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CATIONIC CONDUCTIVITY, WATER SPECIES MOTIONS AND PHASE TRANSITIONS IN $\text{H}_3\text{UO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$ (HUP) AND MUP RELATED COMPOUNDS ($\text{M}^+ = \text{Na}^+, \text{K}^+, \text{Ag}^+, \text{Li}^+, \text{NH}_4^+$)

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$\text{MUO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$ ($\text{M}^+ = \text{Na}^+, \text{K}^+, \text{Ag}^+$) and $\text{MUO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ ($\text{M}^+ = \text{Li}^+$) materials have been studied using calorimetry and vibrational spectroscopy (IR, Raman and neutron between 100 and 360 K). Conductivity has been determined with the complex-impedance method between 250 and 360 K. Except for AgUP, all the materials exhibit a low-activation-energy domain ($E_A \sim 0.3$ eV) at high temperature and a high-activation-energy domain ($E_A \sim 0.6$ eV) below the transition. Various phases or domains are distinguished between 100 K and 350 K, from a quasi liquid state to an ordered (hydrogen-bonded) water-molecule layer. The room-temperature conductivities are 5×10^{-3} , 2.5×10^{-4} and $7 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$, for HUP, NaUP and KUP respectively. The role of cation size on the ordering process and on conductivity mechanisms is discussed. Comparison with HUP, DUP and mixed H/DUP materials is made.

1. Introduction

$\text{H}_3\text{UO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$ (HUP), alternatively represented by $\text{HUO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$, is among the best-known fast-proton solid conductors $\sigma_{RT} \sim 6 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ and is used in microionic devices such as sensors, super-capacitors, electrochromic display, batteries, etc. [1,2]. The structure consists of infinite sheets of $(\text{UO}_2\text{PO}_4)_n$ entities separated by a two-level water-molecule layer, (fig. 1), oxygen atoms of this layer form squares and are hydrogen bonded; one of the four water molecules is replaced by an H_3O^+ ion [3]. H_3O^+ ions can be exchanged by $\text{K}^+, \text{Na}^+, \text{Ag}^+, \text{NH}_4^+$ ions, and these materials also exhibit ionic conductivity [4].

In our previous works [5–7] vibrational studies led us to propose, in particular considering isotopic, diluted

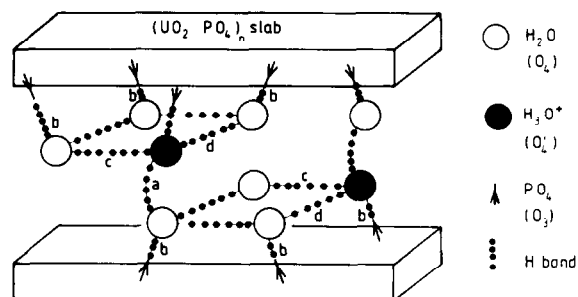


Fig. 1. Schematic representation of the water layers in HUP.

spectra (H/D) as a function of temperature, a phase-transition mechanism for HUP from a bidimensional quasi-liquid state of protonated species in the super-protonic phase to a completely ordered crystal at low temperature. Room-temperature conductivity appears mainly to occur by both H_3O^+ and H_2O jumps in the

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quasi-liquid state. Correlatively $M^+(K^+, Na^+, Ag^+ \dots)$ conductivity could also involve both H_2O and M^+ jumps.

In this paper, we first present conductivity determination of HUP, KUP, NaUP, AgUP and LiUP ($LiUO_2PO_4 \cdot 4H_2O$) compounds; and, on the basis of a detailed vibrational study (using IR spectroscopy, Raman and inelastic neutron scattering), we discuss phase transitions and conductivity mechanisms.

2. Experimental

HUP was prepared as described in [5]. M^+ isomorphs were obtained by ionic exchange in convenient 2 M $MCl(MNO_3)$ aqueous solutions during a few days to a few weeks as a function of the M^+ cations. Compositions and exchange rate (higher than 98%) were determined from chemical analysis done by the Service Central d'Analyse du CNRS (69. Vernaison, France) and from combined ponderal and calorimetric analysis. Deuterated samples were prepared by isotopic exchange in a D_2O atmosphere during a few months as a function of the M^+ cation, as previously described [5,7].

Infrared spectra of suspensions of crystalline powders in Nujol and Fluorolube, taken through CaF_2 and TPX windows, were recorded at various temperatures (between 100 and 350 K) on Perkin Elmer 783, 983 and 180 spectrophotometers on a FTIR Bruker instrument in the mid- and far-infrared region, respectively.

Raman spectra were recorded on a R.T.I. 30 DILOR triple monochromator apparatus in the 50–350 K temperature range. The 647.1 nm line of a Spectra-Physics Krypton ion laser of about 300 mW was selected as the exciting line.

Inelastic neutron scattering was performed at the Laue-Langevin Institute in Grenoble, France with the multichopper time of flight IN6 spectrometer between 80 and 350 K. A 5.1 Å incident wave length was used. The sample thickness was calculated to give 8 to 10% of elastic scattering. Spectra were corrected by the CROSSX [8] standard program of corrections for detector efficiency, sample container, scattering, absorption and self-shielding. A blank run was subtracted. Spectra were normalized by comparison with the elastic scattering from vanadium reference.

