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RAMAN SCATTERING STUDY OF $\text{Rb}_{1-x}(\text{ND}_4)_x\text{D}_2\text{PO}_4$ MIXED CRYSTAL

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Raman scattering spectra of a 71.4% deuterated crystal of $\text{Rb}_{0.52}(\text{ND}_4)_{0.48}\text{D}_2\text{PO}_4$ were studied in a wide range of temperatures down to 5 K. At low temperatures the system forms a so-called glass state, with no long range order transition to either a ferroelectric or antiferroelectric phase.

We have concentrated our study on the vibrations related to the internal modes of the molecular groups (phosphate and ammonium). Special attention is focused on the ν_2 (symmetric deformation mode) of the PO_4 and the libration mode of the ammonia, because they are very sensitive to the ordering of the protons, and to the ferroelectric- or antiferroelectric-like ordering for the former and the glass-like arrangement for the latter.

INTRODUCTION

The mixed crystal of ferroelectric RbH_2PO_4 (RDP) and antiferroelectric $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP), i.e. $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ (RADP), gives in a certain range of concentration a suitable competition among three phases (ferroelectric, antiferroelectric and paraelectric) in such a way that the long range order transition is frustrated, and a glass-like system at low temperatures with a random distribution of dipoles is achieved.¹

RDP and ADP are KH_2PO_4 (KDP) isomorphs at high temperatures (space group $\text{I}\bar{4}2\text{d}-\text{D}_{2\text{d}}^{12}$). In RDP the low temperature phase has long range order and contains the so-called "up-down" Slater configurations, with a spontaneous polarization along the c-axis and a symmetry $\text{Fdd2}-\text{C}_{2\text{v}}^{19}$ in the ferroelectric phase. In ADP by contrast, the acid protons assumed one of four "lateral" Slater configurations in the low temperature phase, with an antiferroelectric ordering of dipoles and a symmetry $\text{P2}_12_1-\text{D}_2^4$. At intermediate concentrations, i.e. $0.22 < x < 0.78$, the long range order transitions are suppressed and no ordering occurs at low temperatures,^{1,2} so that the $\text{O}-\text{H}\cdots\text{O}$ "acid" protons remain disordered. In this concentration range, upon lowering the temperature, freezing of a randomly frustrated system inside a crystalline lattice is obtained. Some authors call such systems "structural glasses", others "dipole glasses". They are similar to some magnetic spin glasses, but with competition between structures in place of spins.^{2,3}

Systems with competing structural orderings have some advantages with respect to their magnetic counterparts. In particular, dielectric dispersion measurements in a broad range of frequencies are very accessible, and specially due to the transparence of RADP any kind of optical measurements are easily obtained in contrast with magnetic spin-glass systems. For example, light scattering experiments in the KDP family are very enlightening because all vibrational modes important for the long range order transitions are Raman active in both phases. A very interesting point is to investigate the site symmetry of molecular groups in KDP-type compounds by Raman scattering. With this kind of information we can study the character of the transition. In RDP the local symmetry of the PO_4 group is C_2 in the paraelectric and ferroelectric phases.⁴ By contrast, in ADP the symmetry of both molecular groups PO_4 and NH_4 was found to be C_2 in the paraelectric phase and C_1 in the antiferroelectric one.⁵ An excellent review for light scattering experiments in the KDP family was presented by Tokunaga and Tatsuzaki.⁶

Raman scattering in RADP mixed crystals can give very important information because the glass formation is usually related to the dynamics of the ammonium groups. In particular, the partial substitution of NH_4 by Rb atoms will induce a laterally off-center NH_4 positions which implies alternatively local "up" and "down" Slater configurations at each NH_4 site,⁷ in place of the usual RDP (or ADP) long range ordering.

The present paper reports the Raman spectra at different temperatures, paying special attention to the local environments and internal vibration modes of the molecular groups.

EXPERIMENTAL

$\text{Rb}_{0.52}(\text{ND}_4)_{0.48}\text{D}_2\text{PO}_4$ (DRADP) single crystals were grown by slow evaporation from solution in an argon atmosphere, showing the typical habit for KDP family single crystals. The deuterium concentration was estimated as 71.4% from mass-spectrometry experiments. The crystal comes from the same batch that V. H. Schmidt *et al.*⁸ used for dielectric measurements. The surfaces of a 2 cm^3 single crystal were oriented perpendicular to the x , y and z tetragonal axes.

