

The Spectroscopic Study of Oxonium Ions in Minerals

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Abstract

Nuclear magnetic resonance (NMR) and infrared spectroscopic studies of some mineral species in which the presence of oxonium ions has been postulated show that it is often difficult to obtain direct evidence of their existence. Clear evidence of oxonium in synthetic hydrogen uranospinite, $\text{H}_3\text{O}(\text{UO}_2\text{AsO}_4) \cdot 3 \text{H}_2\text{O}$, was obtained by infrared spectroscopy. It was not possible either to confirm or disprove the existence of oxonium in synthetic members of the alunite-jarosite group by infrared spectroscopy. Although fine structure characteristic of the presence of oxonium was not obtained in NMR spectra of the uranyl arsenates or alunites, a comparison of 77 K and 298 K spectra for different species revealed a degree of non-vibrational motion in some or all of the protons at room temperature.

Introduction

Oxonium ions have been recorded in a number of minerals including spodumene (Gordienko and Kalenchuk, 1966), vermiculite (Bokii and Arkhipenko, 1962), mica (Brown and Norrish, 1952; White and Burns, 1963), palygorskite (Tarasevich and Ovcharenko, 1965), amphiboles (Ginzburg and Yukhevich, 1962), uranophane (Smith, Gruner, and Lipscomb, 1957), hydrated uranate minerals (Sobry, 1971), troegerite (Ross and Evans, 1964, 1965), hydrogen autunite (Ross, 1965), jarosite (Kubisz, 1961; Brophy and Sheridan, 1965), alunite (Parker, 1962) and several other mineral phosphates and arsenates (Tarte and Paques-Ledent, 1968).

Many more minerals may reasonably be expected to contain oxonium ions, either as an essential constituent or in partial substitution for another cation (Kubisz, 1968), but it is not always easy to obtain evidence supporting their presence. As a result of recent interest in the problem, several useful reviews

have appeared (Brasseur and Peters, 1965; Kubisz, 1968; Mel'nikov and Mel'nik, 1969; Nyrkov, 1968).

The presence of oxonium ions in inorganic compounds is often inferred but rarely demonstrated by direct evidence. One such indirect approach has been the demonstration of isomorphous relationships by synthesis of H_3O^+ , K^+ , or NH_4^+ analogues. An early example of this approach is the work of Kraus (1935) who was able to infer the presence of oxonium in heteropoly acids on the basis of isomorphism of tungstoboric acid and its ammonium salt. It may even be possible to show the existence of a complete solid solution between H_3O^+ and K^+ end members as in jarosite (Kubisz, 1961). Another indirect method is the interpretation of chemical analyses of minerals containing excess water together with a cation deficiency (Brown and Norrish, 1952; Bokii and Arkhipenko, 1962; White and Burns, 1963). Although X-ray structure determination may not reveal hydrogen atom positions, the presence of oxonium may be suggested by symmetry considerations. In this way Johansson (1963) was able to infer the presence of oxonium in basic gallium sulfate from the trigonal symmetry of its probable site in the crystal structure. Halla and van Tassel (1956) have inferred the presence of H_3O^+ in the jarosite group using a similar argument.

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The direct determination of oxonium involves obtaining some structural information on hydrogen atoms in the crystal. Neutron diffraction, proton magnetic resonance, and infrared spectroscopy are therefore applicable techniques. The results, however, are not always unambiguous. Neutron diffraction may give clear results on pure oxonium compounds but positional or rotational disorder leads to considerable complexities in interpretation (Norman, 1962). Proton magnetic resonance spectra will give evidence of 2-spin or 3-spin systems only if the systems are relatively isolated from each other. Infrared spectra should give unambiguous confirmation of the presence of oxonium, but absorption from other components in the compound may overlap the regions of critical interest. This problem will be enlarged upon in the present paper.