Conductivity is determined by means of the com-

plex-impedance method: a Solartron (Schlumberger Inc.) impedance analyzer, monitored by an Apple II microcomputer, was used. Pt electrode (foils) were used, the samples being in the form of room-temperature pressure-sintered disks (200 kg/cm^2). Translucent pellets are only obtained for HUP and NaUP in a few hours. Preferable orientations are observed with the c -axis parallel to the pressing direction. Thus, if conductivity measurements were performed parallel to the pressing direction – the more-adapted setting, the measured value is about one half to one order of magnitude lower than the intrinsic ionic conductivity value measured in a parallel direction to the conductivity layer on a well-oriented disk. Thus conductivity values given in this paper which were measured on polycrystalline, partly oriented samples, are slightly lower than the intrinsic values.

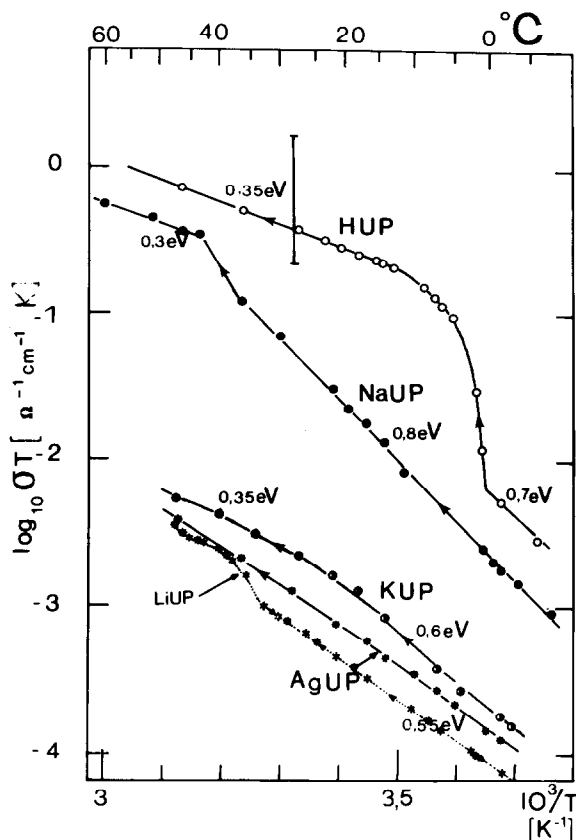
Differential scanning calorimetry runs were done on a Perkin Elmer DSC4 apparatus between 150 and 700 K.

3. ac conductivity

Superprotonic conductivity in HUP has been previously reported by Shilton and Howe both for pressure-sintered pellets [9] single crystals [10]. The unusually high cation mobility in such a structure was expected by Beintema [11] and Wilkins et al. [12]. However, doubts on specific HUP protonic conductivity have been presented [13]. Indeed, the HUP structure could be modified by a water or thermal treatment without any drastic modification of the X-ray powder pattern, but with a lowering both of the phase transition temperature and of conductivity [14,15]. These phenomena are related to water non-stoichiometry and formation of slab stacking faults. Furthermore (i) gradual evolution of the HUP framework into $(UO_2)_3(PO_4)_2 \cdot 4H_2O$ or $(UO_2)(H_2PO_4)_2 \cdot 3H_2O$ ones could occur [15], (ii) use of acetone in order to dry the sample induces modification of the structure, and the HUP material becomes highly hydrophilic [14].

A high mobility of the Na^+ cation in HUP-type structures has been previously pointed out [4], and earlier NMR measurements have shown that the H_2O mobility was important [16].

Fig. 2 shows the conductivity plot ($\log_{10} \sigma T$) as a



function of the inverse temperature. In table 1 our conductivity data are compared with previous literature results. A good agreement occurs, in particular a non-Arrhenius behaviour is observed above the HUP phase transition (II \rightarrow I). The high conductivity of NaUP is confirmed. Except for AgUP, a high (0.5–0.6 eV) and a low (\sim 0.3 eV) activation-energy domain are pointed out for the low-temperature and the high-temperature phases respectively; the transition between the two domains is more or less defined according to the cation nature; in particular a non-Arrhenius behaviour can be observed during the transition.

Weak dsc effects are observed for all these materials (table 2 and fig. 3) in the 260–320 K region. Furthermore, very weak effects are distinguished near 200 K for HUP and KUP (7). The dsc peaks are maximal for well hydrated materials (i.e. a water content close to 3H₂O for Na⁺, H₃O⁺, K⁺) and occur a few degrees or ten degrees below the dehydration process. Thus this phenomenon could be related to the appearance of a water non-stoichiometry. Indeed, for Na, Li, K, AgUP a reversible dehydration could occur without any strong modification of the (UO₂PO₄)_n slab [17].

◀ Fig. 2. Conductivity plot as a function of inverse temperature for MUP pressure-sintered disks (heating cycle). Bars indicate variations as a function of crystallite orientation.

Table 1
ac conductivity of MUP materials.

