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STUDIES ON SYNTHETIC ALKALI-HYDRONIUM JAROSITES III. INFRARED ABSORPTION STUDY

Abstract. Infrared absorption spectra in 400—4000 cm⁻¹ region of synthetic alkali-hydronium jarosites in comparison with those of hydronium and alkali alunite were studied. Basing on deuterated compounds frequencies of three isoelectronic hydrogen-oxygen complexes: H_3O^+, H_2O and OH^- were identified. All frequencies and intensities of absorption bands are lower in jarosite series than in alunites indicating stronger sulphur-oxygen, trivalent metal-oxygen and hydrogen-oxygen bonds, and a greater dipol change connected with corresponding vibrations in the latters. There is but little influence of monovalent cation on the frequencies except on those of O-H vibrations. The strong partial splitting of degenerate modes of SO_4 confirms its C_{3v} symmetry which is due to non-equivalence of sulphate oxygens. The Fe-O-H (Al-O-H) bending vibrations occurring at about 1010 (1070) cm⁻¹ are likely to be confused with v_1 or v_3 of SO_4.

INTRODUCTION

X-ray, chemical and thermal investigations of synthetic alkali-hydronium jarosites so far undertaken (Brophy and Sheridan 1965, Kubisz 1970, 1971) have provided indirect evidence of their chemical constitution. To demonstrate, however, directly the existence of three different types of hydrogen-oxygen complexes in the jarosite (alunite-type) structure the method of infrared absorption spectroscopy in 400—4000 cm⁻¹ region has been applied. Deuteronium (D_3O) jarosites and alunites have been prepared ** to facilitate identification of O-H vibrations.

In the investigated minerals of the jarosite-alunite group of general composition

$$A_xH_3O_{1-x} R_{3-y} [(OH)_{6-3y} (H_2O)_{3y} (SO_4)_2]$$
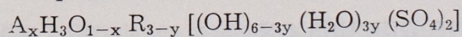
($A = K^+, Na^+; R = Fe^{3+}, Al^{3+}$) five vibrational units have been selected.

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** Fifteen per cent heavy water (99.83% D_2O) solutions of $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$ dehydrated at 560° and 700°C respectively were sealed in glass tubes and heated for 20 hours at 145° and 185°C respectively. These syntheses were carried out by the author in the University Chemical Laboratory at Cambridge.

sulphate tetrahedra, coordination octahedra around R^{3+} ions, trigonal H_3O^+ pyramids, H_2O molecules, and OH^- groups. Although it is true that H_2O and OH^- belong to the $RO_2(OH, H_2O)_4$ octahedron they may be treated separately as hydrogen-oxygen system. The positions of jarosite vibrational units and their molecular as well as site symetry (Γ_s) are given in Tab. 1. The smallest, rhombohedric cell R3m (Hendricks 1937) or R$\bar{3}$m (Rong Wang et al. 1965) was considered for spectroscopic work.

The unambiguous assignment of all absorption bands in the spectrum of jarosites offers some difficulty. It is true first of all for O—H vibrations of the various hydrogen-oxygen complexes especially in the region of torsional and stretching frequencies. The great width of the O—H stretching band and overlapping of O—H bending and torsional oscillations with S—O vibrations exucludes direct identification of the various band components. Therefore the detailed assignment of O—H vibrations as proposed here is based chiefly on analogy with other hydrogen containing substances and comparison of spectra jarosites with different K-Na-H_3O contents. Partial analysis of S—O stretching vibrations in jarosites and alunite has been carried out by Adler and Kerr (1965). These authors, however, assigned R—O—H bending vibration to one of activated S—O degenerate, modes and Si—O vibration (at 911 cm^{-1}) of kaolinite admixtures to ν_1 S—O frequency. Noninterpreted jarosite and alunite spectra have been published by Moenke (1962).

EXPERIMENTAL

The absorption spectra shown on Figs. 2, 3 and 4 were recorded with Zeiss UR-10 spectrophotometer with NaCl, LiF and KBr prisms using KBr pellet technique. The concentration of the sample in the pellet was 0.25—0.31 per cent. To ascertain that no interaction of KBr with jarosite takes place all spectra were repeated using Nujol and hexachlorobutadiene mulls on NaCl plates. One spectrum of D_3O-jarosite taken directly after its synthesis with a Perkin-Elmer Model 21 spectrophotometer (Nujol mull) is shown in Fig. 5 *. Spectrum of the same sample presented in Fig. 4, which was recorded two years later, shows a considerable H for D exchange, this was not the case with D_3O-alunite (S-16C, Fig. 4). In Fig. 3 spectra of natural alunite (H-4), Na, H_3O- (BS-4) and K, H_3O-jarosite (G-5) are shown for comparison. For natural Pb, H_3O-jarosite (Bo-276) only numerical data are given in Tab. 2. These minerals were described by Kubisz (1964).