The purpose of this study was to examine, with infrared and proton magnetic resonance spectroscopic techniques, examples from two mineral groups in which the circumstantial evidence for the presence of oxonium is particularly clear. The two groups selected were hydrogen uranospinite $\text{H}_3\text{O}(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$, abernathyite $\text{K}(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ and related synthetic compounds, and synthetic and natural examples from the alunite-jarosite group.

The crystal structures of $\text{K}(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$, $\text{NH}_4(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$, and $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$ have been described by Ross and Evans (1964). In these compounds NH_4^+ , K^+ and H_3O^+ play essentially the same role (Ross and Evans, 1965). The positions of the hydrogen atoms are not known, but layers which separate the uranyl arsenate sheets are composed of water molecules arranged in what appears to be a tetrahedrally hydrogen-bonded pattern related to the pseudostructure of water (Gurney, 1953). One in four of these molecules are randomly substituted by univalent cations, including oxonium.

The alunite-jarosite group of minerals may be represented by the formula $A^+R^{3+}_3(\text{SO}_4)_2(\text{OH})_6$ where A^+ is usually NH_4^+ , K^+ or Na^+ and R^{3+} is Fe^{3+} or Al^{3+} . On the basis of solid solution studies, a deficiency in the univalent cation content coupled with an analytical excess of water has generally been interpreted to be due to replacement of A^+ cations by H_3O^+ (Shishkin, 1951; Kubisz, 1964; Brophy and Sheridan, 1965). The substitution may be complete, and several oxonium compounds in this group have been synthesized. Hendricks (1937) in

the original structural study on alunite, $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$, and jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$, showed that the compound $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ was isostructural with jarosite.

In the structure of alunite (Wang, Bradley, and Steinfink, 1965), the potassium ion is situated on a site of D_{3d} symmetry. It is surrounded by six equivalent hydroxyl ions, alternatively 2.335 Å above and below the level of the potassium ion. The K-OH bond distance is 2.871 Å. The structure of the oxonium analogue of neither alunite nor jarosite has been studied in detail, but the related gallium salt, $3\text{Ga}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$, has been investigated by Johansson (1963). He concluded that the site occupied by K^+ in alunite is occupied by H_3O^+ in this compound, despite the close juxtaposition of hydroxyl and oxonium ions.

All of the compounds examined were synthesized fairly readily, thus enhancing their value for comparative spectroscopic study. We will show that infrared results from hydrogen uranospinite confirm the presence of oxonium ions, but do not unequivocally confirm oxonium in compounds of the alunite-jarosite group. The resonance results give no evidence of oxonium ions but a useful comparison of the special significance of each technique is obtained.

Experimental

Hydrogen uranospinite³ was synthesized according to the method of Mrose (1953). Sodium, potassium, calcium, and ammonium substituted products were obtained by standing small amounts of the synthetic hydrogen uranospinite in appropriate chloride solutions of molar concentration for a period of four months. Subsequent X-ray diffraction examination showed that the substitution was substantially complete in each case.

Alunites and jarosites were prepared in several ways. The most successful results were obtained using a combination of the methods of Fairchild (1933) and Brophy, Scott, and Snellgrove (1962). A molar ratio of 1:3 for K:Fe or Al in a 0.2N H_2SO_4 solution was heated in sealed pyrex glass tubes at temperatures between 110°C and 160°C for periods of 3 to 10 days. The products were washed several

³ It seems probable that at least two distinct hydrous uranyl arsenates occur as minerals (Shchipanova *et al.*, 1971). Until the position becomes clearer, we prefer not to use the name troegerite for our synthetic material.

times with 0.2N H_2SO_4 , then with distilled water and dried at 60°C. The supposed oxonium analogues formed when the syntheses were repeated without potassium in the solution.

Proton magnetic resonance spectra were taken with a spectrometer which consisted of a marginal oscillator and a 12 in. electromagnet set at about 1650 gauss. The absorption line was obtained directly by continuous averaging techniques using a PDP-8 computer. All specimens were examined as powders at 77 K and 295 K.