All Raman spectra were obtained in a right angle configuration. An argon ion laser operating on the 5145 \AA line with an average incident power of 500 mW probed the sample which was placed in a helium cryostat. The scattered light from the sample was collected and analyzed by a double monochromator and then focused onto a photomultiplier tube. The resulting signal from the electronic detection system was recorded on chart paper.

The thermal stability was estimated as $\pm 0.1\text{ K}$ and the spectral resolution averaged about $2\text{--}3\text{ cm}^{-1}$.

RESULTS AND DISCUSSION

DRADP has the tetragonal crystallographic symmetry (D_{2d}^{12}) with two formula units per primitive cell. Pure ADP has 51 optical branches as indicated by the

factor group analysis.^{5,9} RDP has 40 Raman active branches.¹⁰ The situation in DRADP is much more complicated than in the parent compounds, because of partial deuteration (71.4%) and the fact that also 48% of Rb atoms have been substituted by $\text{NH}_{4-x}\text{D}_x$ groups. In this case, the site symmetry is expected to break much more easily than in the pure compounds (DRDP and DADP),^{4,5} in which this behavior has been observed even at room temperature (RT). The relative abundance of each species due to partial deuteration is calculated in Table I. These results will be used in the assignment of the spectra. Because of all these reasons it is meaningless to make a complete table for all the modes and symmetries from the factor group analysis, as can be made in RDP,¹¹ and ADP.⁵

The modes of symmetries A_1 , B_1 , B_2 and E are Raman active. B_2 and E are also infrared active with polarizations parallel and perpendicular to the tetragonal c -axis, respectively. A_1 , B_2 and E were measured in $x(zz)y$, $x(yx)y$ and $x(zx)y$ geometries, respectively, with the same crystal orientation. In order to measure the B_1 symmetry, the crystal should be rotated for instance to $z(xx)y$ geometry where A_1 and B_1 symmetries are active.

TABLE I
Relative abundance of $\text{NH}_{4-x}\text{D}_x^+$, and $\text{H}_{1-x}\text{D}_x\text{PO}_4^-$ groups due to the partial deuteration (71.4%), see text

Species	Probability	Number of equivalent species	Relative abundance (%)
ND_4^+	0.2599	1	25.99
ND_3H^+	0.1041	4	41.64
ND_2H_2^+	0.0417	6	25.02
NDH_3^+	0.0167	4	6.68
NH_4^+	0.0067	1	0.67
			Total: 100%
D_2PO_4^-	0.0818	1	8.18
HDPO_4^-	0.2042	2	40.84
H_2PO_4^-	0.5098	1	50.98
			Total: 100%

(a) *Low frequency region and internal modes of the D_2PO_4 species (0–1200 cm^{-1}).*

In our DRADP crystal with 52% rubidium (48% ammonium) we will have new external modes i.e. those involving Rb to ND_4 relative motions with respect to D_2PO_4 groups. The low frequency region is thus more complicated than in the pure compounds DRDP and DADP.

In Table II we have made an assignment of the modes, trying to be consistent with the assignments in the pure compounds DRDP^{4,11} and DADP⁵ as well as previous data on RADP.⁷

The internal modes of the PO_4 group are labeled as ν_1 to ν_4 , after Herzberg.¹² The symmetric stretching ν_1 is non-degenerate with A_1 symmetry. At RT, the leakage into other symmetries is practically negligible (See Figure 1.a). By contrast, at low temperatures the leakage is strong compared with the permitted

TABLE II

Low frequency modes at two different temperatures (room temperature and 5 K), with the corresponding assignments, mostly related with the phosphate group