RESULTS AND DISCUSSION

S u l p h a t e   i o n. Rhombohedric alunite type unit cell contains two SO_4^{2-} ions (Hendricks 1937, Rong Wang et al. 1965). Γ_s of their position

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* This spectrum was recorded in University Chemical Laboratory, Department of Inorganic Chemistry at Cambridge.

is C_{3v} both for R3m and R$\bar{3}$m space groups (Tab. 1 This means that symmetry of the local field acting on these ions is lower than their symmetry in the free state (T_d). Consequently A_1 (ν_1) and E (ν_2) modes of the free ion will be activated and its degenerate F_2 (ν_3, ν_4) modes partly split Fig. 1). Each sulphate ion in the unit cell will contribute six vibrations. These vibrations couple together to give twelve modes, out of which only six are infrared active. This may be illustrated by a correlation diagram (Fig. 1) of symmetry properties.

T a b l e 1

Vibrational units in alunite-type structure

Oscillator (vibrational unit)	Z	Γ_m	Γ_p*	Position in the unit-cell
SO_3 (OH)	2	C_{3v}	C_{3v} (C_{3v})	S atom and O_I (or OH) on C_3 axis in OOz positions
$R(OH)_{4/2}$ O_2	3	C_1	C_s (C_{2h})	R on symmetry planes in x$\bar{x}$z; x2xz; 2$\bar{x}$$\bar{x}$z or $\frac{1}{2}$ 0 $\frac{1}{2}$ positions
H_3O	1	C_{3v}	C_{3v} (D_{3d})	O atom on C_3 (or C_{3i} = S_6) axis in 000 position
H_2O	?	$C_{\infty v}$	C_1 (C_s)	in general or in x$\bar{x}$z; ...; positions

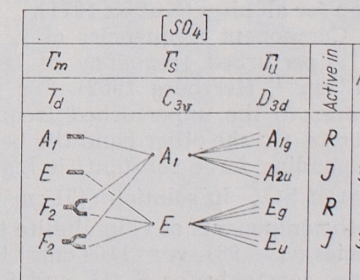*... Γ_p symbols in parentheses are for the R$\bar{3}$m unit-cell symmetry

Fig. 1 Correlation diagram of symmetry properties for SO_4 ion in jarosite-alunite

The C_{3v} site symmetry of SO_4^{2-} ion is emphasized by nonequivalence of its neighbours and S—O bond lengths. Namely three sulphate oxygens (O_{II}) locatedraound C_3 axis, forming the base of the tetrahedron, are in contact with B atoms, and the apical oxygen (O_I), lying on this axis, has three hydrogen bonded OH neighbours (Rong Wang et al. 1965). The

three S—O_{II} bonds are longer (e.g. in alunite, by 5 per cent) than S—O_I bond which has a considerable degree of covalent character. The sulphate ion in this case may be regarded as a SO_3OH grouping. It is to be expected that S—O vibrations involving the double bonded oxygen O_I will have higher fraquencies.

Comparison of spectra of hydrogen and deuterated compounds allowed the sulphate frequencies to be easily identified (Tab. 2 and 3). Splitting of the v_3 and v_4 (Tab. 2) is to strong to be caused only by the crystal field forces of C_{3v} symmetry. Evidently it must be due chiefly to nonequivalence of oxygens i.e. of S—O bond lengths and bond characters. Thus infrared spectroscopic work confirms X-ray analysis results.

Plumbojarosite shows the largest while natrojarosite the smallest splitting (Tab. 2), indicating strongest distortion of sulphate tetrahedra in the former. This is due to the fact that every second A^+ cation position is vacant in plumbojarosite. The splitting of stretching vibration Δv_3 is for alkali jarosites smaller than that of the bending Δv_4 one, $\Delta v_3, < \Delta v_4$, for plumbo- and hydronium jarosites Δv_3 is nearly equal to Δv_4, while for alunites $\Delta v_3 > \Delta v_4$. Thus it is evident that the magnitude of splitting is a complex function of electrongativity of A^+ as well as of R^{3+} cations. Possibly the strength of hydrogen bonds between O_I and OH groups plays here some role too.

In alkali-hydronium jarosite series Δv_3 increases distinctly and Δv_4 decreases (slightly) in the sequence Na > K > H_3O-jarosite:

	Pb	H_3O	K	Na
Δv_3	129	108	94—100	83— 89 cm^{-1}
Δv_4	128	113	113—119	115—122

(The values of Δv given above are based on spectra of synthetic and natural jarosites).

All sulphate frequencies are higher for alunite than for jarosites, indicating weaker (longer) S—O bonds in the latter. It is confirmed by the temperatures of thermal transformations which are lower for jarosites than for alunites (Kubisz 1971).

Component frequencies of v_4 (F_2) bending vibration lie on both sides of unperturbed frequency of tetrahedral (T_d) sulphate ion in solution (613 cm^{-1}, Herzberg 1962). For jarosites the higher component of v_4 is nearer to the unperturbed frequency, whereas the opposite is true for alunite. On the other hand the bending frequency v_2 (E) (and thus the corresponding force constant) is higher in both minerals, as compared with that of SO_4^{2-} in solution (451 cm^{-1}). As for the stretching vibration v_1 and both components of v_3 in alunite they are all shifted towards higher frequencies (v_1 = 981, v_3 = 1104 cm^{-1} in solution). It means that both stretching force constants for S—O_I and S—O_{II} bonds) are higher in this mineral than in solution. In jarosites only the v_1 frequency has increased while components of v_3 are distributed about the unperturbed value. This gives evidence of differences in the structure and surrounding of sulphate tetrahedra in jarosites and alunites.

