Protonic inter-H-bond motion and ionic conductivity in hydrogen-bonded proton glasses

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Low-frequency dynamics of the hydrogen-bonded proton glass $Rb_{1-x}(NH_4)_xH_2AsO_4$ and its deuterated form has been investigated by measuring the decay of the NMR transverse nuclear-spin magnetization of ^{87}Rb nuclei in a spatially inhomogeneous electric-field gradient, ^1H line shape and ^2H two-dimensional exchange NMR techniques. A large difference in the time scales of the decay of Hahn echo and Carr-Purcell echo train was observed between room temperature and 10 K. The Hahn echo decay curves showed an exponential decay with the exponent proportional to the cube of time that is characteristic for random stochastic atomic motions. The proton NMR spectrum demonstrates the presence of mobile protons which produce a motionally narrowed absorption line above 220 K. Two-dimensional exchange NMR experiment on the deuterated glass demonstrated the existence of slow thermally activated deuteron hopping between different hydrogen bonds, the process that represents the ionic conductivity. The same effects were observed also in several pure compounds of the KH_2PO_4 family. The observed low-frequency dynamics is not a peculiarity of the proton glass phase but represents the protonic inter-H-bond motion and ionic conductivity that is a common feature of the KH_2PO_4 family. [S0163-1829(99)02705-8]

I. INTRODUCTION

In the physics of glasses a lot of effort has been made to understand the nature of the glassy phase from the thermodynamic point of view. The question is whether the glassy phase represents a new kind of an equilibrium thermodynamic state or the tremendous slowing down of the structural rearrangement times in glasses is just a kinetic phenomenon and the observed freezing is due to the finite observation time of the experimental measurement techniques. From the experimental side this question still remains open. The main reason is the fact that the glassy structures are characterized by a broad spectrum of correlation times for molecular motions, which cover the range from extremely short times up to the age of the universe. In an experimental observation of the glassy structures one encounters a problem that the observation time of a given experimental measurement technique is finite, i.e., the observations are inevitably made within a finite frequency interval, usually much narrower than the spectrum of the correlation times. The measured physical parameters thus in principle do not represent real thermodynamic quantities but generally observation-time-dependent quantities due to the fact that the investigated system cannot visit the whole phase space within the spectroscopic observation time. Under such conditions the answer to the question on the thermodynamic nature of the glassy phase remains in principle ambiguous. Knowledge of the shape and width of the excitation spectrum is, on the other hand, essential for understanding the physics of glasses.

Among various kinds of glassy structures proton glasses[1,2] represent one of the simplest and most studied examples. Proton glass phase forms in solid hydrogen-bonded ferroelectric-antiferroelectric mixtures (e.g., in $Rb_{1-x}(NH_4)_xH_2PO_4$ abbreviated as RADP-x) where the H bonds represent basic reversible two-position electric dipoles. The dipoles orient randomly between the two possible orientations according to the dominating local ferroelectric or antiferroelectric forces at a particular lattice site. It has been conjectured that the dynamics of the proton glass phase is determined predominantly by the proton motion between the two equilibrium sites of the H-bond double-well potential[3,4] (the proton intra-H-bond motion). This intrabond motion slows down on cooling and gradually freezes out, yielding a static frozen disorder of the H-bond electric dipole moments at low temperatures in the classical model (neglecting tunneling effects). The H-bond double potentials are considered to be asymmetric with the asymmetries A distributed by a symmetric distribution function $\rho(A)$ centered at $A=0$. It is considered that the gradual freeze-out of the proton intrabond motion in proton glasses is a consequence of the distribution of the H-bond potential asymmetries which in turn induces a distribution of the proton intrabond transfer times τ_c. The broad distribution of the autocorrelation times τ_c in proton glasses is thus attributed to a single proton degree of freedom, namely to the proton intra-H-bond motion in asymmetric double-well potentials with distributed asymmetries. This conclusion is supported by the ^{87}Rb NMR spin-lattice relaxation data[5] in protonated $Rb_{0.50}(NH_4)_{0.50}H_2PO_4$ (RADP-50) and deuterated $Rb_{0.56}(ND_4)_{0.44}D_2PO_4$ (DRADP-44) where it was shown that the ^{87}Rb spin-lattice relaxation mechanism originates from the proton and deuteron intrabond motion. A large isotope effect was observed on deuteration that shifted the ^{87}Rb relaxation time minimum from 25 K in the protonated RADP-50 to 85 K in the deuterated DRADP-44 due to the slower O-D···O intrabond dynamics. The temperature dependence of the ^{87}Rb relaxation rates showed an Arrhenius character at temperatures above 50 K in DRADP-44 and above 25 K in RADP-50, whereas below

