

VARIATIONS IN INFRARED SPECTRA, MOLECULAR SYMMETRY AND SITE SYMMETRY OF SULFATE MINERALS

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ABSTRACT

The interaction of the functional molecular group, SO_4^{2-} , in sulfate minerals with its extramolecular environment is usually manifest in the splitting of degeneracies of vibrational modes of the ion. Although symmetry prescribes the number of components of degenerate vibrational modes such as ν_2 , the spectra of sulfate minerals do not always observably reflect symmetry effects, and it is, therefore, not always possible to obtain information about molecular symmetry of sulfate minerals by counting the number of absorptions. The absorption spectra of most sulfate minerals studied, however, give evidence of the modification of the symmetry of the sulfate ion from T_d to various lower symmetries. The spectral data for alunite and jarosite show more vibrational components for ν_3 than permitted by the site symmetry of the sulfate ion, thus indicating the presence of non-equivalent ions.

INTRODUCTION

In recent years there has been increasing interest in infrared application to mineral analysis. As a result the need for more information on factors affecting variation of characteristic molecular group frequencies has become evident, for without this knowledge there is little possibility of deriving unambiguous information of structural significance from complex mineral spectra.

Certain general principles that govern the correlation of the vibrational spectra of molecular ions with their structural features are implicit in every application of absorption spectroscopy. First, each vibrational frequency is associated with a different motion of the vibrating nuclei; second, each specific configuration of the nuclei forming the molecule will produce a characteristic vibrational spectrum; third, the vibrational spectrum is dependent both on the masses of the nuclei and the internal forces that maintain the equilibrium configuration of the molecule; and, fourth, the functional molecules may exist in crystals in differing environments which more or less alter the equilibrium parameters of the molecule. From what has already been done, it is apparent that the interaction of functional molecular groups with their surrounding ions is an important aspect of molecular absorption spectroscopy of minerals.

Recent spectral investigations (Adler and Kerr, 1963a,b) emphasizing the dependence of functional molecular groups on intermolecular environment have shown that the spectroscopic distinction between minerals in both the calcite and aragonite groups has as its basis the modification of

intramolecular forces by the introduction of cations of different sizes and electronic properties between ionic carbonate molecules. The relevant structural effect of these substitutions is thought to be the constriction or dilation of the molecular CO_3^{2-} ion as oxygen atoms of neighboring molecules are either drawn nearer or apart on substitution of extramolecular cations of different size (Weir and Lippincott, 1961). The resultant functional effect is a corresponding increase or decrease in molecular vibration frequency which is evident in spectral shifts. The vibrational frequencies are observed to vary more or less linearly with change in radius of the intermolecular cation, but this relationship appears generally to hold true only for cations belonging to the same periodic group.

Molecular vibrations also respond to the structural arrangement of the adjoining extramolecular ions. These environmental ions provide as a general expression of their geometric configuration the site symmetry of the molecule. The effective property of the site symmetry is the restriction it imposes on molecular symmetry, for, generally, a molecule has lower symmetry in a crystal than in the free state because of the deformational forces exerted by the surrounding ions. It is of considerable importance that the molecular symmetry suggested in almost all inorganic compounds is equivalent to or higher than the site symmetry.

The effects of low symmetry in the molecule are evident usually in splitting of degeneracies and in the appearance of latent bands representing vibrations sensitive to dipole adjustments. These effects account for the spectral differences between calcite and aragonite as well as other structurally dissimilar carbonate minerals (Adler and Kerr, 1963a,b). It is also of considerable importance that in some cases either the magnitude of the splitting is too small or the amplitude of one component is too low to permit resolution of the split degeneracy. The spectra of certain carbonates, *e.g.* aragonite and witherite, vary for this reason, particularly in the character of the ν_4 mode. If it were not for such inconsistencies in the resolution of splitting, the spectral characteristics of a molecule could be treated practically in terms of its site symmetry, *i.e.*, one could predict exactly the nature of the molecular absorption spectrum from site symmetry data. It should be emphasized, however, that in spite of this deficiency site symmetry provides very useful information in that it restricts consideration of molecular symmetry to specific point groups and places certain limitations on vibrational and corresponding spectral variations. These restrictions are an invaluable aid in utilizing absorption spectra to detect the possible presence of non-equivalent molecules in crystals, particularly when the spectral enrichment does not exceed the maximum number of fundamental bands prescribed for non-linear molecules by the 3N-6 relationship.

Although this investigation deals specifically with structural and vibrational aspects and features of the molecular sulfate ion, SO_4^{2-} , the considerations are also applicable to other tetrahedral molecules.