Infrared spectra were obtained with materials dispersed in very thin disks prepared from freshly dried KBr. Blank disks showed no appreciable water absorption. Considerable care was taken with sample preparation of the uranium compounds because spectra are easily modified by excessive grinding. Specimens lightly ground in an agate mortar for no more than a few seconds gave the most satisfactory spectra. Examination of each supposed oxonium compound in nujol and in hexachlorobutadiene provided no evidence of exchange between H_3O^+ and K^+ in the KBr discs.

Results

Nuclear Magnetic Resonance Spectra

The lines obtained from the four samples at 295 K and 77 K are shown in Figure 1. The weight of the specimen was the same in each case and the lines are plotted on the same scale with the exception of those from the two arsenate specimens at room temperature. The widths of the lines at half peak height are indicated.

The lines from hydrogen uranospinite and abernathyite at 77 K have the same width, height, and integrated intensity. The second moment of each line is 24.5 (gauss)^2 . There is a significant difference between these lines and the lines obtained at room temperature. In this case the width of the line from abernathyite is about 1 gauss and that from hydrogen uranospinite less than 0.05 gauss.

The lines from the two alunite specimens at 77 K have the same shape and a second moment of 14.5 (gauss)^2 but the peak height and intensity for the oxonium specimen are about twice those from the potassium specimen. At room temperature both lines consist mainly of broad lines similar in shape to those observed at 77 K, but there is a narrower line superimposed on each. The lines from these two alunite specimens are quite different from proton

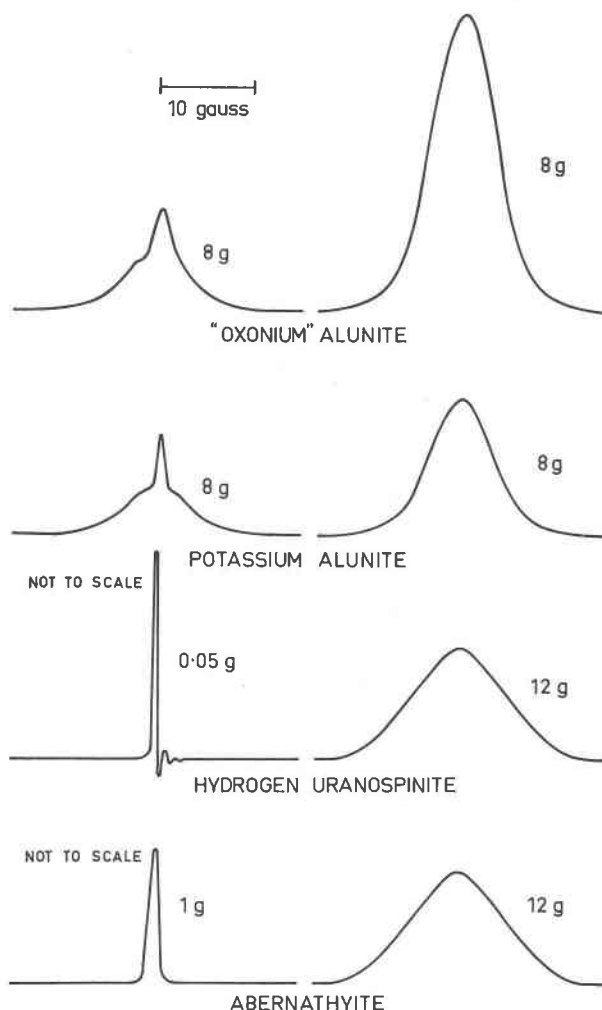


FIG. 1. Proton magnetic resonance spectra of alunites and hydrous uranyl arsenates at 77 K (left) and 298 K (right).

resonance in hydrated gallium sulfate (Kydon, Pintar, and Petch, 1968) so that the assumption that the state of water of hydration in the two systems is similar is not justified.

