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A Deuterium NMR Study of $D(UO_2XO_4)$, $4D_2O$; X = P, As

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Deuterium NMR spectra have been obtained by the solid echo technique for polycrystalline samples of DUO_2XO_4, $4D_2O$, with X = P (DUP) and As (DUAs). Transitions (II → I) were found, by DSC measurements, to occur at 260 and 290 K for DUP and DUAs, respectively. In the high temperature tetragonal phase *I*, the NMR lineshapes are consistent with motionally averaged axially symmetric electric field gradient tensors, with values for $\langle e^2qQ/h \rangle_{av}$ of 39.2 ± 0.2 and 38.2 ± 0.2 kHz for DUP and DUAs, respectively. This requires fast chemical exchange of the deuterium atoms between all of the hydrogen-bond sites in a water layer, and participation of all of the deuterium atoms in the diffusion process. There are no discernible discontinuities in the spectra at the transition temperature suggesting that there is little change in the local structure of the water layers at the transition. The spectra disappeared at about 10 K below T_c and for DUP a distorted broader spectrum became discernible below about 200 K.

Introduction

The layered compound hydrogen uranyl phosphate tetrahydrate HUO_2PO_4, $4H_2O$ (HUP) and the isostructural arsenate HUO_2AsO_4, $4H_2O$ (HUAs) are superionic proton conductors near room temperature (*1*, *2*). Bernard *et al.* (*3*), from powder neutron diffraction studies on DUAs at room temperature, confirmed that DUAs is isostructural with DUP and determined how on average the hydrogen-bond sites are occupied.

The structure of this high temperature phase I (*3*, *4*) consists of planar acidic water networks containing equal numbers of H_4O_2 and $H_5O_2^+$ dimers, interleaved with $(UO_2PO_4)_n^{n-}$ layers. Infrared spectra of HUP and HUAs show peaks in the 2300 cm^{-1} region expected for $H_5O_2^+$ (*5*). In the water network, shown schematically in Fig. 1a, the oxygens belonging to four different dimers are connected through the H bonds to form four- and eight-sided rings. The ends of the dimers are also H bonded to phosphate (or arsenate) oxygens. For each pair of dimers (H_4O_2, $H_5O_2^+$) there are 10 possible H bonds: 4 in the squares (*s* bonds), 2 in the centers of the dimers linking the squares (*d* bonds), and 4 in the bonds directed towards the phosphate (or arsenate) oxygens (*p* bonds). The stoichi-

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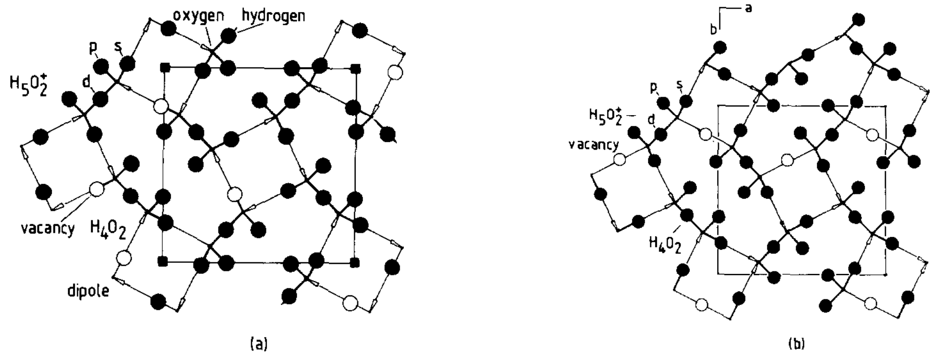

FIG. 1. Two-dimensional water network in HUO_2XO_4, $4H_2O$ with X = P or As. Occupied H bond ●; vacant H bond ○; arrow indicates dipole; oxygens omitted for clarity. For each pair of dimers (H_4O_2 and $H_5O_2^+$) there are 10 H bonds: 4 in the squares, *s*; 2 at the center of dimers, *d*; and 4 next to phosphate (or arsenate) oxygens, *p*; one H bond is vacant. (a) Structure at 305 K based schematically on Ref. (*3*). The *p* sites are fully occupied and vacancies are disordered. (b) Structure at 4 K based on Ref. (*7*). Vacancies are ordered, forming chains of H_4O_2 in the *a* direction, linked by $H_5O_2^+$ in the *b* direction.

ometry requires that only 9 out of the 10 bonds are occupied by hydrogens. There are some similarities with the hydrogen-bonded network in $SnCl_2$,$2H_2O$, but this network contains no vacancies and only half of the oxygens are hydrogen bonded to chlorines.

