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Hydrogen Bonds in α-$Na_3PS_4 \cdot 8H_2O$: X-Ray Diffraction and Vibrational Spectroscopic Study

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Crystal structure and vibrational spectra of α-$Na_3PS_4 \cdot 8H_2O$, monoclinic, space group $P2_1/c$, a = *8.644(2),* b = *12.853(2),* c = *13.586(2)* Å, β = *103.41(1)°,* V = *1468.3* Å^3, Z = *4, have been studied to supplement our investigation on hydrogen bonds in the isostructural $Na_3AsS_4 \cdot 8D_2O$. The thiophosphate differs structurally from the thioarsenate, mainly by the smaller size of the XS_4 tetrahedron ($\langle P–S \rangle$ = 2.043 Å, $\langle As–S \rangle$ = 2.161 Å), while bond lengths of the $Na(H_2O)_4S_2$, $Na(H_2O)_5S$ and $Na(H_2O)_6$ octahedra as well as those of the hydrogen bonds – mainly of O–H···S type – remain almost unchanged. This is reflected in the frequencies of uncoupled O–H(D) vibrations, which are very similar to those of the thioarsenate (at T = 75 K: $\bar{\nu}_{OH}$ = 3275–3620 cm^{-1}, $\bar{\nu}_{OD}$ = 2431–2665 cm^{-1}).*

TABLE I. Crystal Data.

	α-$Na_3PS_4 \cdot 8H_2O$	$Na_3AsS_4 \cdot 8H_2O$ ref. [2]
	monoclinic, space group $P2_1/c$	
a	8.644(2) Å	8.682(2) Å
b	12.853(2)	12.967(2)
c	13.586(2)	13.692(2)
β	103.41(1)°	103.39(1)°
V	1468.3 Å^3	1499.5 Å^3
Z	4	4
Mr	372.3	416.3
Dc	1.68 Mg m^{-3}	1.84 Mg m^{-3}

Introduction

$Na_3PS_4 \cdot 8H_2O$ crystallizes in two different forms which are both monoclinic and which have been designated as I and II [1]. Form II, called α-$Na_3PS_4 \cdot 8H_2O$ in this paper, is isotypic with the only known form of $Na_3AsS_4 \cdot 8(H,D)_2O$, which we recently investigated by X-ray and neutron diffraction and by Raman spectroscopy, paying special attention to the hydrogen bonds [2, 3]. As the thioarsenate was found to contain an unusually broad spectrum of O–H(D)···S type bonds with respect to bond geometry as well as bond energies, it seemed worthwhile to also study the thiophosphate in order to learn whether the replacement of AsS_4 by PS_4 leads to changes in the structure, the hydrogen bonds and/or hydrogen bond strengths. Our recent studies [2, 4, 5] have demonstrated that special X-ray refinement techniques may provide hydrogen atom positions and geometrical data on hydrogen bonds with sufficient accuracy for a correlation with vibrational spectroscopic data.

Crystal Growth

Raw material of $Na_3PS_4 \cdot 8(H,D)_2O$ with 0, 5 and 95% deuteration was obtained [6] from Na_2S, P_2S_5 and the appropriate $H_2O–D_2O$ mixtures. While this method frequently yielded both forms of $Na_3PS_4 \cdot 8(H,D)_2O$, only the α-form was obtained on recrystallizing the raw material from solutions with ~50 weight% $Na_2S \cdot 9(H,D)_2O$ in $H_2O–D_2O$ mixtures at temperatures in the range of 25–40 °C. By controlled slow cooling, well-formed short-prismatic colorless crystals similar to those of the thioarsenate were obtained, with maximum dimensions of about 2 cm.

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TABLE II. Atomic Parameters for α-$Na_3PS_4 \cdot 8H_2O$.