a deviation from the classical thermally activated behavior was observed due to tunneling effects. An attempt to fit the temperature dependence of the relaxation rates within the Arrhenius regime with a distribution of intraband autocorrelation times however yielded a surprising result that the data could be well reproduced by a narrow distribution or, to a good approximation, even without it. This is in contrast to the dielectric relaxation data of DRADP-x where a broad distribution of the relaxation frequencies was observed[6] in that temperature regime. The relaxation frequencies near the high-frequency edge of the distribution obeyed the Arrhenius law whereas they showed a divergent behavior of the Vogel-Fulcher type at the low-frequency edge. The high-frequency part of the relaxation spectrum could be rather unambiguously associated with the intra-H-bond motion by comparing the activation energies of the NMR and dielectric experiments. The low-frequency part of the spectrum is, however, still not well understood. It is evident that the distribution of the proton intraband transfer times is not broad enough to account solely for the observed broad distribution of the autocorrelation times. There exist obviously other protonic degrees of freedom involved in the low-frequency dynamics of these systems, which were not observed in the NMR spin-lattice relaxation experiment, apparently due to their slowness. One possibility is the ''Takagi'' HPO_4 and H_3PO_4 intrinsic defect diffusion[3] that is again connected to the proton intrabond motion. It represents a correlated motion of protons in four hydrogen bonds attached to a given PO_4 tetrahedron. The HPO_4 and H_3PO_4 defects represent a kind of renormalized particle with a larger effective mass so that their dynamics is expected to be considerably slower from the proton intrabond dynamics in uncoupled bonds. Another possibility is the hopping of protons between different H bonds, which represents atomic self-diffusion in space, giving rise to ionic conductivity. This process has been given little attention so far in the study of the proton glass phase dynamics. Bulk ionic conductivity has, however, been already observed in RADP-50 (Ref. 7) as well as in some pure compounds of the KH_2PO_4 (KDP) family.[8]

In this paper we present ^{87}Rb, ^{1}H, and ^{2}H NMR studies of the slow motions in proton glasses $Rb_{1-x}(NH_4)_x H_2 AsO_4$ (RADA-x) and their deuterated analogues which were so far neglected in the dynamics of these systems. We demonstrate that ^{87}Rb NMR spin-echo decay curves show an exponential decay with the exponent proportional to the cube of time, which is characteristic for diffusive motions in a spatially inhomogeneous electric field gradient (EFG). The diffusive character of the motion is also manifested in the fact that the cubic decay could be eliminated in a Carr-Purcell sequence, where the spin echo train showed a much longer exponential decay with the exponent depending linearly on time. The two-dimensional (2D) exchange NMR experiment on deuterons demonstrated that the detected motions correspond to spatial jumps of deuterons between different hydrogen bonds (the deuteron inter-H-bond exchange), representing the ionic conductivity. The frequencies of the interbond jumps were found to be slow, varying from sub-Hz frequencies at 40 K up to several ten kHz at room temperature. The increased probability for the interbond jumps on heating is manifested in the appearance of a motionally narrowed line in the proton spectrum of RADA at temperatures above 200 K. Similar

effects were detected also in the pure compounds RDA, ADA, and KDP, showing that this phenomenon is not a peculiarity of the proton glass phase but a common feature of the KDP family.