Positional order–disorder can be associated with (i) the distribution of hydrogens over the two distinct crystallographic positions in each H bond, which are taken to be asymmetric, (ii) the distribution of vacancies on the *s* bond (this takes into account contributions from the distribution of H_2O_4 and $H_5O_2^+$ dimers over the *d* bonds as well as the two possible orientations of the H_2O_4 dimers). The *p* sites are fully occupied and the hydrogens are ordered, occupying the H-bond sites nearer to the dimers than to the phosphate oxygens. On the other hand, the *d* bonds are also fully occupied but disordered, i.e., there was evidence from the neutron diffraction data for a statistical superposition of the two pairs of dimers of the type $H_2\overset{+}{O}\text{–}H \cdots OH_2$ and $H_2O \cdots H\text{–}\overset{+}{O}H_2$, and $HO\text{–}H \cdots H\text{–}OH$. In other words, the *d* positions are only average positions. The remaining bonds are $\frac{3}{4}$ filled, and the vacant *s* bond corresponds to the absent terminal hydrogen at the HO end of the dimer $HO\text{–}H \cdots OH_2$. The *s* bonds are ordered, for the neutron scattering density clearly shows that only one of the crystallographically distinct *s* sites is occupied. There was no evidence for ordering of the vacancies.

Shilton and Howe (*5*), from powder X-ray diffraction studies, determined that there is a transition from a tetragonal (*P*4/*ncc*) phase I to an "orthorhombic" phase II at 274 and 301 K for HUP and HUAs, respectively. They also proposed an ordering scheme which assumed long range ordering of the hydrogen bonds but disordering of the vacancies that is consistent with the optical properties. Dielectric studies on HUAs reported by Benyacar and Dussel (*6*) indicate a transition at 253 K to a ferroelectric phase.

Fitch *et al.* (*7*) subsequently showed by powder neutron diffraction studies on DUAs at 4 K that phase II is probably triclinic with space group symmetry $P\bar{1}$. The occupation of the hydrogen bonds, as determined by them, is shown schematically in Fig. 1b. The uranyl arsenate framework (not shown) is somewhat distorted from phase I and the vacancies are ordered, forming chains of H_4O_2 dimers in the *a* direction, crosslinked by $H_5O_2^+$ dimers in the *b* direction. In fact, the water oxygens forming the vacant *s* bond sites are too far apart (3.3 Å) for the *s* bonds to be properly called hydrogen bonds, nevertheless, the bonds are shown vacant in Fig. 1b to make comparison with Fig. 1a easier. Despite these differences, however, the local environment of each type of hydrogen is probably very similar in phases I and II.

Bernard *et al.* (*8*) have argued that the mechanisms for transport processes in phase I involve combinations of three elementary steps: (i) ($H_5O_2^+$ rot.) a labeled hydrogen atom is transferred across a $H_5O_2^+$ dimer by the concerted three-fold axis rotation of each end of the dimer; (ii) ($H_5O_2^+$ vac. hop) a vacancy hops between adjacent *s* sites in the same square and exchanges a labeled hydrogen between the dimers $H_5O_2^+$ and H_4O_2; (iii) (H_4O_2 vac. rot.) a vacancy and a hydrogen are simultaneously transferred, in opposite directions, across a H_4O_2 dimer between two squares by the concerted threefold axis rotation of each end of the dimer. Hydrogen self-diffusion probably involves steps (i) and (ii) and/or (iii). Ionic conduction probably involves only steps (ii) and (iii).

Proton relaxation studies (*9*) show that the dipole–dipole interaction between the protons is made time dependent and averaged to zero by hydrogen self-diffusion. Because the averaging is found to occur in one stage the steps involved in the diffusion process must be concerted, and therefore kinetically indistinguishable. It is not known whether the rotations involved in steps (i) and (iii) occur around axes directed along the *p* or vacant *s* bonds. It should be possible to distinguish between these two possibilities because rotations around the *p* bond do not affect the *p* hydrogens whereas rotations around the vacant *s* bond exchange the *p*, *s*, and *d* hydrogens. Proton relaxation studies cannot determine whether or not the *p* hydrogens are mobile because even if they were fixed they would still be relaxed because of the dipole–dipole interaction between the *p* hydrogens and the *s* and *d* hydrogens, which would be made time dependent by the motion of the mobile *s* and *d* hydrogens. On the other hand, deuterium NMR studies on the fully deuterated compounds should be able to tell whether all the deuterium atoms are mobile. This is because the interaction between the nuclear electric quadrupole moment and the electric field gradient of the crystal is likely to be much larger than the dipole–dipole interaction between deuterium atoms, so that the deuterium spectra should be more sensitive to the motion of the deuteriums relative to the lattice than to the motion of the deuteriums relative to each other. The object of the work reported in this paper is to add to our understanding of the mechanisms of molecular motions in DUAs and DUP by studying their deuterium NMR spectra.