$T = 300 \text{ K}$				$T = 5 \text{ K}$				Assignments
$(A_1 + B_1)$ $z(yy)x$	(B_2) $x(yx)y$	(E) $x(zx)y$	(A_1) $x(zz)y$	$(A_1 + B_1)$ $z(xx)y$	(B_2) $x(yx)y$	(E) $x(zx)y$	(A_1) $x(zz)y$	
83	—	83	(75)	80	80	80	80	External modes
(114)	—	—	—	—	—	(100)	—	
—	—	126	—	—	137	135	132	
177	—	170	—	182	175	175	178	PO ₄ libration
—	—	—	235	235	237	241	237	ND ₄ libration
354	—	(360)	350	347	—	345	344	ν ₂ of PO ₄
—	—	—	—	—	358	—	—	
385	379	—	—	388	386	—	—	
—	—	—	—	406	—	400	412	ν ₄ of PO ₄
456	—	—	—	462	462	470	465	
—	490	480	—	—	482	—	—	
—	—	—	—	509	—	507	509	ν ₄ of PO ₄
—	—	526	520	—	520	520	—	
540	—	551	—	550	550	550	556	
—	—	—	—	622	—	—	—	ν ₁ of PO ₄
680	—	—	710	706	718	712	700	
888	887	925	899	881	881	881	881	
—	—	—	—	892	894	887	894	δ(OD)
963	962	975	955	967	962	962	962	
—	1075	1075	—	—	—	1112	—	ν ₃ of PO ₄
—	—	—	1120	—	—	—	—	

Raman modes. The leakage is stronger in the E than in the B₂ symmetry (See Figure 2.a), probably as the result of the lowering from S₄ to C₂ (or even to C₁ site symmetry). Another peculiar characteristic of the ν₁ mode is that at low temperatures it becomes a doublet with a narrow frequency shift of about 12 cm⁻¹ (See Figure 2.a). Because ν₁ is a non-degenerate mode there are only three possibilities for this doublet. First, a Davydov splitting, due to dynamical coupling between the two PO₄ groups in the primitive cell. This can be disregarded because the ratio of intensities is almost the same in all the scattering configurations, so they have the same symmetry. The second possibility for the doublet could be the non-equivalence of the two PO₄ groups. If such is the case, the doublet should appear even in the pure compounds (RDP and ADP), and certainly this is not the case.^{11,5} The third one is that the PO₄ groups have different environments depending on the attaching to NH_{4-x}D_x species or Rb atoms, which will produce slightly different ν₁ vibration frequencies. The third argument is a peculiarity of DRADP mixed crystals, and it is also very reasonable taking into account that the oxygens of the PO₄ groups are bonded to the ammonia groups by hydrogen bonds instead of pure ionic bonding as in the case of the rubidium atoms.

The symmetric deformation ν₂ (doubly degenerated in the free PO₄) has two bands of A₁ and B₂ symmetries. The frequency of the ν₂ mode depends on the proton arrangement around the PO₄ group. If the proton arrangement varies with the temperature the mass of the D₂PO₄ group will change as well as the force