II. ^{87}Rb SPIN ECHO DECAY IN AN INHOMOGENEOUS EFG

It has been demonstrated recently that the NMR decay of the transverse nuclear-spin magnetization[9–11] and the 2D exchange NMR technique[12] provide a very sensitive method for detecting random stochastic (diffusive) motion of resonant nuclei of spin $I > 1/2$ which move in a spatially inhomogeneous EFG. The diffusive motions can be detected on a scale as small as a fraction of a nanometer. The spatial inhomogeneity of the EFG in glasses is a consequence of the topological disorder that destroys the translational periodicity of the EFG at otherwise equivalent lattice sites. As a result, the NMR absorption lines become strongly inhomogeneously broadened, reflecting the fact that the quadruple-perturbed nuclear resonance frequency depends on space; $\omega = \omega(\mathbf{r})$. The NMR spin echo attenuation factor $A(2\tau) = M_+(2\tau)/M_+(0)$ of the transverse nuclear spin magnetization M_+ in a two-pulse experiment with the pulse separation τ is obtained as[10]

$$A(2\tau) = \exp\{-2\tau/T_2\}\exp\left\{-D(\nabla\omega)^2 \frac{2\tau^3}{3}\right\}. \quad (1)$$

The quantity $\nabla\omega$ is the gradient of the EFG (the gradient of a gradient) and D is the diffusion constant. The spin-spin relaxation time T_2 includes all degrees of freedom other than diffusion that contribute to the spin-spin relaxation. The characteristic feature of the diffusion damping term is its dependence on the cube of time.

In structures with nonrandom crystalline order it is in many cases possible to derive an analytical expression for the frequency-space relation $\omega(\mathbf{r})$, so that the gradient $\nabla\omega$ is known and the diffusion constant D can be extracted from Eq. (1). In solids with glassy structure the frequency-space relation can unfortunately not be derived due to the random character of the disorder so that D cannot be determined. One can however still determine the product of the diffusion constant with the square of the frequency gradient $D(\nabla\omega)^2$ (a kind of a renormalized diffusion constant). For the RADP structure the gradient can be assumed to be similar in the X and Y crystalline directions due to the fact that the proton interbond motion takes place within the planar (X,Y) H-bond network of tetragonal symmetry. In our ^{87}Rb spin echo experiment the diffusion of protons is observed via the transverse magnetization decay of the ^{87}Rb nuclei, which are rigidly bound to the lattice, but the EFG fluctuations at their sites are produced by the proton motion. Since the Rb nuclei are ionically bound, they see a large number of protons within a given coherence volume.

An important feature of the diffusion-induced damping is the fact that it can be eliminated by the application of a Carr-Purcell (CP) train yielding the $\exp\{-2\tau/T_2\}$ decay only, the reason being the stochastic nature of the diffusion motion.[13] The difference between the Hahn echo cubic and the CP linear decays is an important criterion[11] to discriminate the diffusion effects from other mechanisms producing
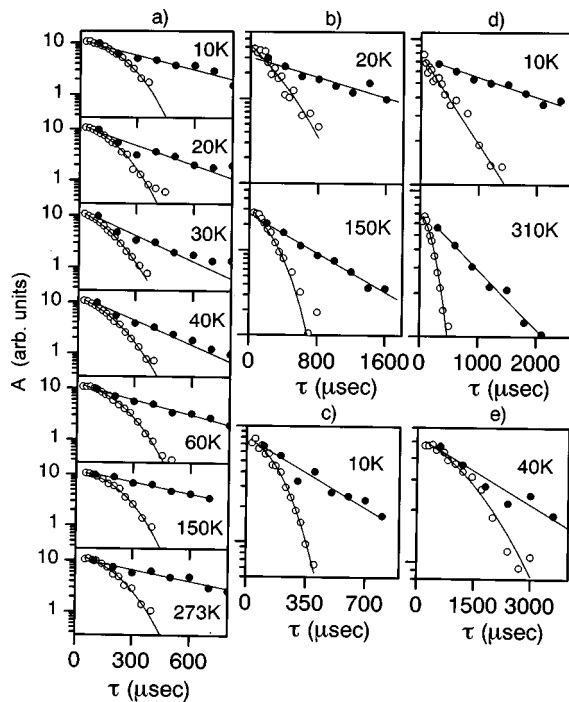
FIG. 1. ^{87}Rb NMR Hahn echo (open circles) versus Carr-Purcell echo (solid circles) decay curves in (a) proton glass RADA-22, (b) deuteron glass DRADA-28 and pure ferroelectrics, (c) protonated RDA, and (d) deuterated DRDA at different temperatures. In (e) the ^{39}K echo decay curves of KDA are shown. Solid lines represent the fits with Eq. (1) for Hahn echo decays and with the T_2 term only for the Carr-Purcell decays.

