$H_3PO_4^+$ and HPO_4^- defects, which propagate through the system in a nearly symmetric double minimum H-bond potential. For bond asymmetries small compared to the potential step and in the long phonon wavelength limit, we get the phonon-induced tunneling rate as[15]

$$\frac{1}{\tau_t}=\frac{1}{\tau_{t0}}\sqrt{1+(A/\Gamma)^2}\coth\left(\frac{\sqrt{A^2+\Gamma^2}}{2k_BT}\right), \tag{2}$$

where Γ represents the tunneling matrix element of the ground state doublet and $\tau_{t0}^{-1}\propto\Gamma^3$. It is assumed that the splitting of the two lowest protonic eigenstates $\hbar\omega_{21}=\sqrt{A^2+\Gamma^2}$ lies within the acoustic phonon bandwidth. The thermally induced incoherent tunneling rate $\tau_t^{-1}$is a sum of a one-phonon absorption and a one-phonon emission rates. It stays finite at zero temperature because of the nonvanishing of the emission rate. The temperature dependence of the tunneling time τ_t is much weaker than that of the hopping time τ_{Ar}. At very low temperatures it becomes independent of temperature.

It is evident that the thermally activated hopping mechanism becomes negligible as compared to the tunneling mechanism at low temperatures, whereas the opposite is true at high temperatures. Because of the exponential change of τ_{Ar}, the crossover regime is narrow and we can use a simple interpolation formula for the proton intrabond correlation time τ_c in the whole temperature range

$$\frac{1}{\tau_c}=\frac{1}{\tau_{\mathrm{Ar}}}+\frac{1}{\tau_t}. \tag{3}$$

In order to test the above dynamic model, we analyze the ^{87}Rb and O–D$\cdots$O deuteron NMR spin-lattice relaxation rates in RADP mixtures. The quadrupole-perturbed NMR spin-lattice relaxation rates W_1 and W_2 of a spin $I=3/2$ nucleus such as ^{87}Rb are obtained from the recovery curve of the nuclear spin magnetization following a radio-frequency pulse. The magnetization recovery of the central transition $(1/2\leftrightarrow-1/2)$ follows the equation $M(t)=M_\infty\{1-2[\exp(-2W_1t)+\exp(-2W_2t)]\}$ (Ref. 16). The rates W_1 and W_2 are the $\Delta m=\pm1$ and $\Delta m=\pm2$ spin transition probabilities and depend on the spectral densities[17]

$$J_n(\omega)\propto(1-p^2)\tau_c/[1+(n\omega\tau_c)^2], \tag{4}$$

(with $n=1,2$) of the time-fluctuating electric field gradient (EFG) tensor elements. It has been shown[9] that the EFG time dependence at the ^{87}Rb sites comes predominantly from the intra-H bond motion of protons, so that we can use Eq. (3) for τ_c. The term $1-p^2$ is the biasing or ''depopulation'' factor and

$$p=(A/\sqrt{A^2+\Gamma^2})\tanh(\sqrt{A^2+\Gamma^2}/2k_BT), \tag{5}$$

is the O–H$\cdots$O bond polarization.[14] The spectral density stays finite at zero temperature because of quantum effects $(\Gamma\neq0)$, which result both in a nonvanishing of the depopulation factor

$$(1-p^2)_{T=0}=\Gamma^2/(A^2+\Gamma^2), \tag{6}$$

and in the finite value of τ_t. This allows for a finite spin-lattice relaxation rate $(W_n\neq0)$ at $T=0$, in contrast to the classical $(\Gamma=0)$ case at $T=0$, where $p=1$ and $1-p^2$ vanishes so that $W_n=0$ in this limit.

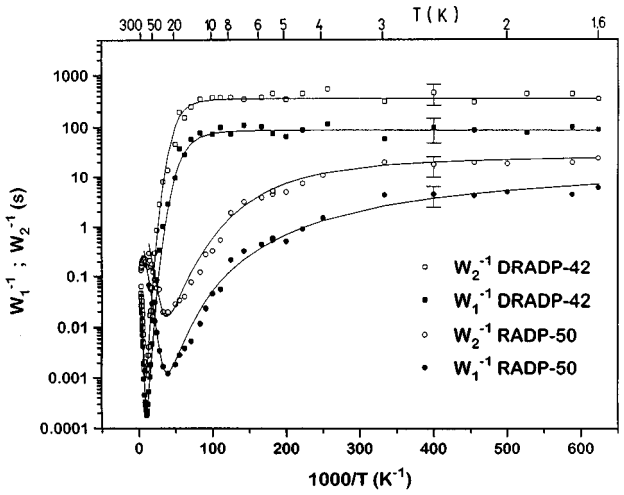

FIG. 1. ^{87}Rb NMR spin-lattice relaxation rates W_1 and W_2 in the temperature interval 290 K$\geqslant T\geqslant$1.6 K in RADP-50 and DRADP-42 [ν_0 (^{87}Rb)=124.3 MHz, crystal orientation $a\perp H_0, c\| H_0$]. Solid lines represent the fits to Eq. (7).