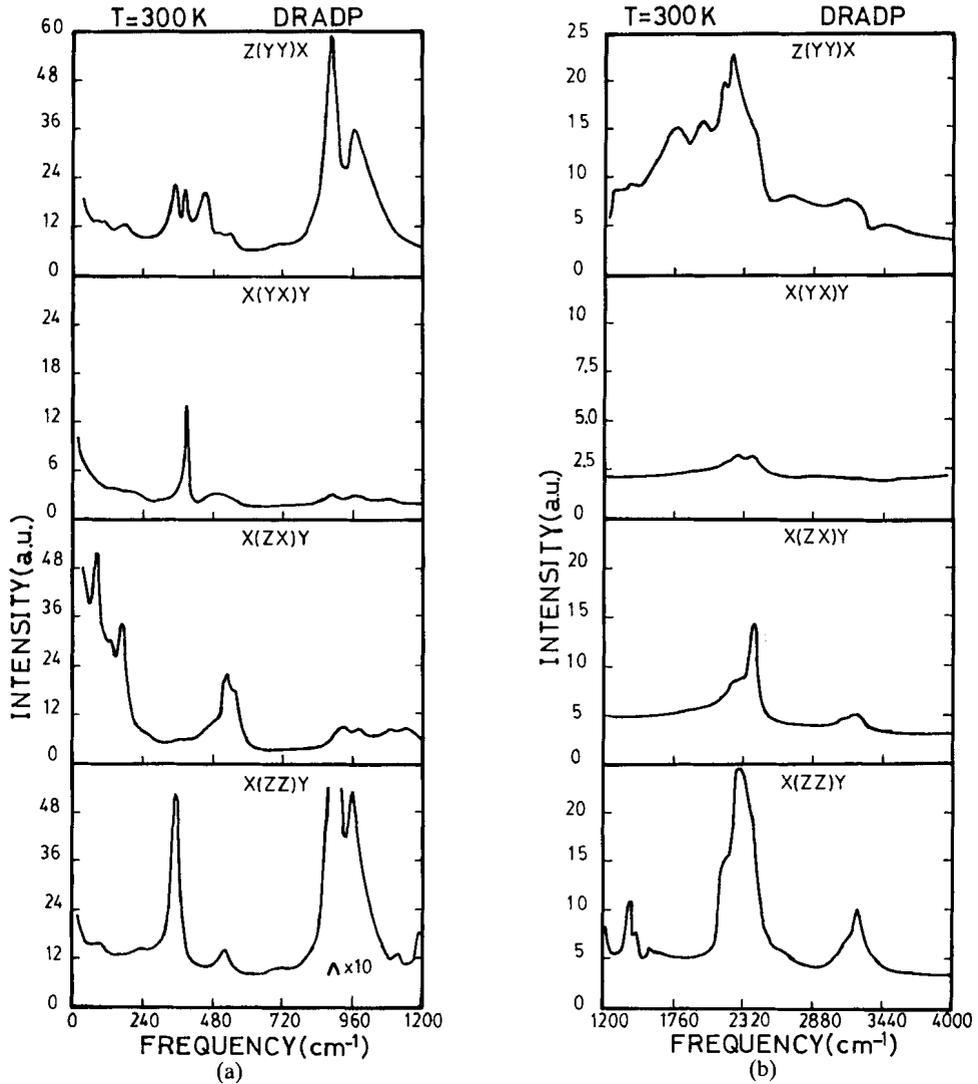


FIGURE 1 Raman spectra of A_1 , B_1 , and B_2 and E symmetries for DRADP at room temperature; (a) Low frequency region ($0-1200 \text{ cm}^{-1}$), (b) High frequency region ($1200-4000 \text{ cm}^{-1}$).

constants, thus changing the frequency of the mode. Figure 3 shows the frequency of the two modes at different temperatures. One can associate the break at approximately 200 K with the glass formation temperature.^{13,14} This result is in very good accordance with very recent dielectric data, from Courtens,¹⁵ in a fully deuterated RADP sample (60% of Rb), which indicate a freezing temperature of 180 K. Otherwise the main trend of the ν_2 frequency is to increase upon lowering the temperature, as we will expect from the strength of the force constants due to the thermal contraction of the crystal.

The ν_3 and ν_4 modes, corresponding to antisymmetric stretching and deformation respectively (triply degenerate modes in the free PO_4), split into two bands