nonmonoexponential echo decays. It was shown[14] that the Hahn echo decay curves of quadrupolar nuclei of noninteger spin exhibit a Gaussian τ^2 decay in the presence of static dipole-dipole coupling among the spins, when measured on the central transition. Experimentally the Gaussian decay can in many cases not be distinguished from the cubic decay. However, unlike the diffusive decay, the dipolarly induced τ^2 decay cannot be eliminated by a CP sequence.

The Hahn-echo and CP-echo decays were measured in a variety of samples; by ^{87}Rb NMR in the protonated glass RADA-22, the deuterated glass DRADA-28, the pure ferroelectrics RDA and DRDA as well as by ^{39}K NMR in the pure ferroelectric KH_2AsO_4 (KDA). The results are summarized in Fig. 1. Figure 1(a) shows the ^{87}Rb (central transition) spin-echo decay curves of RADA-22 in the whole investigated temperature range from 10–273 K. A remarkable difference between the Hahn and CP decays is observed. The CP decays are longer and appear as straight lines on the logarithmic scale, indicating that the decay is monoexponential with the exponent linear in the time variable. They thus represent the pure T_2 decay and the solid lines in Fig. 1(a) represent the fits with the T_2 term only. The Hahn echo decay curves are much shorter and do not yield straight lines in the log plot. They can be well reproduced by Eq. (1) with the dominating diffusion term which has the exponent proportional to the cube of time. The same difference between the Hahn echo and CP decays was observed also in the deuterated glass DRADA-28 [Fig. 1(b)]. The above results demonstrate the existence of slow random stochastic atomic motions, the frequencies of which fall into the observation

window of the NMR transverse magnetization decay experiment. Since the time scale of a typical decay is of the order of a millisecond, the motional frequencies fall into the kHz range. In order to check whether the detected slow motions are a peculiarity of proton glasses, we performed the same experiment also in the pure ferroelectrics RDA [Fig. 1(c)] and DRDA [Fig. 1(d)]. A similar difference in the Hahn and CP decays was observed. Finally we repeated the experiment also on ^{39}K nuclei in pure ferroelectric KDA at temperatures below 40 K [Fig. 1(e)]. ^{39}K nuclei were chosen in order to check whether spin diffusion could produce the observed difference. Due to a very small magnetic dipole moment of ^{39}K nuclei, spin diffusion (of magnetic dipolar origin) should have a negligible effect on the Hahn echo decay in KDA. The same Hahn-CP difference was, however, observed also in this experiment. This difference was found to exist in all the investigated samples regardless of their microscopic (proton glass or ferroelectric) structure and is thus not a peculiarity of the proton glass phase.