Resonance line-shapes in polycrystalline materials for systems of two, three, and four identical nuclei are discussed by Andrew (1955). So-called two-spin systems such as H_2O give rise to a double peaked resonance line, and three-spin systems such as H_3O^+ give rise to a triple peaked line. Crystalline nitric acid monohydrate and perchloric acid monohydrate (Richards and Smith, 1951; Kakiuchi *et al*, 1951) give rise to theoretically predicted triple-peaked curves showing that hydrogen is present in these compounds as H_3O^+ ions. They are assumed to be model oxonium compounds.

It might be anticipated that since both uranyl arsenates contain structural water molecules, the differences between their spectra would be due to the oxonium ion contribution in hydrogen uranospinite. The alunites make a similar pair with structural hydroxyl ions in both materials and oxonium in the analogue compound. It is clear that the line shapes at 77 K are the same for each pair and give no positive identification of oxonium ions in either uranyl arsenates or alunites. An absence of fine structure, however, does not necessarily imply the absence of two- or three-spin systems since fine structure will only be observed with a relatively simple unit cell, and when line-broadening intermolecular effects are small. The sheet arrangements of water molecules and oxonium ions, if present in the uranyl arsenates, and the juxtaposition of hydroxyls and oxonium, if present in the alunites, could result in loss of fine structure in the resonance spectra.

The intensity measurements at 77 K indicate that the uranyl arsenates have a similar number of protons, but this is not consistent with the accepted chemical formulae. The large value of the second moment indicates that the protons are fixed in the structure (Andrew, 1955). The main contribution to the line width at this temperature is the intramolecular interaction within a water molecule with much smaller contributions from intermolecular interaction between different molecules. Sharpening of lines at room temperature implies considerable movement of the water molecules in both arsenates. The spectra indicate that each molecule in the abernathyite water sheets has rotational motion, which eliminates the intramolecular effect. The even sharper line from hydrogen uranospinite suggests that there is some additional diffusional movement of each molecule which eliminates the intermolecular effect. The temperature at which water molecules go into rotational motion has not been determined for the uranyl

arsenates, but an NMR study on synthetic autunites, the related uranyl phosphates (Sugitani, 1971), shows that what is termed random motion of the molecules ceases completely at about -60°C .

The intensity measurements at 77 K for the alunites indicate that there are about twice as many protons in the oxonium compound as in the potassium compound whereas the expected ratio is about 1.5. At room temperature most of the protons are in a situation similar to the low temperature conditions, but some are associated with some form of movement. The most likely interpretation is that the broader lines are associated with hydroxyl protons which are fixed in the crystal structure at room temperature and below, and the narrow line is from protons in water molecules which can rotate.

Infrared Spectra

Vibrational Modes of H_2O and H_3O^+ . Attempts to confirm the presence of oxonium frequently resolve themselves into the question of whether water molecules, oxonium ions, or both are present in the compound being investigated. The oxonium ion, H_3O^+ , is isoelectronic with NH_3 and the symmetry of the free ion is C_{3v} . All four distinguishable normal modes of vibration are infrared and Raman active. By contrast, the water molecule has symmetry C_{2v} with three normal modes of vibration, all infrared and Raman active. Recorded frequencies from the most recent infrared observations on solid acid monohydrates and solutions of the same acids are summarized in Table 1.

The most conspicuous differences between the spectra of the two species are that the stretching frequencies (ν_1, ν_3) of the oxonium ion are lower, the bending frequency (ν_4) of H_3O^+ tends to be higher than ν_2 of water, though not invariably, and ν_2 of H_3O^+ is unique. In a review of more than 450 crystal hydrates Yukhnovich (1963) found that the bending vibration, ν_2 , of water occurs in the range $1590\text{--}1670\text{ cm}^{-1}$, whereas ν_4 of H_3O^+ in acid hydrates and aqueous acid solutions occurs in the range $1670\text{--}1750\text{ cm}^{-1}$. However, in very rare cases frequencies have been recorded outside these limits. We may anticipate, therefore, that even in the presence of water molecules, oxonium ions will usually show a distinguishable infrared spectrum.