(a) Fractional atomic coordinates $\times 10^5$ and equivalent isotropic thermal parameters.[a]

Atom	*x/a*	*y/b*	*z/c*	*Beq*
Na(1)	0	0	0	2.77(2)
Na(2)	50000	50000	0	2.80(2)
Na(3)	33817(7)	55148(5)	40846(4)	2.52(2)
Na(4)	82984(7)	6013(5)	41705(4)	2.73(2)
P	71283(4)	67142(3)	25214(2)	1.52(1)
S(1)	78415(4)	52034(3)	28544(3)	1.89(1)
S(2)	60972(4)	68743(3)	10310(3)	2.16(1)
S(3)	55688(4)	71090(3)	33795(3)	2.45(1)
S(4)	90810(4)	76705(3)	28433(3)	2.15(1)
O(1)	19507(14)	10471(8)	95894(8)	2.89(3)
O(2)	14929(14)	84807(9)	96512(8)	2.78(3)
O(3)	74025(14)	40146(9)	6748(8)	3.05(3)
O(4)	40818(13)	46110(8)	14557(8)	2.50(3)
O(5)	53140(13)	42606(9)	41053(8)	2.64(3)
O(6)	14346(13)	51946(9)	25073(9)	2.72(3)
O(7)	78802(15)	23572(10)	34914(8)	3.25(3)
O(8)	9244(14)	11182(9)	49938(9)	2.92(3)
H(11)	18329	15579	90617	
H(12)	27017	13556	101453	
H(21)	6885	80914	91922	
H(22)	17646	80929	102713	
H(31)	77417	42732	13536	
H(32)	71230	32996	7423	
H(41)	49107	48375	20141	
H(42)	40422	38693	15291	
H(51)	60938	44552	37382	
H(52)	50211	35505	39390	
H(61)	3878	53017	26161	
H(62)	14875	44496	24759	
H(71)	68670	23451	30164	
H(72)	86647	23765	30941	
H(81)	17572	13519	46868	
H(82)	10105	15579	55752	

(b) Anisotropic temperature factors.[b]

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na(1)	320(4)	311(4)	420(5)	−33(4)	141(4)	13(4)
Na(2)	344(5)	394(5)	326(5)	−2(4)	109(4)	−42(4)
Na(3)	297(3)	326(3)	335(3)	53(2)	67(2)	8(3)
Na(4)	386(3)	360(3)	293(3)	−75(3)	97(3)	−14(3)
P	217(2)	179(2)	180(2)	−7(1)	43(1)	2(1)
S(1)	285(2)	196(2)	238(2)	23(1)	64(1)	21(1)
S(2)	372(2)	256(2)	194(2)	−6(1)	3(1)	12(1)
S(3)	325(2)	279(2)	325(2)	25(1)	159(2)	−7(1)
S(4)	257(2)	254(2)	306(2)	−63(1)	32(1)	4(1)
O(1)	419(7)	334(6)	345(6)	−109(5)	132(5)	−5(5)
O(2)	350(6)	370(6)	336(6)	−112(5)	−1(5)	35(5)
O(3)	464(7)	390(7)	304(6)	37(5)	97(5)	−8(5)
O(4)	313(6)	302(5)	333(6)	−20(5)	31(5)	24(5)
O(5)	307(6)	319(6)	377(6)	−11(5)	126(5)	−19(5)
O(6)	323(6)	372(6)	339(6)	32(5)	123(5)	11(5)
O(7)	426(6)	430(7)	379(6)	21(6)	34(5)	−61(6)
O(8)	350(6)	382(6)	376(6)	−54(5)	94(5)	−38(5)

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[a] The parameters of the H atoms were obtained by refining rigid H_2O molecules. The e.s.d.'s of the H_2O rotation angles average 1.5°. The common isotropic temperature factor for all H's refined to 5.1(2) Å^2. $B_{eq} = 8/3\,\pi^2(U_{11} + U_{22} + U_{33})$. [b] The anisotropic temperature factors are in the form: $\exp[-2\pi^2(U_{11}a^{*2}h^2 + \ldots + 2U_{23}b^*c^*kl)]$.

X-Ray Measurements and Results

Preliminary Weissenberg photographs confirmed the monoclinic symmetry, the space group and the approximate cell dimensions as given by [1], but for convenience the unit cell setting of the thioarsenate was adopted in the present study. A crystal, ground to a sphere of 0.3 mm diameter, was employed for data collection on a PHILIPS PW 1100 four-circle diffractometer using graphite monochromatized Mo-Kα radiation. Cell dimensions (Table I) were obtained from least-squares refinement of 50 $2\theta_{hkl}$ values. Intensity data were collected within one half of the reflection sphere ($\sin\theta/\lambda < 0.7$ Å^{-1}) utilizing the $\omega-2\theta$ scan mode with scan widths of 1 + 0.4xtg(θ). A total of about 6000 reflections with intensities significantly above the background, $I_{peak} > 2.5\ \sigma(I_{backg.})$, were measured, while 420 additional reflections with I_{peak} below the given limit were omitted. Averaging of symmetry equivalent reflections yielded 2962 independent observed F_{hkl} which were used in the subsequent calculations.