The general increase of all S—O stretching and bending frequencies in alunite and of only v_1 and v_2 in jarosites, as compared with those of
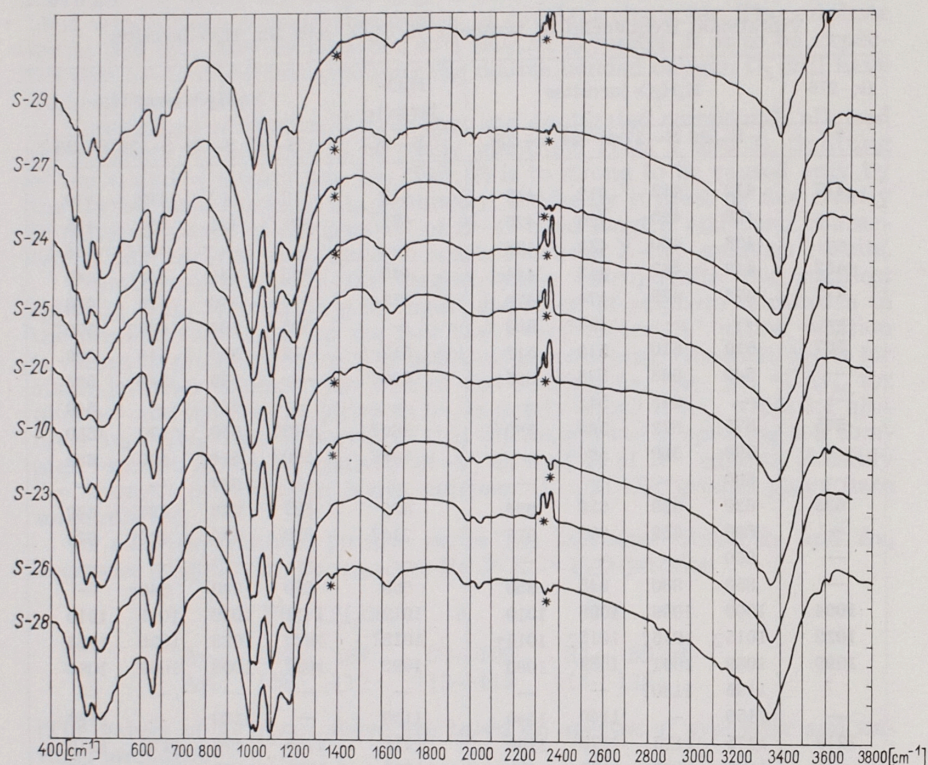
Table 2

Vibrational frequencies of synthetic K, H_3O- and Na, H_3O-jarosites

Bo-276 *	K,H_3O-jarosites S—29	S—27	S—24	S—25	H_3O-jarosite S—2C	Na,H_3O-jarosites S—10	S—23	S—26	S—28
417	412	412	412	412	412	413	412	412	410
—	428	425	420	425	422?	425?	421	430	415
—	438	430	432	435	—	—	—	437?	436
452	447	447	447	444	445	445	445	445	445
477	475	475	474	472	472	475	476	476	476
—	—	—	498?	500	—	505	500	495?	500?
507	510	510	510	512	512	512	510	510	509
—	540	538	538	535?	540?	—	535	540	530
—	—	545	545	—	—	—	544	—	540
575	575	572	565	560?	560?	570?	550	570	550
—	590	590	590	—	585?	590?	570	590	585
—	600	—	—	—	—	—	584	—	—
635	629	629	628	626	625	627	628	628	628
—	660	659	662	675?	710?	680	670	670	670
—	690	—	—	—	—	—	—	—	—
—	850	860	845	850	850	860	840	840?	—
1004	1009	1009	1009	1010	1012	1011	1010	1011	1010
1022	1015?	1015?	1015?	1015?	1015?	1023	1023	1025	1024
1090	1089	1091	1089	1090	1092	1097	1098	1099	1098
?	1125	1130?	—	—	—	—	—	—	—
—	1150	—	1140	1140	1140	—	1130	—	1130
1219	1175	1175	1175	1180	1175	1175	1170	1170	1170
—	1188	1188	1192	1198	1200	1191	1189	1188	1187
—	1390?	1380	1380	1380?	—	1430	1380	1380	1380
?	1590	1590	1580	1570	1575	1585	1580	1590	—
1650	1640	1635	1640	1642	1642	1640	—	1640	1630
—	1960	1960	1960	—	1980?	1980	1980	1988	1988
2050	2015	2015	2015	2000	2020?	2038	2040	2042	2041
—	2080	2075	2075	2080	2080	2080	2080	2080	2080
—	2170	2170	2170	2170	2170	—	2180	2160	—
—	—	—	—	—	—	—	2180	2160	—
—	2860	—	2845	2850	2680	2850	—	2850	2845
—	2920	3160	2915	2920	—	2920	3000	2925	2915
—	3310	3280	3280	3300	3290	3300	3260	3300	3220
—	3350	3330	3320	3330	3320	3320	—	3335	3315
3350	3388	3378	3375	3375	3370	3365	3360	3360	3538
3430	3420	3400	—	3418	3430	3400?	—	—	—

H_3O content

$\longleftarrow$ decreases $\longrightarrow$

* Natural Pb,H_3O-Jarosite (Bo-276).