Abernathyite and Hydrogen Uranospinite. The tetrahedrally hydrogen-bonded arrangement of water molecules in the model structures of abernathyite and hydrogen uranospinite, with random substitution

TABLE 1. Vibrational Frequencies of H_3O^+ and H_2O from Recent Infrared Observations

Compound	State	H_3O^+				State	H_2O		
		$\nu_1(\text{A}_1)$	$\nu_2(\text{A}_1)$	$\nu_3(\text{E})$	$\nu_4(\text{E})$		ν_1	ν_2	ν_3
$\text{OH}_3\text{ClO}_4^*$	s	2820	1020	3220	1670	s(-78°C)	3400	1620	3220
$\text{OH}_3\text{NO}_3^{**}$	s	2780	1135	2780	1680				
$\text{OH}_3\text{HSO}_4^{**}$	s	2840	1160	2840	1620				
Acid *** solutions	l	2900	1205	2900	1750	1(25°C)	3400	1640	3400

*Fournier et al., 1969.

**Savoie and Giguere, 1964.

***Falk and Giguere, 1957.

of oxonium ions for one in four water molecules in the latter mineral, suggests that the infrared spectrum should be closely related to the spectra of oxonium halides in aqueous solution (Fabbri, 1959; Ferriso and Hornig, 1955).

That this is indeed the case is shown in Figure 2 where spectra of abernathyite and hydrogen uranospinite are compared with liquid H_2O and aqueous HCl spectra. Analysis of the synthetic abernathyite for potassium gave 6.91 percent K_2O , which indicates a formula $(K_{0.92}H_3O_{0.08})UO_2AsO_4 \cdot 3H_2O$. The differences between the spectra of the two solids should be due mainly to the presence of H_3O^+ in hydrogen uranospinite. Bands below 1000 cm^{-1} , most of which occur in uranyl and in arsenate spectra, can be assigned as UO_2^{2+} or AsO_4^{3-} absorptions (Table 2). An exception is the broad band in the vicinity of 600 cm^{-1} , which, by reason of its shape and position, is likely to originate in the librational motion of H_2O (ν_R).

Although absorption in the O-H stretching region remains quite intense, the identified oxonium vibrational bands are observed to disappear when the material is heated at 350°C for one hour. Weight loss curves show that water loss occurs soon after the commencement of heating, suggesting that water content is not fixed at exactly three molecules per formula unit at ambient temperatures. Decomposition of oxonium may occur according to the reaction $H_3O^+ + O^{2-} = H_2O + OH^-$. This would explain

TABLE 2. Band Frequencies and Assignments for Hydrogen Uranospinite and Abernathyite

H_3O (UO_2AsO_4) $\cdot 3H_2O$	K (UO_2AsO_4) $\cdot 3H_2O$	Assignment
ν (cm^{-1})	ν (cm^{-1})	
~ 3400	~ 3500	H_2O (ν_1, ν_3)
~ 3400	-	H_3O^+ (ν_1, ν_3)
~ 2300	-	H_2O ($\nu_2 + \nu_R$)
1740	-	H_3O^+ (ν_4)
1635	1645	H_2O (ν_2)
1150	-	H_3O^+ (ν_2)
950	953	UO_2^{2+} (ν_3)
918	900	UO_2^{2+} ($\nu_1?$)
815	818	AsO_4^{3-} (ν_3)
610	590	H_2O (ν_R)
486	497	AsO_4^{3-} (ν_4)
386	372	AsO_4^{3-} (ν_1)

why intensity is maintained in the O-H stretching region during the initial stages of water loss.