Least-squares refinement with the program SHELX [7] started with the non-hydrogen atom parameters of $Na_3AsS_4 \cdot 8D_2O$ [2] and, with anisotropic temperature factors and an isotropic correction for extinction, the refinement converged rapidly to R = 0.03. The hydrogen atoms were then found in a difference map at approximately the same positions as in the thioarsenate. Analogous to our previous studies [2, 4, 5] the H atoms were refined as parts of rigid H_2O molecules with O–H = 0.80 Å for the center of the spherical scattering function of H [8], O–H = 0.96 Å for the nuclear H position, and with H–O–H = 101.9–107.7° using the D–O–D angles found in the neutron diffraction study of $Na_3AsS_4 \cdot 8D_2O$ [2]. A common isotropic temperature factor was refined for all H atoms. The final refinement adjusted 174 parameters and converged with weights $w = 1/[\sigma^2(F_o) + 0.0001 \times F_o^2]$ to $R = 0.020$ and Rw = 0.023. The largest correction for extinction was a factor of 0.93 for the 104 reflection. Complex neutral atom scattering functions of Na, P, O and S were taken from [9]. Final atomic parameters are presented in Table II, interatomic distances and angles in Tables III and IV. A list of observed and calculated structure factors is available from the authors upon request.

The present study proved α-$Na_3PS_4 \cdot 8H_2O$ to be isostructural with $Na_3AsS_4 \cdot 8(H,D)_2O$. Both structures are built up from $Na(H_2O)_4S_2$, $Na(H_2O)_5S$ and $Na(H_2O)_6$ octahedra and XS_4 tetrahedra (X = P, As) which are linked to form corrugated layers of the composition $Na_3XS_4 \cdot 8H_2O$. These layers extend parallel to (010) and are parallel b interconnected exclusively by hydrogen bonds (Figs. 1 and 2). The asymmetric units of both structures each contain 13 straight O–H···S bonds, one O–H···O bond and one bifurcated O–H···S,S bond, while one of the H atoms, H(32), is not hydrogen-bonded from a geometrical point of view (Table IV).

TABLE III. Interatomic Distances (Å) and Angles (°) for Na and P Coordination Polyhedra.

(a) Na^+ ions

Na(1)–S(1)	x2	3.086(1)	Na(2)–S(2)	x2	2.837(1)
–O(1)	x2	2.324(2)	–O(3)	x2	2.424(2)
–O(2)	x2	2.447(2)	–O(4)	x2	2.349(2)
Na(3)–S(3)		3.087(1)	Na(4)–O(3)		2.399(2)
–O(1)		2.535(2)	–O(4)		2.401(2)
–O(2)		2.347(2)	–O(6)		2.401(2)
–O(5)		2.317(2)	–O(7)		2.433(2)
–O(5)		2.473(2)	–O(8)		2.381(2)
–O(6)		2.433(2)	–O(8)		2.504(2)

(b) PS_4 tetrahedron

				∢O–P–O
P–S(1)	2.056(1)	S(1)–S(2)	3.360(1)	110.9(1)
–S(2)	2.025(1)	–S(3)	3.319(1)	108.3(1)
–S(3)	2.040(1)	–S(4)	3.348(1)	109.2(1)
–S(4)	2.052(1)	S(2)–S(3)	3.340(1)	110.5(1)
		–S(4)	3.289(1)	107.6(1)
		S(3)–S(4)	3.361(1)	110.4(1)