MUP	σRT ($\Omega^{-1} \text{ cm}^{-1}$)	E_A (eV)	Remark	Ref.
HUP	6.3×10^{-3}	0.32	single crystal	[10]
	4×10^{-3}	0.32	pellet	[9]
	$1-5 \times 10^{-3}$ a)	0.35 ± 0.03	for $T > 275$ K	this work
		0.65 ± 0.05	for $T < 270$ K	this work
NaUP	10^{-4}		pellet	[4]
	2.3×10^{-4}	0.27 ± 0.02	for $T > 310$ K	this work
		0.81 ± 0.05	for $T < 300$ K	this work
KUP	5×10^{-6}	–	pellet	[4]
	7×10^{-6}	0.35 ± 0.02	for $T > 320$ K	this work
		0.63 ± 0.05	for $T < 305$ K	this work
AgUP	4×10^{-6}	0.55 ± 0.02		this work
LiUP	2.4×10^{-6}	0.30 ± 0.02	for $T > 312$ K	this work
		0.60 ± 0.05	for $T < 305$ K	

a) As a function of sample orientation degree.

Table 2

DSC effects in MUP materials. Experiments are made on powder (heating cycle) scan rate 20 K/mn.

MUP	Tonset (K)	ΔH (cal/g)	Remark
HUP	205 \pm 3	<0.05	III \rightarrow II
	260 \pm 10	1.2	II \rightleftharpoons I (E_A^σ anomaly)
	343 \pm 5	180	} dehydration
	430 \pm 5	20	
DUP	205 \pm 5	\sim 0.05	III \rightarrow II
	260 \pm 5	0.4	II \rightleftharpoons I
H-DUP (H/D = 0.5)	250 \pm 10	<0.1	II \rightarrow I
NaUP	305 \pm 5	0.05–1	II \rightarrow I (E_A^σ anomaly)
	339 \pm 5	250	} dehydration
	344 \pm 5		
	423 \pm 5	70	
KUP	185 \pm 5	\leq 0.01	III \rightarrow II
	315 \pm 10	0.5–1	II \rightarrow I (E_A^σ anomaly)
	350 \pm 5	250	} dehydration
	356 \pm 5		
AgUP	386 \pm 5	250	dehydration
	412 \pm 5		
LiUP a)	203 \pm 5	0.1–0.2	very poor
	310 \pm 5		II \rightarrow I (E_A^σ anomaly)
	353 \pm 5	950	} dehydration
	378 \pm 5		
	443 \pm 5	140	

a) $\text{Li}^+\text{UO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$.

4. Water-molecule disorder

The study of local-disorder variations as a function of temperature allows to state precisely the phase transition occurring in MUP materials. The intramolecular forces within UO_2^{2+} , PO_4^{3-} , H_2O and H_3O^+ being much stronger than intermolecular ones, internal and external modes can be distinguished in a good approximation. In this paper, we only discuss librational and translational modes; internal modes have been previously studied [5–7]. The assignment was based on D/H isotopic shifts, analogy with the spectra of simi-

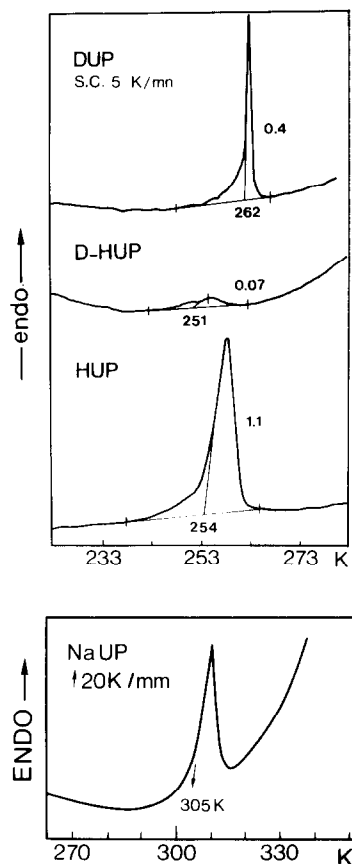


Fig. 3. DSC traces for NaUP (down) and DUP, mixed D-HUP (H/D \sim 0.5) and HUP (up); the heating rates are, respectively, 20 K/mn and 5 K/mn.

lar compounds, and intensity considerations, i.e. modes involving uranyl motions are especially intense on Raman spectra, and only modes involving hydrogen-atom motions give rise to strong (incoherent) inelastic neutron spectra (INS).

4.1. Inelastic neutron spectra

The formalism to treat the INS spectra was established twenty years ago by Egelstaff [19] and was used recently in a comprehensive study of protonic conductivity in β/β'' -aluminas [18]. It consists of extrapolating to the zero momentum transfer the function $\omega^2(S_{\text{incoherent}}/Q^2)(Q, \omega)$, where Q is the

momentum transfer, ω the frequency and S the spectral density. The frequency distribution function

$$P(\omega) = \omega^2 \lim_{Q \rightarrow 0} S_{\text{inc}}(Q, \omega)/Q^2$$

$$= \frac{1}{2} \pi \int dt \exp(-i\omega t) \langle v(0), v(t) \rangle,$$

where $\langle v(0), v(t) \rangle$ is the velocity autocorrelation function. The form of $P(\omega)$ is homogeneous with the $\nu^2 I(\bar{\nu})$ formalism that is now currently used in the analysis of low-frequency infrared and Raman spectra [20,21].

INS spectra are given in fig. 4. They have been calculated with the FLNCE program [8], which allows to obtain respectively the scattering law $S_{\text{inc}}(Q, \omega)$ and the frequency distribution function $P(\omega)$. This latter program also gives the function $P(\alpha, \beta)$, which corresponds to the sum of $\omega^2 S_{\text{inc}}(Q, \omega)/Q^2$.