EXPERIMENTAL METHOD

The infrared spectra shown here were obtained on a Perkin-Elmer Model 21 spectrophotometer using NaCl optics. Samples for spectral runs were prepared from finely ground (minus 300-mesh) material. For most samples an amount varying from 0.75 to 1.5 mg was mixed and ground with 300 mg of KBr in a dental amalgamator; for the heavy sulfates a slightly larger quantity of mineral was used. The mixture was pressed in a tool-steel die at about 19,000 psi to form a translucent pellet approximately 12 mm in diameter. A standard pellet of KBr placed in the reference beam compensated for energy loss caused by KBr in the sample pellet.

It warrants mentioning here that anglesite, PbSO_4 , reacts with the KBr matrix and may yield a range of spectra depending on the degree of interaction and K_2SO_4 formation (Meloche and Kalbus, 1958). The absorption band positions for anglesite may be established, however, if the reaction has not advanced to the stage where the K_2SO_4 band at 9.00μ becomes conspicuous or the intensity of the ν_1 band (10.34μ) for anglesite is considerably diminished.

Mineral specimens for this study were made available from the collections of the U. S. National Museum, Washington, D. C., through the courtesy of Dr. George Switzer, whereas commercially available chemical salts were used to obtain spectra of compounds not available in mineral form. Identification of all mineral species and compounds was confirmed by *x*-ray analysis.

The writers are indebted to Dr. Irving Breger and the U. S. Geological Survey for the use of the spectrophotometer and to Dr. Ralph S. Halford of Columbia University for suggestions concerning alternative interpretations of certain spectral features. Dr. Howard T. Evans, Jr., furnished many helpful comments on crystal structure data.

SPECTRAL FEATURES OF ANHYDRITE AND BARITE-GROUP MINERALS

The barite group consists of the minerals barite, BaSO_4 , celestite, SrSO_4 , and anglesite, PbSO_4 , having cations of relatively large size. The Ca ion, which is comparatively small, does not produce a structurally analogous sulfate but forms instead the mineral anhydrite, CaSO_4 , of different structure type. Infrared spectra of these minerals are shown in Fig. 1 and wavelength data are given in Table 1.

Barite-group minerals yield three intense bands in the 8 to 10μ region

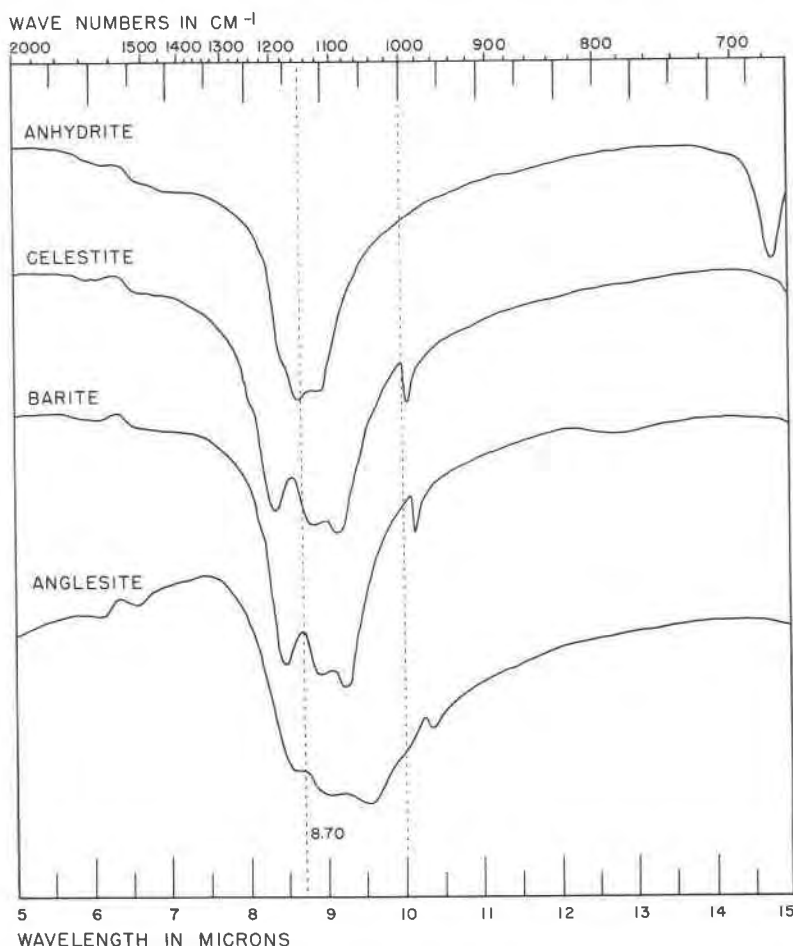


FIG. 1. Infrared spectra of anhydrite and barite-group minerals. The spectral shift of the ν_3 (8.5 to 9.5 μ) and ν_1 (10 μ) modes for the barite group is a function of cation substitution.