The PS_4 anion has a mean bond length of P–S = 2.043 Å which compares well with ⟨P–S⟩ = 2.045 Å found for $CrPS_4$ [10] and ⟨P–S⟩ = 2.050 Å for Li_3PS_4 [11]. As the PS_4 group is significantly smaller in size than the AsS_4 group (⟨As–S⟩ = 2.162 Å [2]), one could expect some larger differences between the thiophosphate and the thioarsenate with regard to bond lengths outside the thioanions. This is not true, however. The structure reacts very flexibly on replacement of AsS_4 by PS_4 by (i) a decrease of unit cell dimensions (*cf.* Table I) and by (ii) suitably small shifts of Na and O positions to preserve the Na–S, Na–O and hydrogen bond lengths as much as possible. As a result, bond lengths of α-$Na_3PS_4 \cdot 8H_2O$ differ from the corresponding ones of the thioarsenate by 0.000 to +0.024 Å for Na–S (average increase 0.010 Å), by –0.024 to +0.002 Å for Na–O (average decrease 0.009 Å) and by –0.041 to +0.035 Å for the O···S,O distances within hydrogen bonds (average decrease 0.007 Å). The H positions found for α-$Na_3PS_4 \cdot 8H_2O$ deviate from those of the neutron diffraction determined D positions of the thioarsenate by 0.03 to 0.10 Å (average 0.054 Å; assuming identical cell dimensions for both compounds) while H···S,O distances of the straight hydrogen bonds differ by –0.047 to +0.040 Å (average decrease 0.005 Å). Apart from random

TABLE IV. Hydrogen Bonds and Ligands to the Water Molecules. [a]

A B C	B–C	A–C	∢BAC	∢ABC	∢BAB′	∢CAC′	L	A–L	∢LAL′
O(1)–H(11)···S(2)	2.717(24)	3.370(2)	41(1)	126(3)	103.9	67.8(1)	Na(1)	2.324(2)	91.9(1)
···S(4)	2.713(12)	3.615(2)	17(1)	157(3)		122.7(1)	Na(3)	2.535(2)	
–H(12)···S(3)	2.408(4)	3.366(2)	3(1)	175(3)					
O(2)–H(21)···S(4)	2.251(8)	3.193(2)	9(1)	167(3)	107.0	113.7(1)	Na(1)	2.447(2)	93.6(1)
–H(22)···O(7)	1.891(4)	2.848(2)	3(1)	175(3)			Na(3)	2.347(2)	
O(3)–H(31)···S(1)	2.348(10)	3.275(2)	13(1)	162(3)	105.5		Na(2)	2.424(2)	89.3(1)
–H(32)···		see below					Na(4)	2.399(2)	
O(4)–H(41)···S(1)	2.569(13)	3.448(2)	20(1)	152(3)	104.9	96.9(1)	Na(2)	2.349(2)	91.0(1)
–H(42)···S(3)	2.287(6)	3.233(2)	8(1)	169(3)			Na(4)	2.401(2)	
O(5)–H(51)···S(1)	2.343(5)	3.294(2)	7(1)	171(3)	107.7	126.5(1)	Na(3)	3.317(2)	95.3(1)
–H(52)···S(2)	2.366(10)	3.290(2)	13(1)	162(3)			Na(3)	2.473(2)	
O(6)–H(61)···S(1)	2.301(6)	3.248(2)	8(1)	169(3)	101.9	85.6(1)	Na(3)	2.433(2)	126.9(1)
–H(62)···S(4)	2.358(8)	3.294(2)	11(1)	165(3)			Na(4)	2.401(2)	
O(7)–H(71)···S(3)	2.504(5)	3.455(2)	7(1)	171(3)	106.0	104.5(1)	Na(4)	2.433(2)	98.8(1)
–H(72)···S(4)	2.591(5)	3.544(2)	6(1)	172(3)			O(2)	2.848(2)	
O(8)–H(81)···S(2)	2.383(3)	3.343(2)	2(1)	177(3)	104.5	113.0(1)	Na(4)	2.381(2)	95.3(1)
–H(82)···S(4)	2.384(7)	3.326(2)	9(1)	167(3)			Na(4)	2.504(2)	

Oxygen and sulfur atoms next to H(32):

	distance		distance	∢O,S–H(31)–O,S
H(32)–O(3)	0.96	O(3)–O(2)	3.404(2)	131(3)
–O(2)	2.693(22)	–S(2)	3.546(2)	101(3)
–S(2)	3.239(29)	–S(3)	3.972(2)	135(3)
–S(3)	3.235(21)	O(2)–S(2)	4.490(2)	98
–S(4)	3.491(33)	–S(3)	4.335(2)	94
		S(2)–S(3)	3.759(2)	71

[a] O–H = 0.96 Å and H–O–H = ∢BAB′ = 101.9–107.7° were fixed during the rigid-body refinement of the H_2O molecules. The H–O–H angles are those obtained by neutron diffraction on $Na_3AsS_4 \cdot 8D_2O$ [2].