Fig. 2. Infrared absorption spectra of synthetic K, H_3O^- (S—29, 27, 24, 25) and Na, H_3O-jarosites (S—10, 23, 26, 28). The H_3O content increases from S—25 to S—29 and from S—10 to S—28; S—2C ...H_3O-jarosite

sulphate ion in solution, can be explained by comparatively weaker hydrogen bonds between sulphate oxygens and shorter S—O bonds in crystals investigated than in solution (only weak hydrogen bonds are directed towards O_I in all jarosites and alunites and towards O_{II} in hydronium minerals). The coordination of O_{II} to different metal atoms (R) and probably unequal S—O_I ... H- bond lengths could play some role here too.

The v_1 and the lower components of v_3 stretching frequencies shift slightly to higher wave numbers as the ionic radius of A ions (and thus the jarosite unit cell height) decreases, or as the electronegativity of A increases (Tab. 2). This phenomenon is commonly observed in oxy-acid salts (e.g. Adler and Kerr 1965). Contrary to this the bending frequencies v_2 and v_4 seem to be independent on electronegativity of the monovalent cation. There is, however, some correlation between them and a_o parameter. It has the highest value in pure hydronium jarosite ($a_{Na} < a_{H_2O} < a_K$) and correspondingly v_2 and the higher component frequency of v_4 are lowest in H_3O- jarosite while the other v_4 component is highest in this mineral.

The bands at about 2170 in jarosites and 2180 in alunites were assigned to overtones of the lower component of v_3.

Trivalent cation R^{3+} octahedra. Somewhat distorted coordination octahedron around R^{3+} ions in formed by two O_{II} oxygens and four OH^- groups. In the alunite-type rhombohedric cell three such polyhedra join together by sharing OH corners (e.g. Rong Wang et al. 1965). For octahedral, seven-atom molecules, there are only two infrared active vibrations possible. More than two, however, frequencies are to be expected because of presumable distortion of the octahedron and its low site symmetry (Tab. 1).

The R—O bonds in jarosite and alunite are rather weak with considerable degree of ionic character (Hrynkiewicz et al. 1964). Hence the R—O vibrations should emerge in the region rather below 700 cm^{-1}. The corresponding frequencies lie between 400—650 in haematite and magnetite, about 450—800 in corundum (Moenke 1962) and at 720—780 cm^{-1} in aluminium oxy-hydroxides (fide Kolesova and Ryskin 1962).

There is only one absorption band in the jarosite (412 cm^{-1}) and alunite (422 cm^{-1}) spectra (Figs. 2—4) which could possibly correspond to R—O vibrations (Tabl. 2). It is very weak in jarosite and strong in alunite spectra, which may confirm the proposed tentative assignment. The dipol change connected with Al—O vibrations should be greater than that of Fe—O vibrations. Other R—O frequencies expected lie probably below the range covered here.

Hydronium ion. Only one H_3O^+ ion in C_{3v} (or D_{3d}) position on C_3 axis is present in the smallest rhombohedric cell of hydronium jarosite (alunite). It is located below sulphate tetrahedra and has twelve neigh-
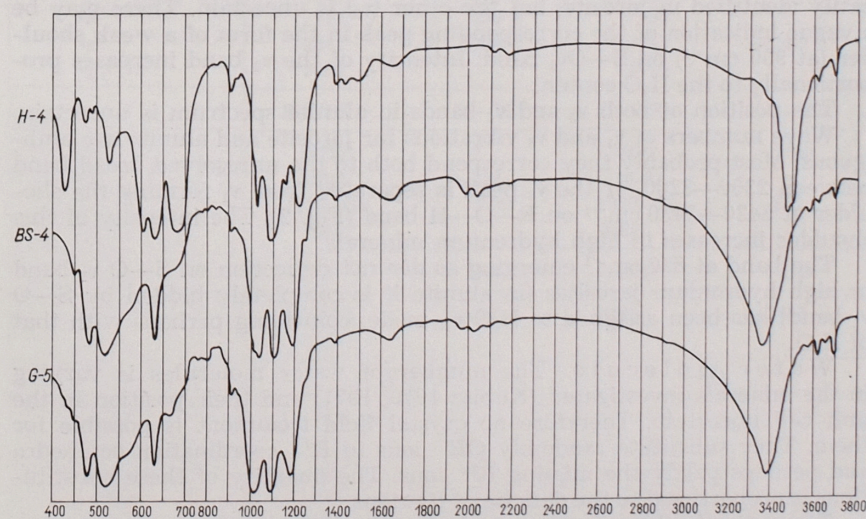

Fig. 3. Infrared absorption spectra of natural Na, H_3O-jarosite (BS-4), K, H_3O-jarosite (G-5) and alunite (H-4)

bours: six O_{II} oxygens, and six OH^- ions (Johanssohn 1963). Most probably it is rotated statistically (disordered among several orientations) forming three normal or bifurcated (with pairs of O_{II}) hydrogen bonds.