Alunite and Jarosite. It is generally agreed that oxonium ions may substitute for potassium in the alunite and jarosite structures. Potassium occupies a site of D_{3d} symmetry. Degenerate vibrations of a C_{3v} ion (H_3O^+) are not resolved in a crystal field of this symmetry. The usual four vibrations of this ion should therefore still be observed, but ν_2 , which coincides with the intense ν_3 absorption of the sulfate ion, will be obscured. There is also overlap between the regions of stretching vibrations of hydroxyl ions and those of oxonium ions. The fine structure visible in the $3000\text{--}3600\text{ cm}^{-1}$ region of jarosite and alunite (Figs. 3, 4), is probably due to

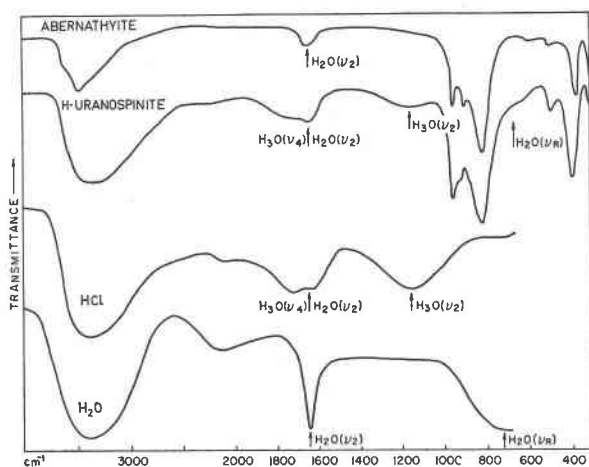


FIG. 2. Infrared spectra of compounds containing H_3O^+ or H_2O . (a) $(K_{0.92}H_3O_{0.08})UO_2AsO_4 \cdot 3H_2O$ synthetic; (b) $(H_3O)UO_2AsO_4 \cdot 3H_2O$ synthetic; (c) aqueous HCl; (d) water. Both (c) and (d) redrawn from data in Fabbri (1959).

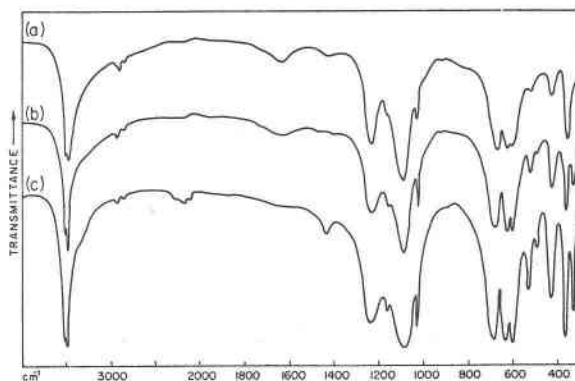


FIG. 3. Infrared spectra of synthetic and natural alunites. (a) $(H_3O)Al_3(SO_4)_2(OH)_6$ synthetic; (b) $(K_{0.99}H_3O_{0.11})Al_3(SO_4)_2(OH)_6$ synthetic; (c) natural alunite, Muzay, Hungary.

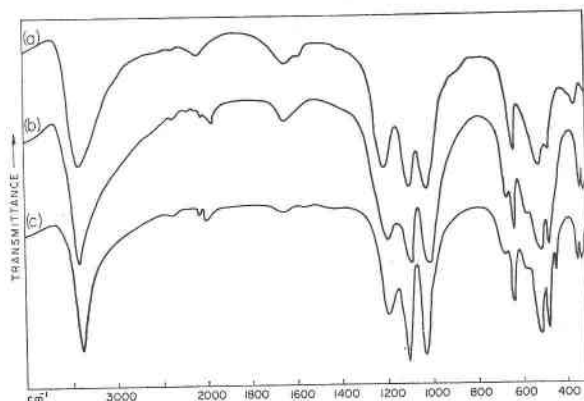


FIG. 4. Infrared spectra of synthetic and natural jarosites. (a) $(\text{H}_3\text{O})\text{Fe}^{3+}(\text{SO}_4)_2(\text{OH})_6$ synthetic; (b) $(\text{K}_{0.82}\text{H}_3\text{O}_{0.18})\text{Fe}^{3+}(\text{SO}_4)_2(\text{OH})_6$ synthetic; (c) natural jarosite, Mt. Morgan, Queensland, Australia.

coupling of the motions of adjacent hydroxyl ions. Variation in the sharpness of the main absorption peak, and in the intensity of the low frequency tail, was observed in samples synthesized at different temperatures. Despite repeated attempts to prove the presence of an absorption band ($\text{H}_3\text{O}^+\nu_{1\nu_3}$) in the 2800–3000 cm^{-1} region in the supposed oxonium alunite (by comparing its spectrum with the spectra of synthetic potassium alunites), it remained uncertain whether a distinct absorption due to H_3O^+ existed. This leaves the 1600–1700 cm^{-1} region as one of critical interest, since in these compounds only H_3O^+ should absorb in this range.