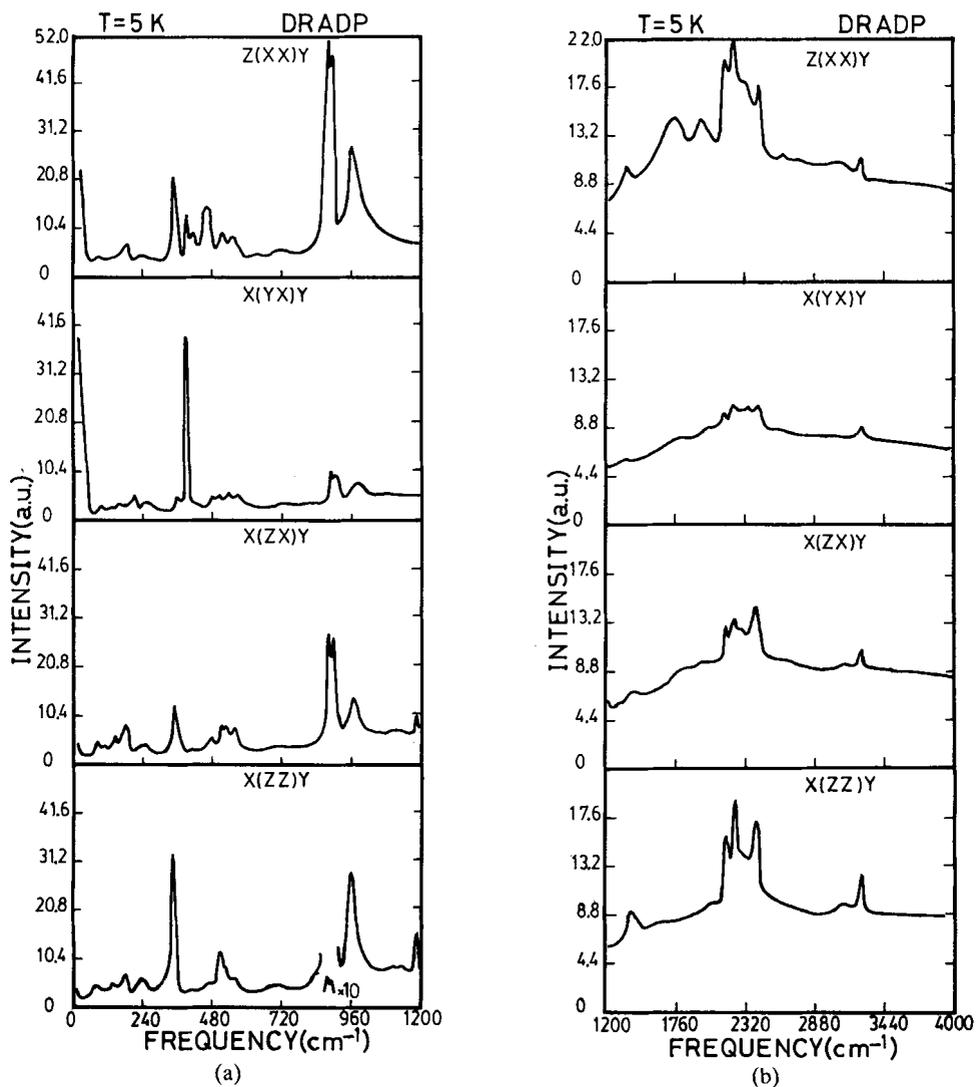


FIGURE 2 Low temperature Raman spectra for DRADP in A_1 , B_1 , B_2 and E symmetries; (a) Low frequency region ($0-1200\text{ cm}^{-1}$), (b) High frequency region ($1200-4000\text{ cm}^{-1}$).

of B_2 and E symmetries. At RT both modes leak into the A_1 symmetry as an indication of the C_2 site symmetry. At low temperatures, there is a total lifting of the site symmetry.

We also assign the 962 cm^{-1} mode to the in-plane bending $\delta(\text{OD})$ in accordance with the pure DRDP.⁴

Also in this region of frequencies we have the external translational modes of the Rb and $\text{NH}_{4-x}\text{D}_x$ against the D_2PO_4 group, as well as the librations of the D_2PO_4 and $\text{NH}_{4-x}\text{D}_x$ groups.

In accordance with Kasahara *et al.*⁵ for DADP we assign the 175 cm^{-1} mode to the libration of the phosphate group. Also after Courtens and Vogt⁷ the 237 cm^{-1}

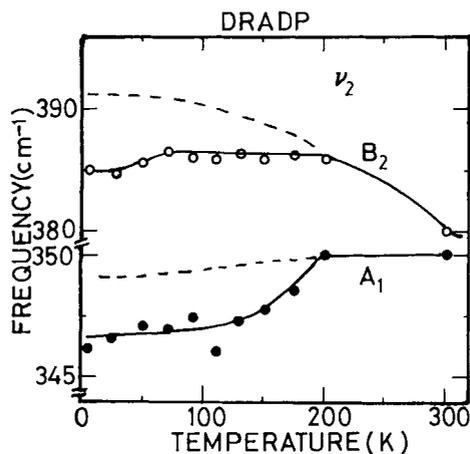


FIGURE 3 Temperature dependence of the frequency of the symmetric deformation ν_2 mode for the phosphate group. Curves are just a guide to the eye. Broken line is a qualitative extrapolation of the anharmonic Debye behavior. The break at approximately 200 K is associated with the glass formation temperature.

mode can be assigned to the ammonia libration, due to its peculiar temperature dependence and the ratio $1/\sqrt{2}$ related with the deuteration effect. Figure 4 shows the temperature dependence of the ammonia libration in the E symmetry. At RT the libration band is very weak, but the peak intensity clearly increases with passing through the glass formation temperature. As pointed out by Courtens and Vogt,⁷ this is an indication that the glass formation in RADP should be associated with the fixation of the ammonium groups, because such fixation is necessary in order to have a well defined libration peak. Also the forbidden ν_2 peaks have a remarkable temperature dependence, growing in intensity even below 70 K, in agreement with the Courtens and Vogt⁷ data for the hydrogenated isomorph.