The infrared spectrum of the pyramidal H_3O^+ ion ($\Gamma_m = C_{3v}$) has been studied by many authors (the most complete revue of references can be find in Savoie and Giguère 1964, or Kubisz 1967). According to the theory H_3O^+ ion which has a trigonal equilateral pyramidal structure may contribute two totally symmetric A_1 vibrational modes, ν_1 (stretching), and ν_2 (bending) and two doubly degenerate antisymmetric E modes, ν_3 (stretching) and ν_4 (bending) (Herzberg 1962, Kubisz 1967). In the monohydrates of oxyacids they lie in the regions (see references above):

ν_1 and ν_3 2445—3400 cm^{-1} — very strong and broad, unresolved band ν_1 should be weaker and of lower frequency tan ν_3),

ν_4 1577—1705 — weak band,

ν_2 950—1175 — strong band; due to Fermi resonance between 2 ν_2 and ν_1 the 2 ν_2 band may have considerable intensity.

The translational frequencies lie at about 100—400, and the librational ones (ν_R) at 600—800 cm^{-1}. All bands may be split due to inversion doubling (Herzberg 1962). As $\Gamma_p = \Gamma_s$ in jarosite no interaction of the crystal field with that of the vibrating H_3O molecule is to be expected.

Identification of H_3O bands in the spectra investigated offers some difficulty. The librational ν_R, and bending frequencies (ν_2, ν_4) coincide with S—O stretching or H_2O bending ones, and the stretching frequencies lie in the same region as those of OH and H_2O molecules. The assignment proposed here (Tab. 3) is based on comparison of spectra of minerals with varying H_3O content (Figs. 2—4).

Of the bending vibrations only the antisymmetric one (1575 cm^{-1}) is easily identified in jarosite, but the other (ν_2) is uncertain. There may be a vague indication of the corresponding peak in the form of a weak shoulder (at 900 cm^{-1}) on S—Oν_1 band. Intensity of the ν_4 band increases proportionally to the H_3O content.

The position of both ν_2 and ν_4 bands in alunite spectrum is uncertain.

Wave numbers of ν_1 and ν_3 vibrations for jarosite and alunite are ambiguous. Most probably they correspond both to the unresolved broad band between 2300—3200, or the ν_3 peak is separated from ν_1 forming the shoulder at 3420—3430 cm^{-1} on R—O—H band (Fig. 2). The intensity of this shoulder increases in high hydronium minerals.

The band at 850 cm^{-1} emerging as distinct deflection on S—O ν_1 band in high hydronium jarosites (in alunite it is completely hidden by S—O ν_1 band) has been assigned to H_3O ν_R mode, coinciding perhaps with that of H_2O.

W a t e r   m o l e c u l e. The number of water molecules is varying in the minerals investigated (Kubisz 1970, 1971) and their position in the unit cell uncertain. Therefore no crystal field treatment is possible for them. They substitute randomly OH^- ions in R^{3+} coordination octahedra and perhaps partly the missing R^{3+} ions. The quantity of these substitutions is proportional to the deficite of R^{3+} ions.

Theoretically three fundamental vibrational infrared active modes are possible for free H_2O. Attaching of H_2O to metal atom (R^{3+}) should give rise to librational (Boutin et al. 1964, Oswald 1965), rocking and wagging

frequencies (Sartori et al. 1958) which for hydrates lie in the region 480—930 cm^{-1}.

In all spectra (Figs. 2—4) characteristic ν_2 band of H_2O is easily identified at about 1640 cm^{-1} (Tabs. 2—3), increasing in intensity with R^{3+} ions deficite. It is most intense in hydronium alunite which shows the highest deficite of R^{3+} ions. The ν_1 and ν_3 bands could not be identified as they nearly coincide with OH^- stretching band extending from 3200 to 3500 cm^{-1}. Similarly, the rocking and wagging frequencies are hidden by strong ν_2 and ν_4 S—O bands. The restricted rotations (librations) of H_2O about the two axes of inertia are most probably due to weak bands at 447—470 (ν_R), and 710—790 cm^{-1} ($\nu_{R''}$) (Tab. 3). Their intensity increases

Table 3

Assignment of vibration in H_3O/D_3O-jarosites and H_3O/D_3O-alunites

Vibrational unit / Assignment	Hydronium Jarosite H_3O	Deuteronium Jarosite D_3O	Hydronium Alunite H_3O	Deuteronium Alunite D_3O
ν_R	~850	635	~840	~620 ?
ν_2 (δ_s)	1175	890—870	1172 ?	?
ν_4 (δ_d)	1575	1200—1160?	1140 ?	~1100 ?
ν_1 (ν_s?)	2300—3100	1700—2300	~2400—3200	1800—2400
ν_3 (ν_d?)	~3430	2520	~3420	2520
	H_2O	D_2O	H_2O	D_2O
ν_R'	447	>400	470	> 400
ν_R''	710	550 ?	790	?
ν_2	1642	1200 ?	1645	~1200 ?
$\nu_2 + \nu_R'$	2080		2115	
	R—OH	R—OD	R—OH	R—OD
ϱ_w	(572)	?	(628)	(435)
ν_R	(662)	(~485)	(675)	?
ν_d	1010—20	770	1070—80	852
$2x\ \nu_d$	2020		2180	
	OH	OD	OH	OD
ν_s	(1980?) 3370	2485	3480	2565
	SO_4		SO_4	
ν_2 (δ_d)	472		517	
ν_4 (δ_d)	512		600	
ν_4 (δ_d)	625		664	
ν_1 (ν_s)	1012		1035	
ν_3 (δ_d)	1092		1123	
ν_3 (δ_d)	1200		1235	
$2x\ \nu_3$	2170		2230	

with increasing water content. In liquid water they lie at 500 and 710 cm^{-1} respectively (fide Walrafen 1964). Combination band of deformation and libration frequencies occurs at about 2080 in jarosites and 2115 cm^{-1} in H$_3$O-alunite.