The infrared spectra of both potassium and oxonium jarosites and alunites, however, show absorption at about 1640 cm^{-1} . In addition, the H_3O^+ , Na^+ , K^+ , Rb^+ , NH_4^+ and Tl basic gallium salts of the alunite type figured by Petrov, Pervykh, and Bol'shakova (1966) *all* absorb in this region. Several natural alunites and jarosites, varying from opaque to optically clear, all showed some absorption in this region, even after drying at 160°C before the spectra were taken.

Since extinction coefficients for some oxonium absorptions are small (Tarte and Paques-Ledent, 1968), it is necessary to consider the origin of otherwise minor spectral features. It seems most likely that weak bands at about 1400–1450 cm^{-1} and 2000–2400 cm^{-1} are respectively due to carbonate impurities and to overtones of sulfate stretching vibrations. Associated with the prominent 1640 cm^{-1} band is another minor feature at 1730 cm^{-1} in the alunites and 1575 cm^{-1} in the jarosites. The latter band in particular cannot be easily dismissed, since

there is a correlation between the degree of potassium deficiency and intensity of absorption. It will be observed that the 18 molar percent of oxonium impurity in the potassium compound has contributed intensity to the low frequency tail of the 1640 cm^{-1} band. The spectra must either be interpreted as resulting from two different water molecule environments or the minor absorptions flanking the 1640 cm^{-1} band are due to the presence of oxonium ions.

Discussion

The interpretation of our data on abernathyite and hydrogen uranospinite is fairly straightforward. The close similarities between infrared spectra of hydrogen uranospinite and aqueous solutions containing oxonium ions confirm the existence of oxonium in an environment related to that of liquid water. NMR spectra neither confirm nor disprove the existence of oxonium in this compound, but show the presence of much proton mobility in the interlayer at room temperatures. Our spectroscopic data are therefore consistent with the structural model of the interlayer proposed by Ross and Evans (1965).

The experimental evidence on alunites and jarosites is much more difficult to interpret. Since the characteristic ν_2 absorption of H_3O^+ overlaps with ν_3 of the sulphate ion, the infrared spectral analysis depends on the proper interpretation of minor features in the 1500–1700 cm^{-1} region. The absorption at about 1640 cm^{-1} , which occurs in the spectra of most normal and oxonium alunites and jarosites and has no correlation with potassium deficiency, can only be due to structural water molecules. The anomalous amount of water usually contained in synthetic alunites and jarosites has been the subject of comment (Parker, 1962; Brophy and Sheridan, 1965). The removal of this water by heating results in substantial changes in cell dimensions. It must therefore be structurally combined, not adsorbed or included water. The existence of a trivalent cation deficiency, tending toward the composition $\text{KR}^{3+}_2(\text{SO}_4)_2(\text{OH})_3(\text{H}_2\text{O})_3$ would explain this excess water content. A trivalent cation deficiency is a feature of synthetic alunite analyses (Parker, 1962), and there is one analysis on record (by Parker in Brophy *et al.*, 1962, Table 1) which shows a marked excess of water and deficiency of aluminum that may represent a substantial amount of this substitution.

The only infrared band which appears to correlate

in intensity with the degree of potassium deficiency is the 1575 cm^{-1} absorption in the jarosites. This band is outside the normal range of oxonium ν_4 frequencies but there are some other well substantiated cases (Paques-Ledent and Tarte, 1969) where this is known to occur. Alternatively, this band could result from the bending vibration of water molecules situated within the site occupied by potassium in normal jarosites.