III. THE PROTON LINE SHAPE

In order to elucidate the microscopic origin of the detected slow motions we performed a proton NMR study of the protonated samples RADA-22, RDA, KDA, and ADA. The last sample was not included in the ^{87}Rb CP-Hahn echo difference experiments as it does not contain rubidium. The ^{1}H line shape experiment was chosen as the frequency observation window of this technique falls into the kHz range, so that the detected slow motions should affect the proton line shape. The shape and width of the ^{1}H NMR spectrum are predominantly determined by the proton-proton magnetic dipole interaction. This interaction depends on the angle θ between the direction of the external magnetic field and the spatial vector joining the two interacting protons as $1 - 3\cos^2\theta$. Protonic motion may thus produce motional averaging of this interaction resulting in a narrowing of the spectrum. The temperature dependence of the ^{1}H spectrum of the proton glass RADA-22 is displayed in Fig. 2(a). At $T=80$ K the spectrum shows a featureless broad shape extending over 30 kHz. It represents the ''rigid lattice'' proton spectrum. On heating a narrow component in the center of the spectrum appears at $T=225$ K and increases in intensity towards higher temperatures. This line represents the motionally narrowed part of the spectrum and arises from mobile protons whose motional frequencies are higher than the rigid lattice spectrum width. From this condition we can estimate the order of magnitude of the motional frequencies to be in the kHz range in the temperature interval between 225 K and room temperature. The increase of intensity of the motionally narrowed part on heating demonstrates that the process is thermally activated. The fact that only a part of the proton spectrum is motionally narrowed demonstrates that not all of the protons participate in this dynamic process and the number of mobile protons increases with increasing temperature. In the RADA-22 sample there are two kinds of different chemically bound protons—the acid O-H···O and the ammonium NH_4 protons. In order to understand their
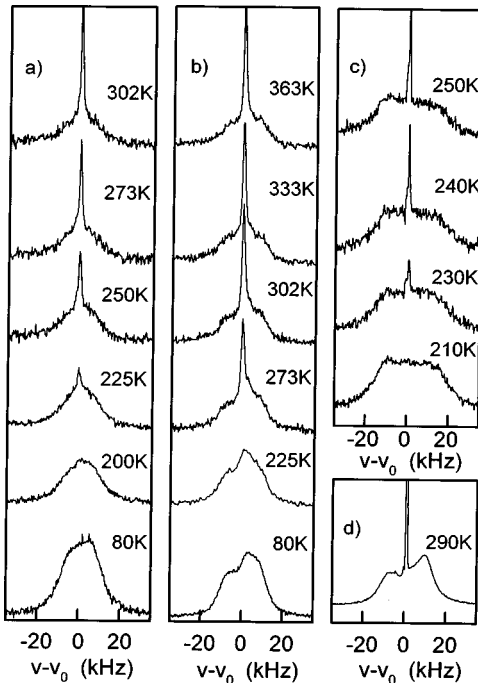
FIG. 2. Temperature dependence of the proton NMR spectrum in (a) proton glass RADA-22, (b) ferroelectric RDA, (c) antiferroelectric ADA, and (d) ferroelectric KDA.

respective role in the detected slow motion, we repeated the ^{1}H line shape experiment on the pure ferroelectric RDA, which contains the acid protons only. We observed an almost identical motional narrowing which started to show up above 250 K in the paraelectric phase [Fig. 2(b)]. A similar narrowing effect was observed also in the paraphase of the antiferroelectric ADA above 230 K [Fig. 2(c)]. The same superposition of the rigid-lattice and motionally narrowed proton spectra was observed also at room temperature (in the paraphase) of the ferroelectric KDA [Fig. 2(d)]. The motional narrowing of the proton spectrum thus exists in all the investigated samples and is thus not a peculiarity of proton glasses. The presence of this effect in the RDA and KDA samples that contain no ammonium protons demonstrates that it originates from the O-H···O protons. The acid protons—or at least a part of them—undergo a motion that is thermally activated with frequencies increasing from sub-kHz below about 220 K up to several kHz at room temperature. The fact that a part of the spectrum shows an almost complete motional narrowing indicates that the associated protons move rather freely in space.