errors, part of the differences concerning hydrogen bond geometry must be attributed to different kinds of systematic errors in neutron and X-ray diffraction, such as shortening of O–D distances by thermal vibration (*e.g.* O(2)–D(32) = 0.920(5) Å for $Na_3AsS_4 \cdot 8D_2O$, while the corresponding bond in the title compound was assumed to be 0.96 Å), or small deviations between nuclear and electronic scattering centres of oxygen atoms (*cf.* [2]). Only the largest differences, concerning H(12)···S(3) (2.408 Å in $Na_3PS_4 \cdot 8H_2O$; 2.455 Å in $Na_3AsS_4 \cdot 8D_2O$ according to neutron diffraction), H(61)···S(1) (2.301 and 2.326 Å, respectively), and H(72)···S(4) (2.591 and 2.551 Å, respectively) appear to be significant, while all other differences are within the estimated limits of error. The environment of H(32), which is not involved in any specific hydrogen bond (Table IV), is also similar to that of the thioarsenate.

Raman Spectra

Single crystal Raman spectra of H_2O, D_2O and isotopically dilute samples were measured in the temperature range T = 75–295 K. Since no significant differences were observed between room temperature and low temperature spectra, structural changes at decreasing temperature can be certainly excluded and the room temperature structural data may be used without serious objections for the interpretation of the low temperature spectra. With the exception of the internal anion vibrations the spectra were found to be very similar to those of the isostructural $Na_3AsS_4 \cdot 8(H,D)_2O$; the frequency range $\tilde{\nu} < 2000$ cm^{-1}, which is outside the scope of this paper, is reported elsewhere [12]. The frequency range of D_2O, HOD and H_2O stretching vibrations is shown in Fig. 3. Assignments of the uncoupled O–H(D) frequencies of the isoto-

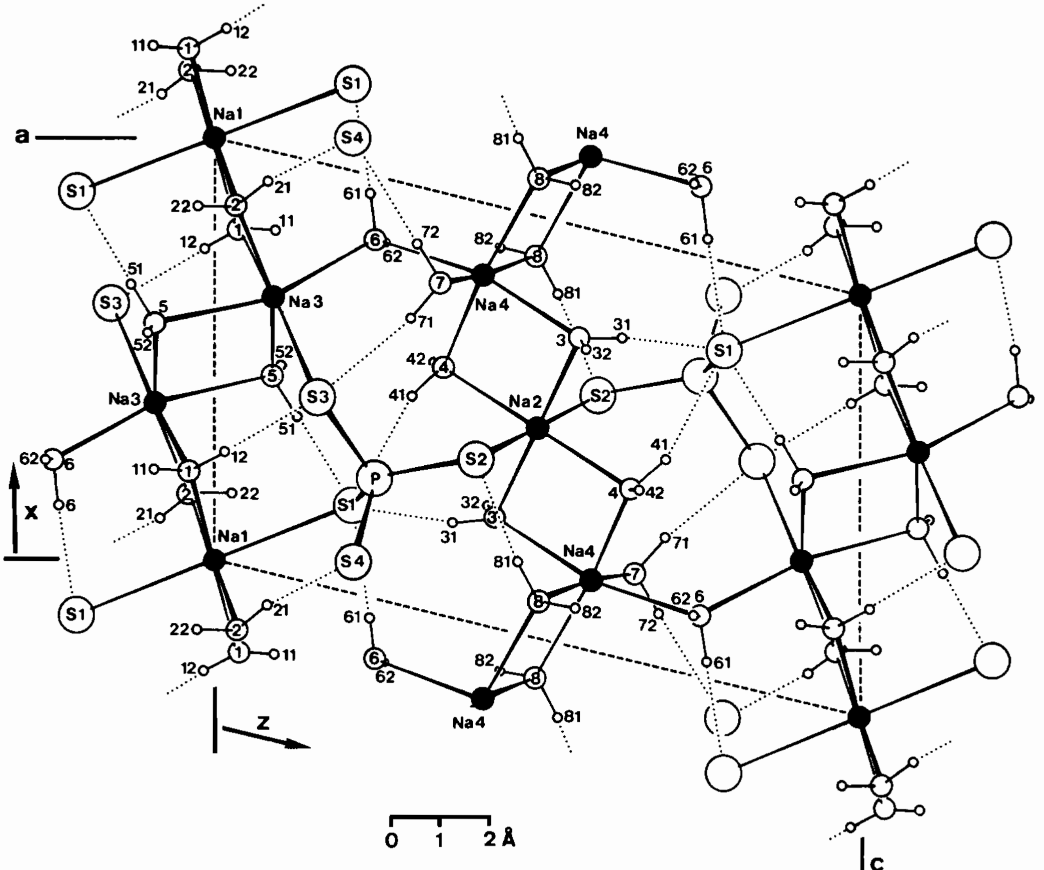

Fig. 1. (010) projection of a α-Na$_3$PS$_4$·8H$_2$O layer at y ~ 0 with intralayer hydrogen bonds. The smallest circles represent H atoms, the next smallest O atoms.