Experiments and Results

Materials

Samples of DUP and DUAs were prepared by exchanging the corresponding polycrystalline hydrogen-containing samples three times with small amounts of D_2O for about one day. Exchanged samples were quickly dried on a filter paper in air and transferred to NMR sample tubes. Before sealing the tubes, the samples were reequilibrated in an atmosphere saturated with D_2O.

The extrapolated onset temperatures for the transition from phase II to I were, as measured using a DuPont 990 differential scanning calorimeter, 260 ± 1 K for DUP and 290 ± 1 K for DUAs. The value for the latter is in good agreement with that previously reported (*5*).

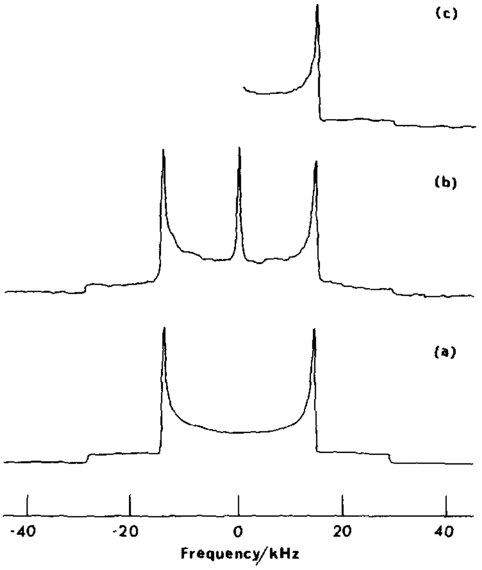

FIG. 2. Deuterium NMR spectra of DUO_2XO_4, $4H_2O$, with X = P (DUP) and As (DUAs), obtained by Fourier transformation of the solid echo. (a) Theoretical "Pake" powder spectrum for $I = 1$ calculated using $e^2qQ/h = 38.4$ kHz, $\eta = 0$ and convoluting with a gaussian broadening function of 0.1 G^2. (b) Spectrum of DUAs (9.8 MHz) at 295 K. The central peak is free D_2O. (c) Spectrum of DUP (54.7 MHz) at 328 K.

NMR Measurements

The ^2H spectra shown in Fig. 2 were obtained by Fourier transformation of the solid echo produced by the sequence $P_y(90°)$–τ–$P_x(90°)$ and starting the transform at $t = 2\tau$ (*11*). Measurements on DUAs were made at 9.8 MHz using a Bruker SXP spectrometer. Quadrature detection was employed with CYCLOPS and 180° phase alternation of the first pulse to eliminate systematic errors and magnetoacoustic ringing following the second pulse; the pulse duration was 3 μsec and τ was 100 μsec. The spectrum at 295 K is shown in Fig. 2b and was obtained by averaging 2900 signals at a repetition rate of 0.016 sec^{-1} into 1 K of memory per channel with a dwell time of 2 μsec. The spectrum was found to be independent of repetition rate up to 2 sec^{-1} (T_1 = 1.5 msec) and there was no evidence for any additional "peaks" in the range ±250 kHz.

The central peak arises from liquid heavy water indicating that the sample was not completely dry, and therefore, was fully hydrated. The remainder of the spectrum is consistent with an axially symmetric "Pake" spectrum calculated using a quadrupole coupling constant $e^2qQ/h = 38.4$ Hz and $\eta = 0$ convoluted with a gaussian line broadening function of 0.1 G^2 (see Fig. 2a). On cooling from 315 K the separation of the singularities was unaffected, but the intensity of the spectrum relative to the central "liquid" component began to decrease at 295 K and completely disappeared at 280 K; a concomitant distortion in the shape of the spectrum was also observed. No echo could be detected at temperatures down to 140 K.