The intrabond correlation time τ_c depends on the bond asymmetry A. In the glass phase the asymmetries are distributed randomly over the H-bond network in a way that the average bond asymmetry is zero. The asymmetry distribution function $\rho(A)$ is Gaussian[2] with a variance σ_A. The NMR relaxation rates in the proton-glass phase are obtained by integrating the spectral densities over the distribution function $\rho(A)$

$$W_n=K_n\int_{-\infty}^{\infty}dA\rho(A)(1-p^2)\frac{\tau_c}{1+(n\omega_0\tau_c)^2};\quad n=1,2. \tag{7}$$

Here ω_0 is the nuclear Larmor frequency and K_n is a constant. The above discussion and Eqs. (4)–(7) apply also to the case of deuteron spin-lattice relaxation, where, however, the spin-lattice relaxation rate is given by $T_1^{-1}=W_1+2W_2$.

The ^{87}Rb spin-lattice relaxation rates W_1 and W_2 have been determined in RADP-50 and DRADP-42 from room temperature down to 1.6 K. The experimental conditions were nominally the same for both substances [ν_0(^{87}Rb) $=124.3$ MHz, $a\perp H_0, c\| H_0$], the basic difference being the different O–H$\cdots$O and O–D$\cdots$O intrabond correlation times seen by a given ^{87}Rb nucleus. Pulsed NMR inversion recovery and, at very low temperatures, saturation-recovery techniques have been used in a 9 T magnet. Temperature stability was within 0.1 K in the whole temperature range.

The inverse ^{87}Rb relaxation rates W_1^{-1} and W_2^{-1} of DRADP-42 (Fig. 1) are dropping continuously from room temperature down to 90 K, where a minimum is observed. Below 90 K they start to increase. The appearance of a minimum (occurring at $\omega_0\tau_c=1$) is a typical sign of the slowing-down of the O–D$\cdots$O intrabond dynamics. In the interval 290 K$\geqslant T\geqslant$55 K, the thermally activated hopping mechanism dominates and reproduces correctly the experimental data. The activation energy $E_a=70.4$ meV and the inverse attempt frequency $\tau_\infty=6\times10^{-13}$ s have been determined

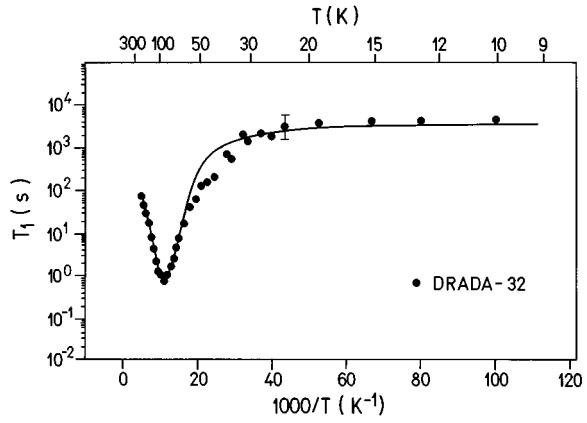

FIG. 2. Acid deuteron NMR spin-lattice relaxation time T_1 in DRADA-32 as a function of temperature [$\nu_0(^2\mathrm{H})=58.3$ MHz, crystal orientation $a\perp H_0, \angle c, H_0=45°$]. The solid line represents the fit with $T_1^{-1}=W_1+2W_2$, where W_n is given by Eq. (7).

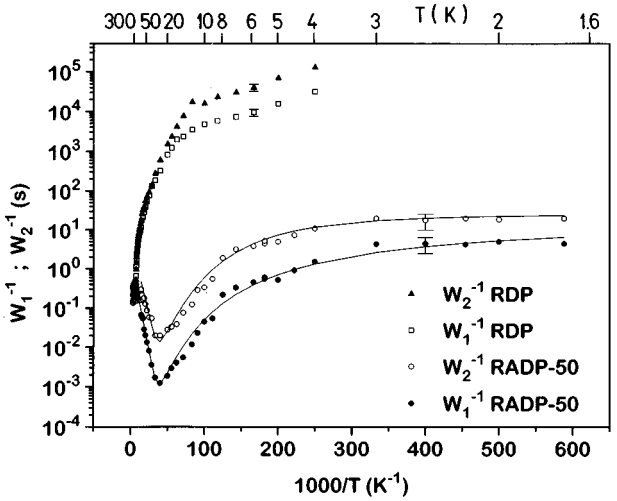

FIG. 3. A comparison of the ^{87}Rb NMR spin-lattice relaxation rates W_1 and W_2 of proton glass RADP-50 and ferroelectric RDP [$\nu_0(^{87}\mathrm{Rb})=124.3$ MHz, $a\perp H_0, c\|H_0$]. The inverse relaxation rates W_n^{-1} of RDP are at low T by a factor 10^4 longer than those of RADP-50.

from the T dependences of W_1^{-1} and W_2^{-1} on the high-temperature side of the minimum. These values agree well with the ones determined on pure KD_2PO_4.[18] The constants $K_1=8.7\times10^{12}$ s^{-2} and $K_2=3.7\times10^{12}$ s^{-2} have been determined from the values of the relaxation rates in the minima.