The presence of distinct ν_2 band in pure hydronium jarosite (S-2C) is inocomprehensible at first. For contrary to K, Na, H$_3$O-jarosites it shows a slight excess of Fe$_2$O$_3$ (see analysis in Kubisz 1970). Hence no H$_2$O for OH$^-$ substitution is to be expected. If, however, an admixture of haematite were present, which is commonly the case in synthetic jarosites, the possible Fe^{3+} vacancies might remain unrecognized.

Hydroxyl ions. Isolated heteronuclear linear OH molecules of C∞_v symmetry have only one fundamental mode. The corresponding band lies in metal hydroxides in the range 2800—3700 cm^{-1} (e.g. Glemser and Hartert 1956). If attached to another atom (R^{3+} in alunite-jarosite) they may contribute R—O—H vibrations, e.g. bending (700 do 1100 cm^{-1} in hydroxides, Hartert and Glemser 1956), wagging (400 do 600 cm^{-1}) and torsional oscillations (600—700 cm^{-1} in SO$_3$OH$^-$, Savoie and Giguère 1964).

The rhombohedric alunite-jarosite cell contains six OH$^-$ ions in equivalent C$_1$ or, if $\Gamma_p = D_{3d}$, C$_s$ positions (Tab. 1). They couple between each other to give a very intense band at about 3400 cm^{-1} corresponding to the stretching vibration. (Tabs. 2—3). Its position depends upon the strength of metal-hydroxyl oxygen (R—OH) and hydrogen-sulphate oxygen (—O—H...OSO$_3$) bonds, and kind of A$^+$ and R^{3+} cations. Namely the O—H frequency is higher in alunite (3480) than in jarosites (3358 do 3388 cm^{-1}). On the other hand in the K—H$_3$O—Na—(Pb)-jarosite series it is highest in K, H$_3$O-members (Tab. 2, S-29, 27, 24, 25).

The bending R—O—OH vibration may easily be confused with S—O ν_1 (in jarosite) or ν_3 vibration (in alunite), if no spectra of deuterated compounds are available. It has a higher, by about 60 cm^{-1}, frequency in alunite than in jarosite (Tab. 3), due to weaker (longer) R—OH bonds in the latter. According to Hartert and Glemser (1956) bending frequency shift of 100 cm^{-1} towards higher values corresponds to shortering of R—OH band by about 0.1 Å. As the bending R—O—OH frequency in jarosites nearly coincides with ν_1 of SO$_4$ it was impossible to establish its dependence on the kind of monovalent (divalent) cation A$^+$ (A^{2+}). It seems to shift to higher velues from K, H$_3$O- to Na, H$_3$O- and Pb-jarosites (Tab. 2) with rising electronegativity of A$^+$ (A^{2+}). It must be kept in mind that hydrogen is held in position by repelling forces of neighbouring R^{3+} ions, resisting stronger the bending of O—H bond than its stretching: —R—O—R—. The second order of R—OH deformation frequency emer-
    H
ges at about 2020—2050 cm^{-1} in jarosites and at about 2180 cm^{-1} in H$_3$O-alunite.

Of all bands only weak shoulders on S—O bands at 572 and 662 cm^{-1} in jarosites, and 628, 675 cm^{-1} in alunites are unaccounted for. They have been tentatively assigned to rocking or wagging frequencies of R—OH (or R—OH$_2$) (compare Sartori et al. 1958). These bands decrease in intensity with diminishing H$_3$O content (Fig. 2). It may be that formation

of hydrogen bonds between H$_3$O$^+$ and OH$^-$ (or OH$_2$) restrains oscillation of the latter.

Isotope shift. The deuteration shift of O—H frequencies is for jarosite and alunite of the same order as that for liquid water (Tab. 3, Figs. 4 and 5). Unfortunately only R—OH frequencies and ν_1/ν_3 of H$_3$O were shifted to spectral regions free of other bands. The R—OD shift is slightly higher for stretching (ν) than for bending (δ) and librational (R) modes, similarly as in hydrated sulphates (e.g. Oswald 1965):

$$\frac{\nu \ (R—OH)}{\nu \ (R—OD)} = 1.36 \text{ for hydronium jarosite and alunite,}$$

and

$$\frac{\delta \ (R—OH)}{\delta \ (R—OD)} = 1.32 \text{ for hydronium jarosite,}$$

$$= 1.27 \text{ for hydronium alunite.}$$

Other O—H/D bands are too broad, hence no accurate calculations were possible.