The spectrum for DUP at 328 K (Fig. 2c) was similarly measured, but at 54.7 MHz (at Heidelberg, West Germany) and using single channel detection and on-resonance excitation. The pulse duration was 3.5 μsec and τ was 50 μsec. Typically 128 signals were averaged at a repetition rate of 5 sec^{-1} into 1 K of memory with a dwell time of 2 μsec. Behavior analogous to that for DUAs was observed. A temperature independent effective quadrupole coupling constant of 39.2 ± 0.2 kHz was measured down to 250 K at which temperature the spectrum disappeared (again some 10 K below the transition temperature). The echo became discernible once more at 200 K. The corresponding spectrum was much broader and severely distorted and is not reproduced here.

Discussion of Results

The spectra reproduced in Fig. 2 are determined by the nuclear quadrupole–electric field gradient interaction of the deuterium spins. In making inferences from those spectra concerning the motion of the

TABLE I

DIFFUSIONAL CORRELATION TIMES $\tau_c = \tau_0 \exp(E_a/RT)$ FOR HUP (T_c = 274 K) (9, 13) AND HUAs (301 K) (9).

	τ_0/sec	E_a/kJ mole^{-1}
	Phase I	
HUP	2.2×10^{-14}	29
HUAs	2.2×10^{-14}	29
	Phase II	
HUP	1.0×10^{-15}	42.6
HUAs	3.0×10^{-15}	42.6

spins it is essential to recognize that in the polycrystalline samples used in our experiments each inequivalent deuterium spin will contribute to the observed spectrum a distinct tensor bandshape characterized by a quadrupole coupling constant e^2qQ/h and asymmetry parameter η (9). Measurements on single crystals at low temperatures would be required to determine the actual values for these parameters; nevertheless, values in the ranges $200 < e^2qQ/h < 400$ kHz and $0 < \eta < 0.3$ are expected for these materials (12). If the tetragonal phase I were assumed to be rigid the observed spectra would be a superposition of bandshapes in the intensity ratios 4:3:2 corresponding to deuterium spins in the *p*, *s*, and *d* hydrogen-bond sites. Therefore the observation of a single Pake bandshape with an effective coupling constant of only 38–39 kHz and $\eta = 0$ shows that there is fast exchange of deuterium atoms between *all* of the available sites in each crystallite. By fast exchange we mean that $1/\Delta\omega\tau_c \gg 1$, where $\Delta\omega$ is the difference in the quadrupole splittings at the sites visited by the diffusing deuterium ions, and where the diffusion motion is described by the correlation time τ_c. This condition is well satisfied in phase I for both DUP and DUAs since Table I shows that $\tau_c < 10^{-8}$ sec and since we have estimated above that $\Delta\omega/2\pi < 400$ kHz.

^{31}P-NMR studies also show that the *p* hydrogens are mobile (13). Fast chemical exchange of the *s*, *d*, and *p* hydrogens shows that threefold axis rotation occurs around the vacant *s* bond axis.

The observed average quadrupole coupling tensor is axially symmetric ($\eta = 0$) on account of the tetragonal symmetry of the crystal. The principal axis of the tensor is expected to be oriented normal to the planes containing the water networks.

The absence of any detectable changes in the separation of the singularities in the spectrum of either DUP or DUAs accompanying the phase change I → II, shows that the exchange rate is still fast in phase II near T_c ($1/\Delta\omega\tau_c \gg 1$, with $\tau_c \sim 10^{-6}$ sec) and that the average quadrupole coupling tensors are the same in phase II as in phase I. This must mean that the local environments of each type of deuterium are very similar in the two phases and are negligibly affected by the small changes in the unit cell dimensions and the onset of ordering of the water network which accompany the phase change.

The rapid, yet continuous, loss in intensity and distortion in the shape of the spectra for both materials on cooling in the neighborhood of T_c is a phenomenological effect associated with the motion of the spins. There will be an exchange contribution to the transverse relaxation rates and hence to the echo decay rate given by

$$1/T_{2\varepsilon} = \Delta\omega^2\tau_c.$$

Thus the spin–echo amplitude is expected to decrease and, since $\Delta\omega$ for a given crystallite depends on its orientation with respect to the static field B_0, its associated spectrum is expected to distort when the pulse separation $\tau \sim T_{2\varepsilon}$. For DUAs at 295 K, $\tau_c = 2 \times 10^{-9}$ sec which in conjunction with $\tau = 10^{-4}$ sec gives $\Delta\omega/2\pi \approx 360$ kHz. This implies that $e^2qQ/h \approx 240$ kHz which is in the expected range (12). The behavior of DUP can be similarly explained.

The NMR results show there to be rapid exchange of deuterium between all the hydrogen bond sites in DUP and DUAs, and that all the deuteriums participate in the transport process.

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