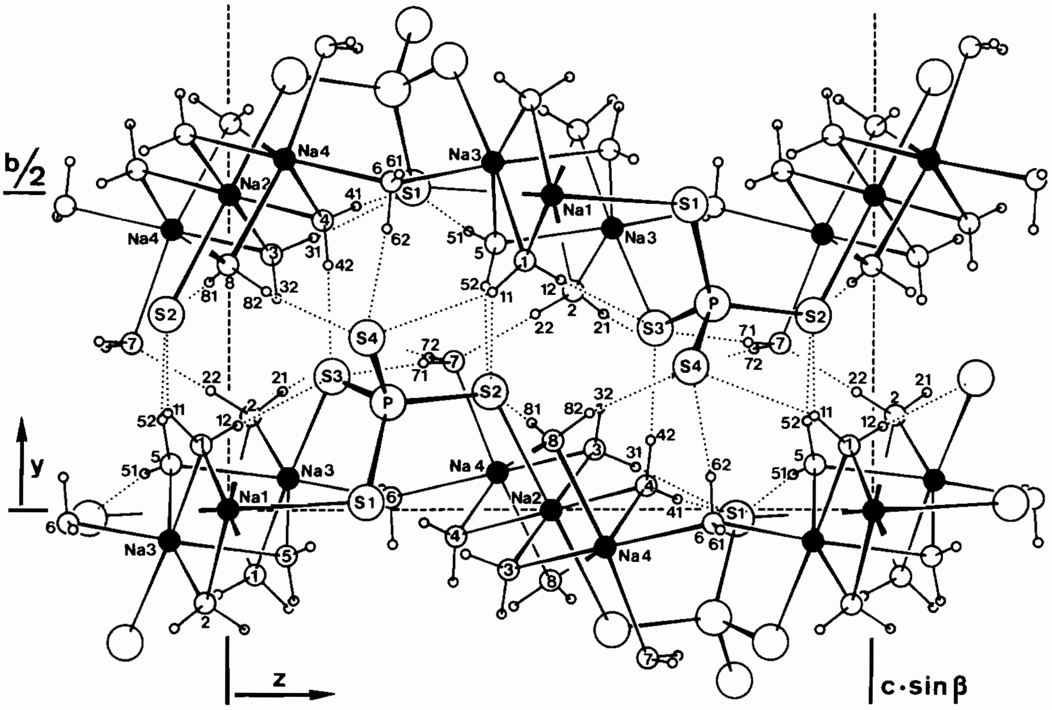

Fig. 2. α-Na$_3$PS$_4$·8H$_2$O in a (100) projection showing intra- and interlayer hydrogen bonds.

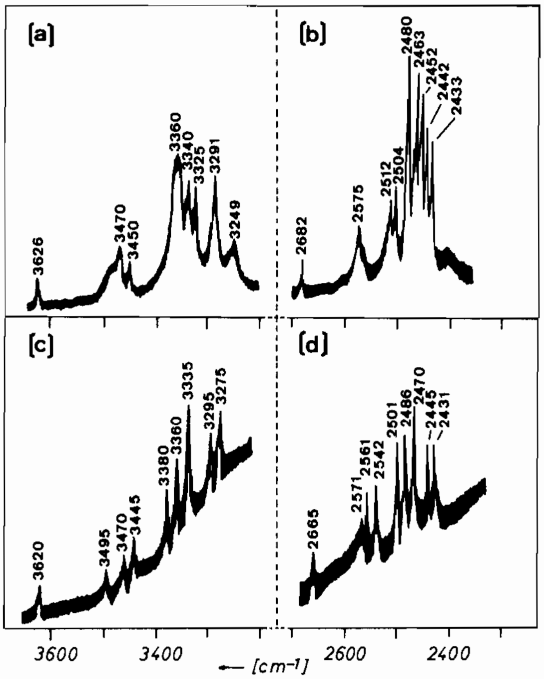

Fig. 3. Raman spectra of α-$Na_3PS_4 \cdot 8(H,D)_2O$ in the frequency range of O–H(D) stretching vibrations (laser excitation at λ_{exc} = 647.1 nm; slit width = 4 cm^{-1}; T = 75 K). (a) 100% H_2O; (b) >99% D_2O; (c) 5% H_2O; (d) 5% D_2O.