It should be mentioned that the deuteration was not complete. The reverse, H for D, exchange in jarosite took place in about two years period, although all D$_3$O-jarosites available were stored in closed tubes. The D$_3$O-alunite remained unchanged. (Fig. 4, 5).

The S—O stretching frequencies (mainly ν_3) were slightly lowered in deuterated minerals.

The O—H distance in H$_3$O$^+$ ion in crystals varies between 0.78 and 1.10 Å (mean value 0.96), the H—O—H angle between 113 and 118° (me-
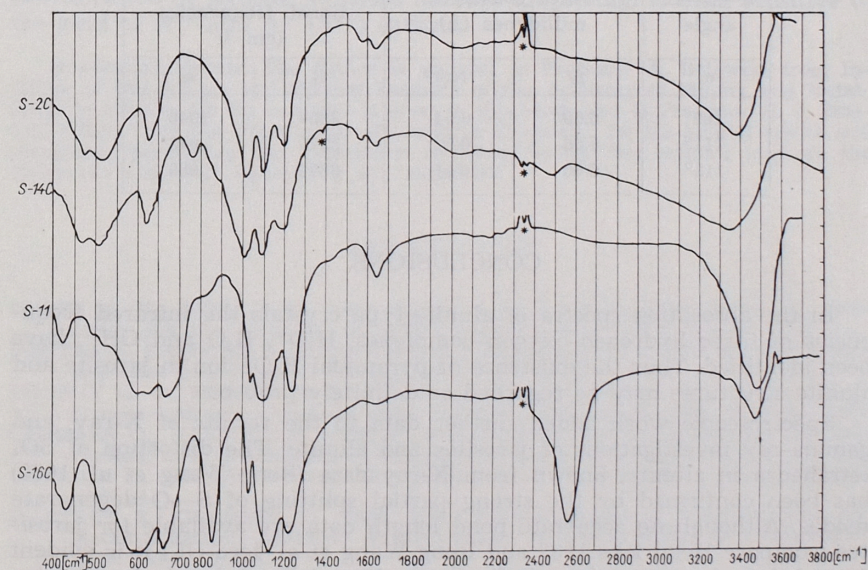

Fig. 4. Infrared absorption spectra of synthetic H$_3$O-jarosite (S—2C), D$_3$O-jarosite (S—14C — taken in two years after its synthesis), H$_3$O-alunite (S—11C) and D$_3$O-alunite (S—16C)
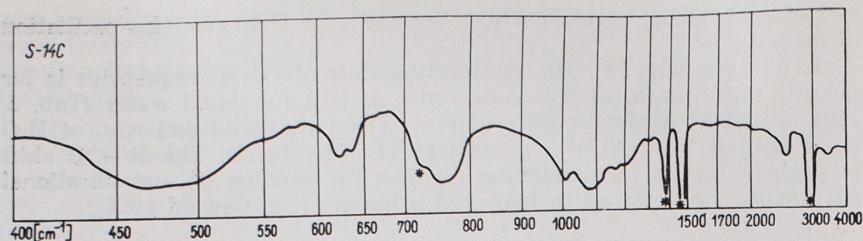
Fig. 5. Infrared absorption spectrum of D_3O-jarosite taken immediately after synthesis (Nujol mull)

an value 112°), the height of the pyramid between 0.16 and 0.36 Å (mean value 0.27) (Kubisz 1967). Using Lechner's equations for XY_3 molecules (fide Herzberg, 1962) the valence force constants of hydronium ion were evaluated basing on ν_3 and ν_4 frequencies. These constants were then applied to calculate ν_1 and ν_3. The results for various H—O—H angles and O—H distances are given in Tab. 4.

Table 4

Force constants and vibrational frequencies of H_3O^+ ion

H—O—H angle	Force constants millidynes (Å)		Calculated vibrational frequencies (cm^{-1})	
α	f_r	$f\alpha/r^2$	ν_1	ν_2
109°	6.69	0.54	3394	1040
111°	6.66	0.52	3379	948*
112°	6.60	0.51	3372	899

CONCLUSIONS

In the absorption spectra of alunite-type crystals the infrared frequencies of three hydrogen-oxygen complexes, H_3O^+, H_2O and OH^-, have been identified. Thus the existence of pyramidal H_3O^+ ion in jarosite and alunite structures may be regarded as definitely proven.

Spectroscopic work added further data to the results of X-ray, and gamma-ray investigations of jarosites and alunite. The distortion of SO_4 tetrahedra in alunite, known from X-ray data (Rong Wang et al. 1965) has been confirmed by the strong partial splitting of S—O degenerate modes. Although no accurrate bond length data are available for jarosites (compare Hendricks 1937 and Rong Wang et al. loco cit.) it is evident from infrared spectra that all S—O, O—H and R—O bonds are shorter (stronger) in alunite (R = Al^{3+}) than in alkali-hydronium jarosites (R = Fe^{3+}). On the other hand S—O (and R—O) bond lengths seem not to alter significantly in K—H_3O—Na-jarosite series. The kind of monova-

lent cation A^+ has but little, although measureable influence on these bonds. Since, as it seems the sulphate tetrahedra and $FeO_2(OH)_4$ octahedra have very similar dimensions in K—H_3O—Na-jarosites the differences in the size of their unit cells are chiefly due to different packing of these structural units.