Below 55 K thermally activated hopping no longer describes properly the T dependence of the relaxation rates. At the low-temperature side of the minimum, the classical hopping model yields a straight line in the $\log W_n^{-1}$ vs inverse temperature plot, whereas the experimental points deviate increasingly from this line and become nearly T independent below 16 K. Below 55 K tunneling starts to dominate the intra-H bond deuteron transfer. W_1^{-1} and W_2^{-1} are determined by the tunneling rate τ_t^{-1}. Below $T=4$ K, W_1^{-1} and W_2^{-1} reach an almost constant plateau, which is determined by the parameter τ_{t0}. The occurrence of this plateau is a typical sign for the existence of tunneling. The plateau reflects the quantum effects of the saturation of the tunneling rate τ_t^{-1} and the finite value of the depopulation factor $1-p^2$ at low temperatures. The temperature dependence of W_1^{-1} and W_2^{-1} in the region between 55 and 4 K is determined by the value of the tunneling matrix element Γ and the width of the asymmetry distribution σ_A. The fit (solid lines in Fig. 1) yielded the values $\tau_{t0}=(2\pm0.9)\times10^{-3}$ s, $\Gamma=2.7$ meV and $\sigma_A=25.6$ meV, where σ_A is T independent within experimental accuracy. The deuteron-glass phase dynamics below 55 K in DRADP-42 is determined by phonon-assisted tunneling.

Completely analogous conclusions are obtained from the O–D···O deuteron spin-lattice relaxation time T_1 measurements in the glassy phase of the isomorphous DRADA-32 (Fig. 2). Here too a T_1 minimum is observed at $T=90$ K and T_1 becomes T independent below 20 K. The values of the parameters obtained from the fit (solid line in Fig. 2) are $E_a=84.4$ meV, $\tau_\infty=8\times10^{-14}$ s, $\Gamma=3.4$ meV, and $\tau_{t0}=1.6\times10^{-3}$ s.

The ^{87}Rb results of deuterated DRADP-42 can be contrasted with the ones of protonated RADP-50 (Fig. 1). The relaxation rates show a qualitatively similar behavior. The minima in W_1^{-1} and W_2^{-1} are shifted to $T=25$ K demonstrating that the proton motion is much faster than the deuteron one. The high-temperature side of the minimum can be again well described by thermally activated proton hopping, yielding $E_a=18.9$ meV, $\tau_\infty=7.5\times10^{-13}$ s, $K_1=2\times10^{12}$ s^{-2} and $K_2=3\times10^{11}$ s^{-2}. Below 25 K phonon-assisted proton tunneling starts to dominate the relaxation. A plateau is observed below 3 K yielding $\tau_{t0}=(3.0\pm3.1)\times10^{-5}$ s. The clear evidence for tunneling—the weakly temperature dependent plateau—can be observed in protonated RADP-50 only at sufficiently low temperatures and this explains the lack of experimental evidence for tunneling so far. The other parameters are obtained from the fit as $\Gamma=8.2$ meV and $\sigma_A=9.5$ meV. The dynamics of RADP-50 at low temperatures is determined by the phonon-assisted O–H···O proton tunneling.

In Fig. 3 the ^{87}Rb spin-lattice relaxation rates of RADP-50 are compared to those of pure RDP, which undergoes a proton order-disorder transition to a ferroelectric state at $T_c=147$ K. Below T_c all H-bond potentials become strongly asymmetric so that $1-p^2\approx0$ and $W_n\to0$. The large H-bond asymmetries effectively prevent tunneling. The observed plateau in RDP is by a factor 10^4 higher than in RADP-50, demonstrating that the strong T-independent relaxation mechanism found at low temperatures in the glass compounds is absent in the long range ordered ferroelectric state. The observed plateau in RDP is probably because of dipolarly mediated spin diffusion to paramagnetic impurities. In order to check whether spin diffusion plays any role also in RADP-50 and DRADP-42, we performed magnetization recovery measurements on the central transition of ^{85}Rb ($I=5/2$) (Ref. 19). From the difference in the magnetic dipole moment, nuclear electric quadrupole coupling constant eQ, and natural abundance with respect to ^{87}Rb, one can calculate the W_n^{-1} ratios for the two mechanisms. For quadrupolar relaxation we get $W_n^{-1}(^{85}\mathrm{Rb})/W_n^{-1}(^{87}\mathrm{Rb})=0.03$; whereas for spin diffusion this factor is about 10. The experimentally obtained ratio was close to 0.03 so that spin diffusion can be safely excluded.

Our results show that the O–H···O dipoles in proton and deuteron glasses at low temperatures are not completely frozen out and static, but show the dynamic features characteristic for the presence of tunneling. This classifies RADP and DRADP among quantum glasses. It also should be pointed out that the present study provides the first quantitative evidence for intra O–H···O hydrogen tunneling at low temperatures in any KH_2PO_4-type hydrogen-bonded material.

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