IV. DEUTERON 2D EXCHANGE NMR

The proton NMR line shape experiment has demonstrated that the observed slow protonic dynamics originates from the acid protons. There still remains the question which protonic degree of freedom—the intra-H-bond motion, the inter-H-bond motion (the ionic conductivity) or both—is involved in this process. An elegant spectroscopic method to answer this question is the 2D exchange NMR experiment on deuterons.[15] In the deuterated glass DRADA-x the ND_4 and the O-D···O deuterons give resolved lines in the spectrum. The ND_4 deuteron lines are located at the center of the spec-

trum whereas the O-D···O deuterons yield two outer pairs of satellites. These two pairs correspond to the so called X and Y deuterons, referring to the H-bonded chains of the AsO_4 tetrahedra propagating along the crystalline a (X) or b (Y) directions. In the 2D exchange spectrum the deuteron resonance lines corresponding to lattice sites with different resonance frequencies are located at the diagonal of the (ω_1, ω_2) plane. The deuteron motion between these sites is detected by the appearance of peaks at the cross positions of the two lines between which the exchange is taking place. The deuteron exchange is monitored coherently during the ''mixing period'' (t_{mix}) of the 2D exchange experiment. For t_{mix} short compared to the deuteron jump time τ_{exch} the cross peaks are absent, whereas for $t_{mix} \gg \tau_{exch}$ the cross peak intensity reaches a saturated value.