Experimental conditions on the INS time-of-flight spectrometer involve two limitations: (i) the resolution is not constant and strongly decreases above 40 meV (320 cm^{-1}), which prevents discriminating details in the water-molecule librational-mode region, (ii) at low temperature, long counting durations are necessary and the intensity of spectra is dependent on the state population, only the energy-gain side of the inelastic part being obtained.

Fig. 4 compares $P(\omega)$ spectra of NaUP and KUP materials at 263 and 313 K respectively. As for KUP, well defined modes, assigned to translational and librational modes, are observed at 313 K, in the case of NaUP; even at 263 K only a broad feature centered

at 95 cm^{-1} is visible in the 0–350 cm^{-1} region. The same features are observed in super protonic conductors such as HUP [22], NH_4 and $\text{H}^+(\text{H}_2\text{O})_n$ β/β'' -alumina, $\text{Zr}(\text{H}_3\text{OPO}_4)_2$, H_2O , $\text{H}_3\text{O}^+\text{ClO}_4^-$ or CsHSO_4 [18,24,25]. This is consistent with the existence of a strong rotational and translational disorder of the H_2O species in NaUP. In particular, in the low-energy region (0–50 cm^{-1}), the $P(\omega)$ spectra are more similar to those observed in liquids than in solids (Debye law) [18]. The intense band at about 500 cm^{-1} (table 3) corresponds to rotational modes.

4.2. Librational modes of water molecules

IR spectra give a more detailed view of the region of water-molecule rotational motion. Fig. 5 compares IR spectra of MUP materials and of deuterated derivatives in the 200–1300 cm^{-1} region. Frequencies and assignments are given in table 3. Previous studies on HUP and KUP [7] have assigned the bands near 550 and 650 cm^{-1} to $\text{R}'\text{H}_2\text{O}$ motions. This is consistent with the inelastic-neutron spectra (fig. 4).

These modes decreased with the appropriate ratio on deuteration (fig. 5), and line narrowing occurs at low temperature in the case of HUP, KUP and LiUP material. The effect is not straightforward for NaUP.

It has been shown previously [7] that the PO_4^{3-} ion librational modes narrow at low temperatures as well as the external motions such as metal-ligand $\text{U}(\text{O}-\text{PO}_3)$ modes (narrow bands in the 400–520 cm^{-1} regions). These bands are observed in the case of ordered UO_2-PO_4 slabs.

Fig. 5 compares the low-frequency Raman spectra

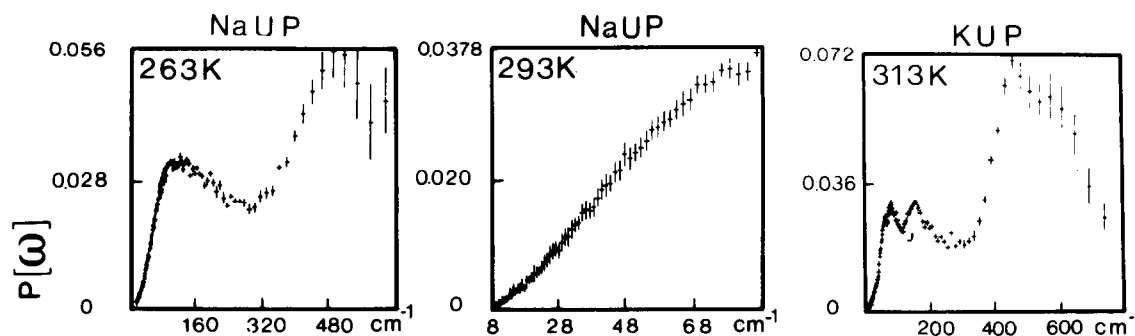


Fig. 4. Inelastic neutron scattering spectra ($P(\omega)$) for KUP at different temperatures.

Water and external modes in MUP materials.

a) Not studied.
b) s: strong, m: medium, w: weak, b: broad, v: very, sh: shoulder.
c) Frequencies in brackets correspond to internal modes.