(b) *Internal modes of the ammonium species, high frequency region (1200–4000 cm^{-1}).*

The internal modes of the ammonium ions are very difficult to assign in the present case due to the complexity introduced by the partial deuteration. In Table I we have listed the five possible ammonium species together with their estimated relative abundance, supposing that the deuterium has the same probability to substitute for acid protons as for ammonium ones. We have also made the assumption that the deuteration of one bond of the ammonium is not affected by the previous deuteration of neighbouring bonds.

Under these circumstances we have made tentative assignments in Table III, trying to be consistent with the previous assignments of Kasahara *et al.*⁵ for ADP and DADP, and Courtens and Vogt⁷ for RADP. We can distinguish clearly two zones for the stretching modes. One corresponds to N–H stretching and the other to N–D stretching, with the proper frequency relation $1/\sqrt{2}$ between them. In the former, the most intense bands must correspond to the N–H stretching of the

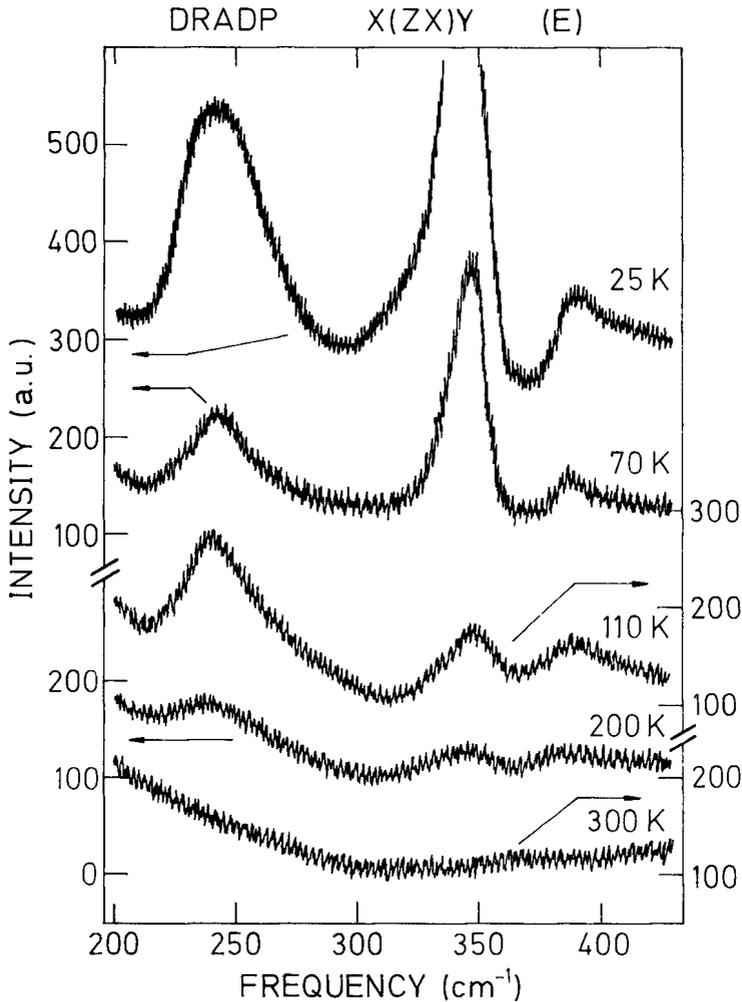


FIGURE 4 Libration mode ($\sim 247 \text{ cm}^{-1}$) of the ammonium groups at different temperatures. The other two peaks showed in the spectra are two forbidden vibrations of the phosphate group (ν_2), which are not allowed in the E symmetry if the symmetry rules are fulfilled.

most abundant species ND_3H (41.64% abundance, one bond) and NH_2D_2 (25.02% abundance, two bonds). ν_1 and ν_3 bands of pure NH_4 are unlikely to be seen due to their low relative abundance. In the latter the most intense band must correspond to the coupled N–D stretching of ND_3H and the others to ν_1 and ν_3 bands of pure ND_4 and coupled N–D stretching of ND_2H_2 species.