The deuteron 2D exchange NMR experiment was performed in DRADA-32 at temperatures 40 and 293 K. The orientation was chosen such that the outer pair of the O-D···O lines corresponded to the Y deuterons and the inner pair to the X deuterons (Fig. 3). At 40 K the ND_4 lines are too broad to be detected whereas they are observed at 293 K. The same experimental conditions were used at both temperatures except for the mixing time which was taken $t_{mix} = 5$ s at 40 K and $t_{mix} = 0.4$ s at 293 K. At 40 K [Fig. 3(a)] each of the O-D···O lines shows additional splitting (the so-called $X_\pm$ and $Y_\pm$ splittings). This is due to the fact that each of the X and Y H-bonded AsO_4 chains consists of two kinds of H bonds making an angle $\pm 0.5°$ with the crystalline (a,b) plane. The deuteron EFG tensors at the two sites of a given H-bond double potential differ and yield the additional structure in the $X_\pm$ and $Y_\pm$ subspectra. In Fig. 3(a) one observes that at 40 K no cross peaks between the X and Y lines are present for the given choice of t_{mix}, demonstrating the absence of the $X \leftrightarrow Y$ interbond exchange on the time scale of the experiment. When the measurement is repeated at 293 K [Fig. 3(b)] one finds first that the $X_\pm$ and $Y_\pm$ splittings are averaged out by a fast deuteron intrabond motion. Single sharp time-average X and Y deuteron lines are observed instead. In addition, cross peaks between these two lines appear, demonstrating the existence of the $X \leftrightarrow Y$ interbond exchange and the associated deuteron ionic conductivity. The frequency scale of this motion at room temperature is within the observation window of the 2D exchange experiment, which is limited by the inverse mixing time $t_{mix}^{-1} = (0.4\,\mathrm{s})^{-1} = 2.5$ Hz at low frequencies and by the splitting of the X and Y lines ($2\pi \times 48$ kHz) at high frequencies. Motions with higher frequencies would average the X and Y lines into a single line at a time-average position. The frequency range of the detected deuteron $X \leftrightarrow Y$ interbond exchange is thus consistent with the frequencies of the dynamic process which produced the motional narrowing of the proton lines in Fig. 2. This leads us to the final conclusion that the detected slow motions corresponds to the proton and deuteron thermally induced transfer between different H bonds. This is a kind of a spatial diffusion and represents the microscopic mechanism of protonic and deuteronic ionic conductivity as a hopping process over well defined lattice sites. At room temperature this process involves atomic jumps with kHz frequencies. The motion, however, persists down to much lower temperatures where the jump frequencies are considerably slower. Indeed, the 2D exchange experiment in DRADA-32 per-
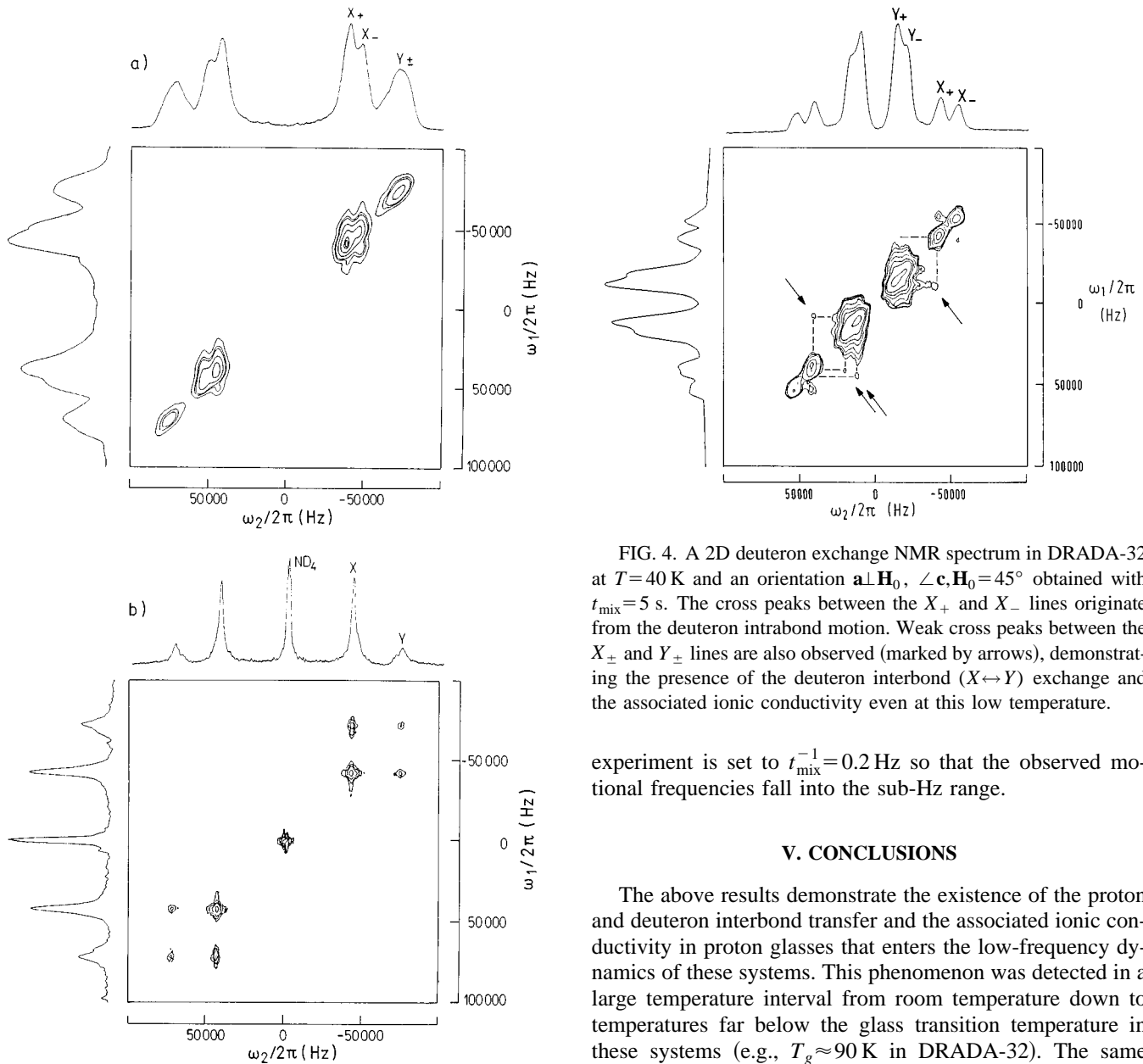
FIG. 4. A 2D deuteron exchange NMR spectrum in DRADA-32 at $T = 40$ K and an orientation $\mathbf{a} \perp \mathbf{H}_0$, $\angle \mathbf{c}, \mathbf{H}_0 = 45°$ obtained with $t_{\mathrm{mix}} = 5$ s. The cross peaks between the X_+ and X_- lines originate from the deuteron intrabond motion. Weak cross peaks between the $X_\pm$ and $Y_\pm$ lines are also observed (marked by arrows), demonstrating the presence of the deuteron interbond ($X \leftrightarrow Y$) exchange and the associated ionic conductivity even at this low temperature.