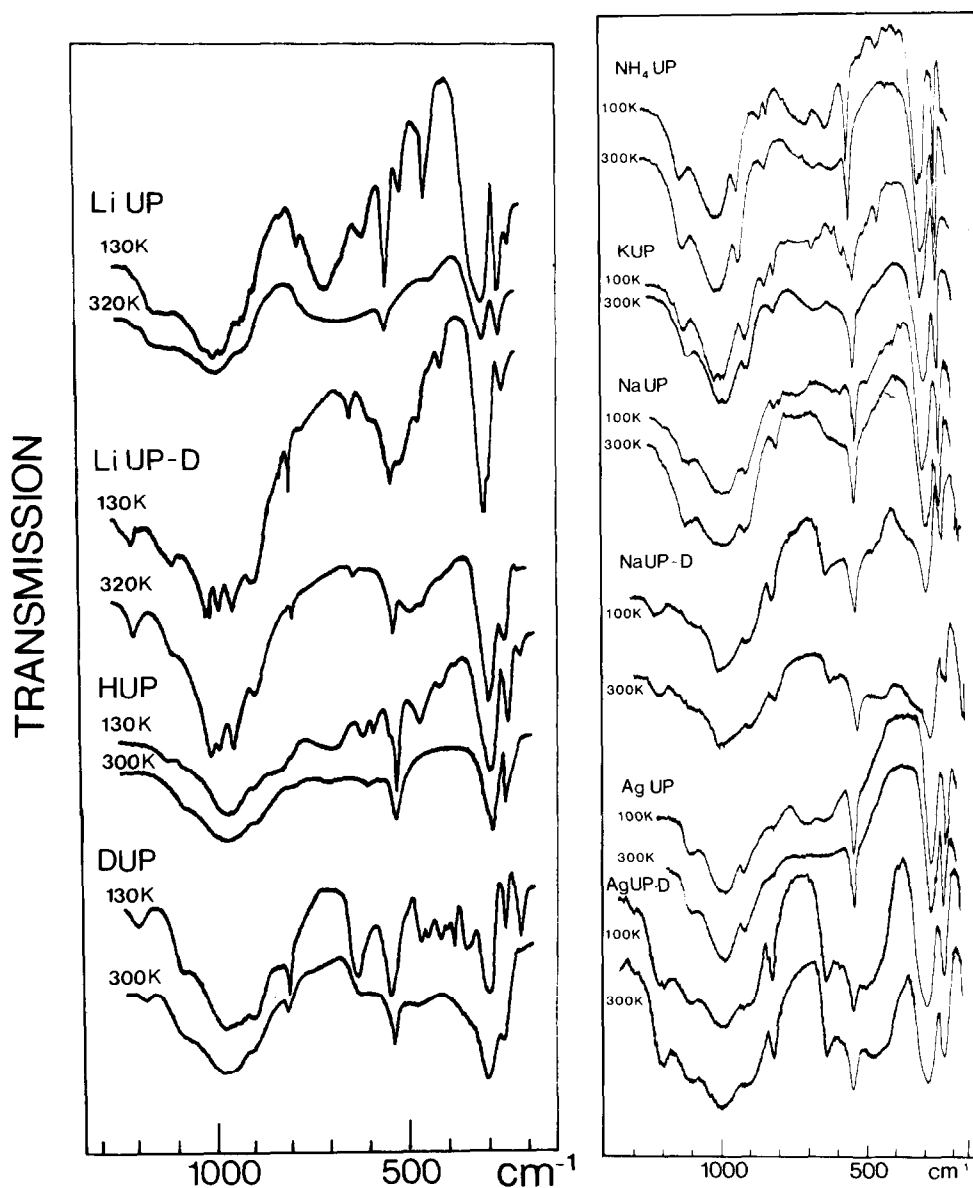


Fig. 5. Infrared spectra ($1300\text{--}200\text{ cm}^{-1}$) of MUP and deuterated derivatives for different materials at 130 and 300 K (320 K).

at room temperature. Previous studies [7] have demonstrated that the mode near $100\text{--}110\text{ cm}^{-1}$ corresponds to PO_4^{3-} librational motion. This mode is large for HUP and NaUP, indicating a PO_4^{3-} orientational disorder associated with disorder of the water-molecule layer. Translational cation modes are only observed for Ag^+ and NH_4^+ cations.

4.3. Isotopic diluted spectra

In order to have a more precise description of the water-layer ordering, νOH spectra isotopically diluted in $\text{MUO}_2\text{PO}_4 \cdot 3\text{D}_2\text{O}$ ($\text{H/D} < 10\%$) have been studied (fig. 6). This method has been fruitfully used for HUP [23] or other superprotonic conductors

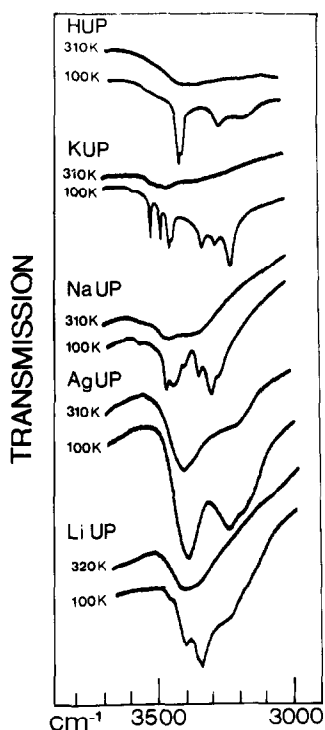


Fig. 6. Infrared OH stretching region of isotopically diluted samples ($H/D < 0.08$) at various temperatures for different MUP materials.

[25,26]; indeed, diluted OH vibrators are free of intramolecular coupling, and their frequencies allow to determine the distance between oxygen atoms of water molecules and of the surrounding oxygen cage, according to the $\nu_{OH} = f(d)$ correlation curve [27]; furthermore the bandwidth is mainly dependent on local disorder (crystal field). Whereas, for all these compounds at room temperature one broad band (with some shoulders) is observed, well defined bands are observed at low temperatures for HUP and KUP; NaUP and LiUP show intermediate features between the first two materials and AgUP.

According to structure refinements [3,28–30], bands are assigned to the different OH vibrators hydrogen-bonded with water molecules, phosphates ions or H_3O^+ ions (table 4).

For all the materials, two kinds of O–H vibrators are distinguished: the more intense modes above 3350 cm^{-1} are assigned to the O–H...O intermolecu-

lar water-molecule bonds, whereas lower-frequency modes ($3350\text{--}3200\text{ cm}^{-1}$) correspond to O–H...(O– PO_3) hydrogen bonds. As in the case of HUP [23], comparison of O...O distances in MUP, deduced from Novak's correlation curve [27], with those given by structural refinements [28] allows assignment of the different hydrogen bonds, especially in the room-temperature phase.