The suggestion that H_3O^+ can exist in a crystal when OH ions are present in the near vicinity may be considered to be surprising. The ionic product of liquid water is 10^{-14} at 25°C and although a different value in a crystal would be expected, a change of some 12 orders of magnitude would be necessary for both H_3O^+ and OH^- to exist in appreciable concentration at equilibrium.

Perhaps for this reason, Hendricks (1937) proposed the structural formula $\text{H}_2\text{O} \cdot \text{Fe}^{3+}_3(\text{SO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$ for the compound $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ which has the jarosite structure. He believed the potassium sites in the jarosite structure to be occupied by water molecules with charge balance maintained by the coupled substitution of water molecules for one in six hydroxyl ions. Subsequently most authors have inclined to the opinion that H_3O^+ in the potassium site and OH^- can exist in these compounds in juxtaposition.

It is important to recognize that wherever oxonium and hydroxyl ions are supposed to coexist in a mineral structure, indirect methods cannot distinguish whether the protons are arranged into groups of one and three (OH^- , H_3O^+) or only groups of two (H_2O). Indeed, if the protons are mobile, the exchange $\text{H}_3\text{O}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{H}_2\text{O}$ may occur continuously and, if the period of existence of the ion or molecule is greater than the vibrational frequency, it will be recorded in the infrared spectrum. In addition, the possible existence in these compounds of higher hydrates of H^+ such as H_5O_2^+ (Gilbert and Sheppard, 1973) cannot be entirely overlooked although it does add further complexity to the interpretation of the spectra. It would therefore seem to be impossible with the data at hand to come to any firm conclusion.

The NMR spectra do not provide evidence of oxonium ions in any of the compounds studied. It is possible to distinguish, however, between protons which are essentially in fixed positions in the crystal structure and those which are involved in some sort of rotational or diffusional motion. Since the latter

component is present in both potassium and oxonium alunite spectra, it seems most likely to be due to rotational motion of some of the excess water molecules in the structure, depending on the type of substitution involved. The discrepancy between theoretical and observed relative intensities must also be related to additional water substituted in these structures.

Conclusion

Due to strong intermolecular interactions resulting from the relative structural complexity of common minerals which may contain oxonium, it is unlikely that nuclear magnetic resonance spectra will often show fine structure characteristic of oxonium ions, even if they should in fact exist in these materials. This problem may be overcome to some extent by the use of single crystals. The exceptions to these observations are where oxonium ions, perhaps in substitution for large univalent cations, are in structural isolation from other proton-containing species. On the other hand, nuclear magnetic resonance gives a powerful indication of the degree of mobility of the protons, information which is difficult to obtain in other ways.

Similarly, application of infrared spectroscopy to the determination of oxonium is limited by the chemistry of the compound. From the examples we have studied, it is possible to anticipate areas where infrared analysis will be most fruitfully applied. The only oxonium frequency which cannot be confused with those deriving from water molecule vibrations is ν_2 at about 1150 cm^{-1} . The absorption band corresponding to this frequency is commonly broad and weak. This frequency corresponds, in part, with that of the intense asymmetric stretching vibration, ν_3 , of some common tetrahedral anions such as sulfate, phosphate, and silicate and possibly with vibrations of other anions. In these materials, unless it is possible to prove the presence of a hydrogenic absorption in this region by deuterium substitution, attention must be concentrated on the $1500\text{--}1700\text{ cm}^{-1}$ region in which the bending vibration of H_2O also occurs. This may lead to insuperable difficulties of interpretation, especially if water molecules are present as impurity, or if hydroxyl and oxonium exist together in the same structure. Materials containing only anions of heavy elements, such as arsenate, however, which have their highest fundamental frequency vibration below 1000 cm^{-1} , make ideal subjects for infrared examination. Our investi-

gations also suggest that minerals with oxonium ions in interlayer water molecule sheets are especially favorable for study, provided anion absorptions allow observation of the 1100–1200 cm^{-1} region.

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