experiment is set to $t_{\mathrm{mix}}^{-1} = 0.2$ Hz so that the observed motional frequencies fall into the sub-Hz range.

V. CONCLUSIONS

The above results demonstrate the existence of the proton and deuteron interbond transfer and the associated ionic conductivity in proton glasses that enters the low-frequency dynamics of these systems. This phenomenon was detected in a large temperature interval from room temperature down to temperatures far below the glass transition temperature in these systems (e.g., $T_g \approx 90$ K in DRADA-32). The same phenomenon was found to exist also in the paraphase of the pure members of the KDP family so that it is not a peculiarity of the proton glass phase. The frequency scale of the deuteron interbond exchange in DRADA-32 is in agreement with that determined by Schmidt and Uehling[8] in the pure ferroelectric DKDP where the deuteron $X \leftrightarrow Y$ exchange time was found to be $\tau_{XY} \approx 0.4$ s at room temerature and 15 msec at 343 K. The fact that the ionic conductivity takes place in the RADA and RADP proton glasses in a similar way as it does in the pure KDP family members is not surprising. The structure of the glass compounds is in many respects identical to the pure KDP structure and the macroscopic paraphase symmetry of the glass is preserved down to the lowest measured temperatures. The important issue for the ionic transport is the structure of the H-bond network (a stack of 2D H-bonded planes, each consisting of two sets of mutually perpendicular H-bonded chains), which is the same in the pure KDP members as well as in their mixtures. The substitutional disorder of Rb and NH_4 ions in proton glasses seems to be of marginal importance for the interbond hopping pro-

FIG. 3. (a) A 2D deuteron exchange NMR spectrum in DRADA-32 at $T = 40$ K and an orientation $\mathbf{a} \perp \mathbf{H}_0$, $\angle \mathbf{c}, \mathbf{H}_0 = 65°$ [$\nu_0(^2\mathrm{H}) = 41.46$ MHz] obtained with the mixing time $t_{\mathrm{mix}} = 5$ s. The $X_\pm$ deuteron lines are partially resolved, whereas the $Y_\pm$ lines overlap at this orientation. No cross peaks between the X and Y lines are observed. (b) The same experiment repeated at $T = 293$ K with $t_{\mathrm{mix}} = 0.4$ s. At this temperature the $X_\pm$ and $Y_\pm$ splittings are averaged out by the fast O-D$\cdots$O intrabond motion yielding sharp time-average X and Y lines. The cross peaks between the X and Y lines give a direct proof for the existence of the dueteron interbond ($X \leftrightarrow Y$) exchange.

formed at 40 K at a slightly different orientation using the mixing time $t_{\mathrm{mix}} = 5$ s has detected the interbond cross peaks (Fig. 4) even at this low temperature. The cross peak intensities are, however, very weak even for such a long mixing time, demonstrating the very small probability of thermally activated deuteron $X \leftrightarrow Y$ jumps at such low temperatures. The low-frequency limit of the observation window in this

cess. On the other hand, it plays the dominant role in the proton intrabondmotion due to the biasing of the H-bond double potentials. Our results show that the proton glass dynamics is not determined by a single proton degree of freedom—the intra-H-bond motion—as widely assumed so far. It includes at least one more degree of freedom—the proton interbond transfer, representing the ionic conductivity. This process enters the dynamics of the proton glass phase in the low-frequency part of the glassy excitation spectrum.

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