For AgUP, an important disorder remains at low temperature; for LiUP a narrowing is observed. The situation is more complex on the case of NaUP, where broad and narrow bands are simultaneously observed in the low-temperature spectra: this indicates the existence of different configurations for H_2O species, one kind of water molecules being ordered, at local scale ($\nu = 3340\text{ cm}^{-1}$, $\nu = 3345\text{ cm}^{-1}$), the other kind being disordered ($\nu = 3280\text{ cm}^{-1}$, $\nu = 3425\text{ cm}^{-1}$). It is possible that the Na^+ ions are also located in two kinds of environment: i.e. the center of the water square and the square-edge such as K^+ ions. Detailed assignments are proposed in table 4.

4.4. PO_4^{3-} ions librational disorder

Disordering of the water-molecule layers induces a librational disorder of the hydrogen bonded PO_4^{3-} ions. Fig. 7 compares the low-frequency Raman spectra of different materials. Previous studies, on the basis of H/D and $^{18}O/^{16}O$ isotopic shifts, have assigned the band at about $100\text{--}110\text{ cm}^{-1}$ in the room temperature spectra to a PO_4^{3-} librational mode ($R'PO_4$). Except for KUP and NH_4UP , the broadness of the $R'PO_4$ mode is higher than 30 cm^{-1} (FWHH: full width at half height). This indicates the existence of an orientational disorder. At low temperature, previous studies of HUP samples have pointed out considerable splitting and narrowing [7,23]; furthermore, "metal-ligand" $UO'-PO_3$ mode, corresponding to the coupling between UO_2^{2+} and the surrounding PO_4^{3-} ions appears visible on IR spectra at low temperature (see fig. 5 and table 3). A similar feature is clearly evidenced in the case of LiUP and KUP. The modification is not straightforward for NaUP samples.

Table 4
 ν OH isotopically diluted vibrators in MUP materials.

	ν OH (cm^{-1})		$d = f(\nu)$ a)		$d(\text{A})\text{O}\dots\text{O}$ (X-ray)	Assignments
	100 K	310 K	100 K	310 K	300 K	
KUP	3480 m		2.86			
	3450 m	3440 w, b)	2.83	2.82	2.83 [3]	$\text{O}_4-\text{H}_3 \dots \text{O}_4'$ (inter square) b)
	3420 m		2.80			
	3410 sh		2.80		2.80 [3]	$\text{O}_4-\text{H}_2 \dots \text{O}_4$ (intra square)
	3316 w	3320 w, b)	2.74	2.75	2.75 [3]	
	3270 w		2.715			$\text{O}_4-\text{H}_1 \dots \text{O}_3$ (phosphate)
	3225 m		2.70			
NaUP	3550 w		2.94			H_2O (adsorbed)
	3455 m		2.83			$\text{O}_4-\text{H}_3 \dots \text{O}_4'$
	3425 m, b)	3430 w, b)	2.805	2.81		$\text{O}_4-\text{H}_2 \dots \text{O}_4$
	3340 w	3340 sh	2.755	2.755		$\text{O}_4-\text{H}_1 \dots \text{O}_3$
	3280 m		2.72			
AgUP	3375 m, b)	3380 m, b)	2.775	2.78		$\text{O}_4-\text{H}_3 \dots \text{O}_4$
	3325 m, b)	3320 sh	2.74	2.75		$\text{O}_4-\text{H}_1 \dots \text{O}_3$
	3230 sh		2.70			$\text{O}_4-\text{H}_3 \dots \text{O}_4'$
LiUP	3395 w		2.795		2.95 [30]	O_4-O_4
	3395 m	3370 m, b)	2.74	2.77	2.78	$\text{O}_4-\text{H}\dots\text{O}_3$
	3230 sh		2.70			

a) Ref. [27]. b) O_4 : number 4 corresponds to the X-ray description [7]. For a, b, c, d see fig. 1.

5. Phase transitions and conductivity mechanisms

From the spectroscopic point of view, two kinds of materials are recognized: (i) HUP (DUP) and LiUP in which a modification of symmetry is observed, (ii) other materials in which only a librational-mode ordering occurs without any change of the external UO_2 modes (see fig. 7). The first group corresponds to structures where dipoles induce long-range order. In the second group, only a local ordering occurs, and phase-transition effects are suppressed (see fig. 2 and table 2). The substitution of half a deuteron by a proton in HUP samples induces a drastic lowering of the ΔH value measured on the DSC curves (fig. 3). Furthermore, comparison of the evolution of characteristic modes (i.e. the $\text{U}-\text{O}'$ metal-ligand mode at about 480 cm^{-1}) as a function of temperature shows that only a partial ordering occurs (fig. 8).

In the case of materials in which one alkali ion replaces H_3O^+ ($\text{M}^+ = \text{K}^+, \text{Na}^+$), the situation is similar to those of mixed H/DUP samples. All the techniques reveal the existence of different phases. We have chosen to discuss the kinetics for KUP and LiUP.