With respect to the bending modes the most probable will be ND_2 (NH_2) of the species ND_2H_2 . Also we will have some probability to see the NHD bending.

Because the peaks themselves are very broad and all the ammonium species should give very close frequencies for the internal modes, the assignments in this region of the spectra are difficult, in spite of the increase of resolution.

TABLE III

High frequency modes at two temperatures (room temperature and 5 K) with the more probable assignments mostly for the internal modes of the ammonium species

$T = 300 \text{ K}$				$T = 5 \text{ K}$				Assignments
$(A_1 + B_1)$ $z(yy)x$	(B_2) $x(yx)y$	(E) $x(zx)y$	(A_1) $x(zz)y$	$(A_1 + B_1)$ $z(xx)y$	(B_2) $x(yx)y$	(E) $x(zx)y$	(A_1) $x(zz)y$	
—	—	1155	—	—	—	—	1132	} ν_4 of ND_4
—	—	—	1190	—	—	1187	1186	
1381	—	—	—	1375	1350	—	—	} ν_2 of ND_4
—	—	—	1410	—	—	1425	1400	
—	—	—	1468	—	—	—	—	} NH_2 deformation of $\text{NH}_{4-x}\text{D}_x$ species
—	—	—	1570	—	—	—	—	
1763	—	—	—	1750	1800	1770	1740	
1955	—	—	—	1962	—	1950	1940	
2160	—	—	2163	2162	2162	2162	2169	} ND stretching of $\text{NH}_{4-x}\text{D}_x$ species ν_1 and ν_3 of ND_4 groups.
2233	—	—	—	2231	2237	2235	2236	
—	2250	2245	—	—	—	—	—	
—	—	—	2280	—	—	2300	—	
—	2375	—	—	2350	2350	—	—	
—	—	—	—	—	—	2400	2400	
2410	—	2408	—	—	—	—	—	
—	—	—	—	2425	2431	—	—	
2720	—	—	—	2625	—	—	—	
—	—	—	—	3090	3100	3100	3100	} NH stretching of $\text{NH}_{4-x}\text{D}_x$ species
3230	—	3230	3235	3255	3250	3250	3250	
—	—	3245	—	—	—	—	—	

CONCLUSIONS

We have made the initial assignments of the Raman spectra in deuterated RADP. Special attention was paid to the internal modes of the molecular groups (phosphate and ammonium). In the case of the ammonium, the assignments are only tentative due to the complexity of the partial deuteration (71.4%) which produce some probability for the different ammonium species ($\text{NH}_{4-x}\text{D}_x$).

A very peculiar characteristic of the DRADP Raman spectra was detected in a narrow splitting (12 cm^{-1}) in the ν_1 mode of the phosphate group. An interpretation of this doublet was made in terms of the different environments of the PO_4 groups formed by different proportions of Rb and NH_4 . This is a peculiarity of the DRADP mixed crystals and should be dependent on the Rb concentration.

From the temperature dependence of the frequency of the ν_2 mode of the phosphate groups, the break at approximately 200 K was associated with the onset of freezing, which is the temperature where the system starts to fix the low temperature glass-like state. This temperature is in excellent agreement with recent dielectric data in DRADP (100% deuterium, 40% rubidium)¹⁵ where the freezing temperature was reported at 180 K.

Finally, the temperature dependence of the libration mode of the ammonium species have been carefully studied. The intensity of this mode start to grow at approximately the same temperature (200 K) where the ν_2 frequency deviate

from the anharmonic Debye behavior. In the other hand, the intensity of the libration mode of the phosphate group is much higher than the ammonium one. This is probably due to a bigger distortion of the phosphate group and also to the higher polarizability of the oxygen atoms, in contrast to the hydrogen ones, thus the Raman tensors for the former should be higher.

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