Disregarding the indirect influence of R—O bond length on R—O—H frequencies it may be seen that, contrary to the above, the O—H distances in hydroxyls are significantly affected by A^+ ions. From frequency shifts of O—H stretching and R—O—H bending vibrations follows that O—H bond length is inversely proportional to the ionic radius of A^+, and to Görlich's electrostatic electronegativity (Görlich, 1965). On the other hand it is directly proportional to that of R^{3+} ions. In this respect the behaviour of H_3O^+ complex ion, which has strong hydrogen bonding property, does not differ from that of simple spherical K^+ and Na^+ ions. Evidently the A^+ cations with high electronegativity diminish the strength of R—OH bonds. It is confirmed by the temperatures of jarosite dehydroxylation, which is the lowest for natrojarosite in the investigated series (Kubisz 1971).

The shift of both the stretching and bending frequencies towards higher values in alunite as compared with that of jarosite inspite of stronger R—O bonds may be due to weakening of H—bonds of OH groups. Similar phenomenon was observed in γ-AlO · OH and γ-FeO · OH (Hartert and Glemser 1956).

The O—H stretching band may be used as an „analytical band" in identification of jarosite minerals because its position is most sensitive to the kind of R^{3+} and A^+ (A^{2+}) cations.

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BADANIA SYNTETYCZNYCH JAROSYTÓW ALKALICZNO-HYDRONIOWYCH III. ANALIZA ABSORPCYJNA W PODCZERWIENI

Streszczenie

W pracy przedstawiono wyniki analizy widm absorpcyjnych w podczerwieni syntetycznych jarosytów alkaliczno-hydroniowych (tab. 2, 3 i fig. 2—5) w odniesieniu do widm ałunitów. Na podstawie spektrogramów deuteryzowanych połączeń zidentyfikowano pasma absorpcyjne odpowiadające drganiom trzech izoelektronowych kompleksów wodorowo-tlenowych: H_3O^+, H_2O i OH^-, jak również drganiom zginającym Fe—O—H (Al—O—H), które dotychczas przypisywano drganiom ν_1 lub ν_3 jonu SO_4^{2-}. Stwierdzono, iż częstości drgań i intensywności wszystkich pasm są niższe w jarosytach niż w ałunitach. Wskazuje to na silniejsze wiązania S—O i R^{3+}—O oraz większe zmiany momentu dipolowego w minerałach drugiej grupy. Zmiana rodzaju kationu jednowartościowego A (= Na^+, K^+, H_3O^+) lub dwuwartościowego (np. Pb^{2+}) wywiera wpływ głównie na częstości drgań grup OH. Typ i wielkość rozszczepienia zdegenerowanych drgań jonu SO_4^{2-} wskazuje na jego symetrię C_{3v} wynikającą z nierównoważności atomów O tego jonu.

Ян КУБИШ

ИССЛЕДОВАНИЕ СИНТЕТИЧЕСКИХ ЩЕЛОЧНО-ГИДРОКСОНИЕВЫХ ЯРОЗИТОВ III. АНАЛИЗ ИНФРАКРАСНЫХ СПЕКТРОВ ПОГЛОЩЕНИЯ

Резюме

В статье представлены результаты анализа нифракрасных спектров поглощения синтетических щелочно-гидроксониевых ярозитов (табл. 2, 3 и фиг. 2—5) в сопоставлении со спектрами алунитов. По спектрограммам дейтеризированных соединений определялись полосы поглощения, соответствующие колебаниям трех изоэлектронных гидроксильный комплексов: H_3O^+, H_2O и OH^-, а также колебаниям деформационных Fe—O—H (Al—O—H), которые до сих пор принимались в качестве колебаний ν_1 или ν_3 иона SO_4^{2-}. Констатировано, что частота колебаний и интенсивность всех линий ярозитов меньше чем у алунитов. Это является признаком более сильных связей S—O и R^{3+}—O и более значительных изменений дипольного момента в минералах второй группы. Изменение типа одновалентного катиона A (= Na^+, K^+, H_3O^+) или двухвалентного катиона (например Pb^{2+}) оказывает влияние, главным образом, на часбаний групп OH. Характер и величина расщепления деформационных колебаний иона SC_4^{2-} указывают на его симметрию C_{3v}, обусловленную неоднородностью атомов кислорода этого иона.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Корреляционная диаграмма симметрии иона SO_4 в ярозите-алуните

Фиг. 2. ИК-спектры поглощения синтетических К, H_3O-ярозита (S—29, 27, 24, 25) и Na, H_3O-ярозита (S—10, 23 26, 28). Содержание H_3O возрастает от S—25 до S—29 и от S—10 до S—28; S—2C . . . H_3O-ярозит

Фиг. 3. ИК-спектры поглощения естественных Na, H_3O-ярозита (BS—4), К, H_3O-ярозита (G—5) и алунита (H—4)

Фиг. 4. ИК-спектры поглощения синтетических H_3O-ярозита (S—2C), D_3O-ярозита (S—14C — выполнено в два года после его синтеза), H_3O-алунита (S—11C) и D_3O-алунита (S—16C)

Фиг. 5. ИК-спектр H_3O-ярозита, выполненный непосредственно после синтеза