5.1. Local-ordering mechanism in KUP

In order to have a description of the water-layer evolution as a function of temperature, the bandwidth (FWHH) variations have been determined. They are given in fig. 9. Four domains are recognized: above 330 K the OH-vibrator bands assigned to $\text{O}_4 \dots \text{O}_4$ and $\text{O}_4 \dots \text{O}_3$ hydrogen bonds are broad, and this is characteristic of a rotational and translational disorder of the water molecules; this is consistent with the broad $\text{T}'\text{H}_2\text{O}$ and $\text{R}'\text{H}_2\text{O}$ bands on IR and $P(\omega)$ spectra (table 3). In domain II, the OH vibrators of the differ-

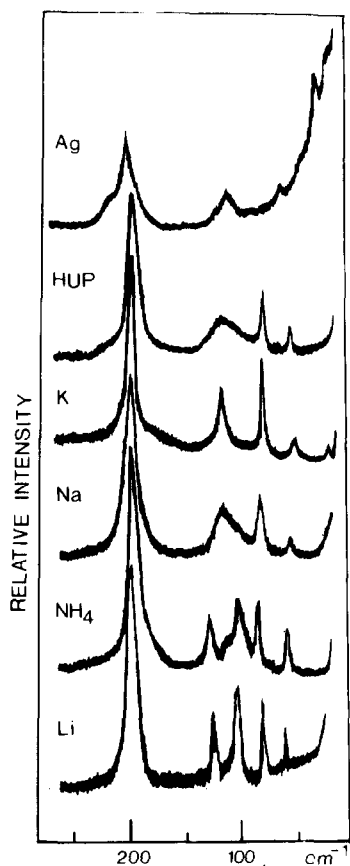


Fig. 7. Low-frequency Raman spectra at room temperature for different MUP materials.

ent hydrogen bonds within the water-molecule squares are distinguished, and the translational disorder is drastically decreased. Simultaneously, the bandwidth of the phosphate-hydrogen-bonded OH vibrators gradually decreases, which indicates that rotational disorder disappears. In phase III, these hydrogen bands are well defined, and only a rotational disorder along the $O_4 \dots O_3$ axis remains. Finally, in domain IV, the last degree of freedom disappears and the H_2O molecules become non-equivalent. This ordering process is similar to those observed for all MUP materials. The transition $II \rightarrow I$ gives rise to a weak DSC effect (table 2) whereas for the transition $III \rightarrow II$ a very small anomaly is occasionally detected. In the case of HUP the strong $H_2O \dots H_2O$ hydrogen bond induces a more pronounced transition when the bond is broken [7,23].

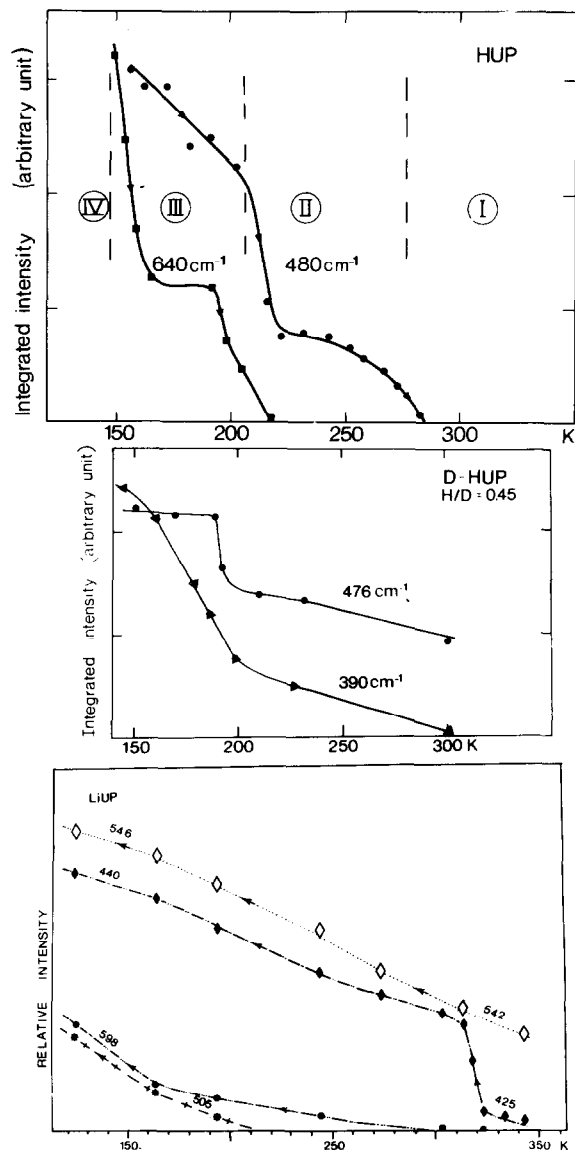


Fig. 8. Comparison of relative-intensity variations as a function of temperature for some characteristic modes in LiUP, HUP and D-HUP materials.

This description is consistent with the evolution of the water-molecule and PO_4^{3-} -ion modes ($200-800 \text{ cm}^{-1}$ region) as a function of temperature (fig. 5). We underline that external UO_2 modes are not modified in KUP (fig. 7).