TABLE V. Raman Frequencies of Uncoupled O–H,D Stretching Vibrations at 75 K (cm^{-1}) and Assignments.

O–H[a]	O–H/O–D	O–D[a]	Assignments[b]
3620	1.358	2665	(32)
3495	1.359	2571	(72)
3470	1.355	2561	(41)
3445	1.355	2542	(71), (22)
3380	1.352	2501	(81), (82), (12)
3360	1.352	2486	(62), (52)
3335	1.350	2470	(51), (31)
3295	1.348	2445	(42), (61)
3275	1.347	2431	(21)

[a] Isotopically dilute HOD. [b] The numbers in parentheses are the identifiers of hydrogen atoms. $\tilde{\nu}$O–H(D)(11) ≤ 3380 cm^{-1} (H) and 2501 cm^{-1} (D).

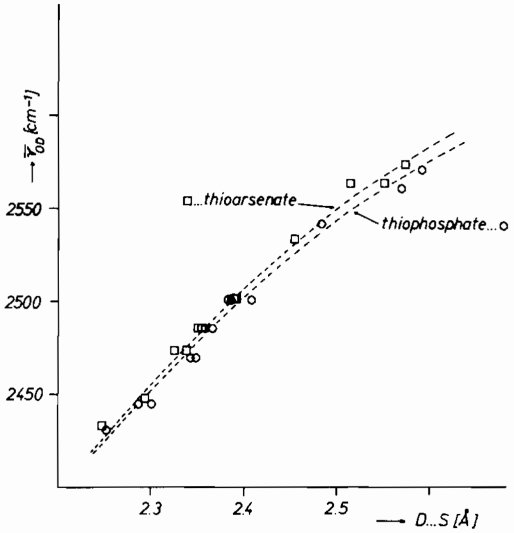

Fig. 4. Comparison of the correlation between uncoupled O–D stretching frequencies and H(D)···S bond distances in α-$Na_3PS_4 \cdot 8(H,D)_2O$ and $Na_3AsS_4 \cdot 8(H,D)_2O$ [2, 3]. Fitted correlation curves are shown as hatched lines (see text).

pically dilute samples [13] to the distinct O–H(D) groups are given in Table V. These assignments are based on the same criteria and approximations which have already been used in the study of the thioarsenate [2, 3]: (i) the frequency of the bifurcated O(1)–H(D)(11)···S,S bond should exhibit a negative temperature coefficient [14]; (ii) the frequency of the O(2)–H(D)(22)···O bond can be estimated to a first approximation from the data on H-bonds in ices [15]; (iii) the highest frequency line should be due to the almost free O(3)–H(D)(32) group; (iv) for the approximately linear H-bonds of O–H(D)···S type a monotonic relationship between frequencies and bond distances H(D)···S is assumed.

The correlation between uncoupled O–D frequencies and bond distances D···S of the approximately linear O–D···S bonds is shown in Fig. 4, which also contains the data from the thioarsenate.

The hatched lines are correlation curves of the type $\tilde{\nu}_{OD}$ = 2727 – A × exp (–B × R) which have been computed by a least-squares fit to the experimental points. It should be noted that the consequent application of the above mentioned criterion (iv) results in somewhat different assignments for the two isostructural compounds. Although these differences may be due partly to actual differences between the H-bond geometries in the two compounds, they most probably mainly reflect the limits of accuracy of the assignment method. These limits can be estimated from the scatter of points usually obtained in correlation plots like those of Fig. 4, and it has been shown in reference [3] that standard deviations of about 10 cm^{-1} and maximum deviations of the experimental points from the computed correlation curve of about ±20 cm^{-1} and ±0.02 Å respectively seem to be characteristic. The differences between the two compounds are only of minor significance, either as far as the different assignments are concerned, but also for the differences between the two correlation curves.

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