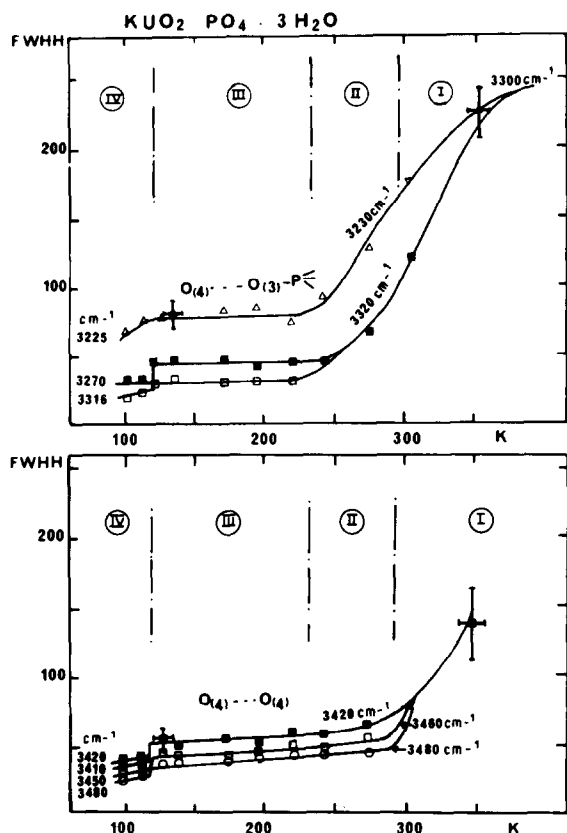


Fig. 9. Bandwidth (FWHH) variations of different OH stretching bands as a function of temperature in the case of an isotopically diluted KUP sample ($H/D < 0.05$).

5.2. Phase transitions in LiUP

Isotopic, diluted ν_{OH} spectra at 100 K (fig. 6) reveal the existence of defined modes whereas only a broad feature is observed at 320 K. Evolution of some characteristic modes is given in fig. 8: (i) a $\nu_2 PO_4$ tetrahedral mode ($\nu = 546 \text{ cm}^{-1}$), (ii) a librational $R'H_2O$ mode ($\nu = 598 \text{ cm}^{-1}$ and (iii) a metal-ligand $U-O'-PO_3$ mode ($\nu = 440 \text{ cm}^{-1}$). The $R'H_2O$ mode, straightforward at 100 K in phase III, disappears above 200 K. This is consistent with a water-molecule layer ordered at 100 K as, for example, in KUP.

A strong modification of the 440 cm^{-1} mode occurs at the $II \rightarrow I$ transition with the formation of the quasi-liquid state. On the other hand, this ordering process does not strongly influence the ν_2 internal PO_4 modes.

5.3. Role of the cation size on phase transition and ordering

The ferroelectric ordering of HUP (HUAs) material is well established [31]. On the other hand, the similarity and the differences between MUP materials have not been discussed.

Steric constraints appear to play an important role in the phase transition. The ordering is built up by the water-molecule arrangement, and the possibility to respect the square symmetry plays a leading part in the ordering energy where a substituted cation is quite smaller (Ag^+ , Na^+) or bigger (NH_4^+) than a water molecule, a static disorder appears to persist at low temperature. In the case of H_3O^+ and K^+ ions, which have a similar size to that of the H_2O molecule, the water layer is well ordered at low temperature. A similar case takes place for LiUP material, where the Li^+ cation is located in the center of the four-water-molecule square at a different z value [30]. However, in the latter case, the possibility to have a Li^+-H_2O solvation process [32] could decrease the degree of order.

Ordering of the water-molecule layer occurs in the same temperature range as observed in ionically doped ice [33,34]. Local or large-range order appears as a result of competing interactions of different strengths: crystalline fields induced from the $(UO_2PO_4)_n$ slab, size and polarization effect of the M^+ cation, and hydrogen bonding.

5.4. Conductivity mechanisms

In all the materials, the highly conducting, low-activation-energy phase is observed for the highly disordered phase. In this phase, the water molecules and the M^+ ions are in a quasi-liquid state, as is revealed by spectroscopy, X-ray [3,11,28] or NMR [35]. Higher conducting properties have been observed for HUP and NaUP. These properties are confirmed by quasi-elastic neutron scattering; among the KUP, NaUP and HUP materials studied, only the latter two show a broadening effect assigned to protonic reorientations [24,36].

The weak conductivity difference between NaUP and HUP – 0.5 order of magnitude at 300 K – disappears if we consider the displacement of the phase-transition temperature (fig. 2). This indicates that Na^+ and H_3O^+ jumps in the quasi-liquid state are the main conducting mechanism. Of course, water

molecules move simultaneously. However, the weak difference could also be related to the proton-transfer contribution (Grotthus mechanism). On the other hand, the difference between NaUP and KUP conductivity properties is important. We have shown that, even at 100 K, a static disorder remains visible in NaUP. This is consistent with the location of one part of the sodium ions in interstitial sites, i.e. the square centers. However, Na^+ ions are smaller than K^+ and H_3O^+ ions, and an intermediate situation between the case of big and small cations such as Li^+ , could occur.

In phase II, where the quasi-liquid state does not exist, a higher activation energy is observed (0.6–0.8 eV). This value is nearly equal to the value of the potential well determined from the frequency of the translational oscillation mode [7]. A M^+ -cation jump associated with an H_2O jump is the more probable mechanism.

Anyway, complementary studies (i.e. accurate structure refinements, quasi-elastic neutron scattering experiments...) are required before definitive conclusions can be drawn about the conducting process: in particular, the conducting pathways, the role of the water stoichiometry, and the partial occupation of the different sites must be carefully specified.

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