(Fig. 1), which correspond to the ν_3 vibrations of the sulfate ion. Although this fundamental is triply degenerate when the sulfate molecule has the ideal tetrahedral configuration, it is here resolved into its three component modes because of the low molecular symmetry imposed by the environment of the sulfate ion. The weak band slightly above 10 μ corresponds to the ν_1 vibrational mode which is non-degenerate and, therefore, yields only one band. The anhydrite spectrum shows a doubly split ν_3 band but is lacking apparent absorption corresponding to ν_1 . Absorption at 14.8 μ is attributed to the ν_4 mode.

The barite-group shows a spectral shift of the ν_3 and ν_1 modes which is dependent on cation substitution. Several features of this shift are worthy of emphasis. With substitution of larger cations, for example Ba for Sr, ν_3 and ν_1 are displaced to lower frequencies (longer wavelengths). Substitution of Pb causes further lowering of the vibrational frequencies, though consideration of radius effects alone dictates a position between celestite and barite. These trends are qualitatively similar to those observed (Adler and Kerr, 1963a) for the isostructural anhydrous normal carbonates of these metals. The seemingly anomalous position of the anglesite spectrum may be caused by a mass effect, but in accord with our conclusions derived from studies of calcite- and aragonite-group minerals it is more likely related to the dissimilarities in electronic configuration between Pb and Group II ions. The frequency-mass and frequency-ionic radius trends for the barite group are depicted in Figs. 2, 3, 4 and 5. They are remarkably similar to the trends for carbonate minerals of the aragonite group shown in the paper previously mentioned.

Omori and Kerr (1963) recently published the spectra of saline sulfate minerals and noted qualitative differences in their infrared absorptions.

TABLE 1. INFRARED ABSORPTION MAXIMA (IN MICRONS AND CM^{-1}) OF ANHYDRITE AND BARITE-GROUP MINERALS

Mineral	Locality	ν_3	ν_1	ν_4
Anhydrite	Champo, Isere, France, ¹ 46393 ²	8.65, 8.92 1156, 1121	—	14.78 677
Anhydrite	Lyon Co., Nevada	8.67, 8.94 1153, 1119	—	14.82 675
Celestite	Lampasas, Texas, ¹ 46918	8.36, 8.84, 9.13 1196, 1131, 1095	10.05 995	
Celestite	Mt. Bonnell, Texas	8.38, 8.83, 9.15 1193, 1133, 1093	10.06 994	
Barite	Buck Creek, N. C., ¹ 18160	8.48, 8.93, 9.23 1179, 1120, 1083	10.15 985	
Barite	Felsobanya, Roumania	8.54, 8.98, 9.26 1171, 1114, 1080	10.18 982	
Anglesite	Monte Poni, Sardinia, ¹ C4587	8.59, 9.06, 9.53 1164, 1104, 1049	10.34 967	

¹ Infrared spectra are shown in Fig. 1.

² U. S. National Museum number.

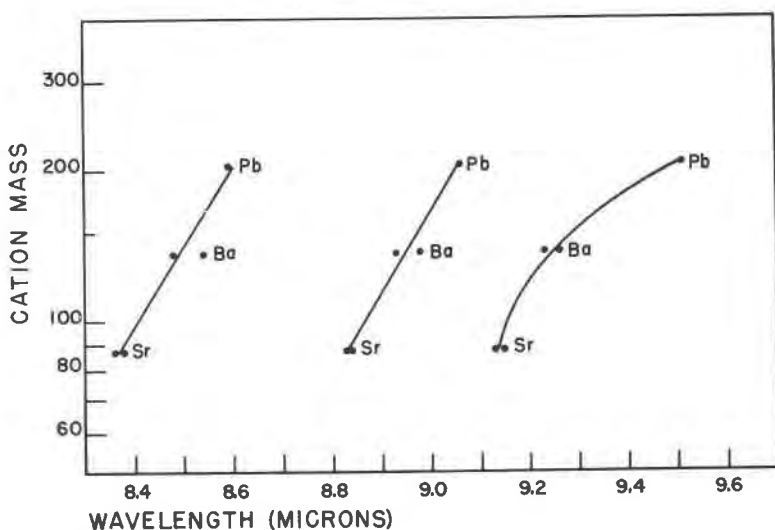


FIG. 2. Variation of the barite-group ν_3 sulfate absorption bands with change in cation mass.

The absorption bands of the barite group assigned here to the ν_1 mode and to the high frequency component of the ν_3 mode were considered by them as possibly originating with the metabisulfite ($S_2O_5^{2-}$) ion. The principal difficulty with this interpretation is that although $S_2O_5^{2-}$ molecules form various inorganic salts their presence in minerals has evidently not been confirmed by *x*-ray diffraction studies. Moreover, the bands attributed to $S_2O_5^{2-}$ ions are readily identifiable with the normal vibrations of the ν_3 and ν_1 modes of the SO_4^{2-} ion. We can expect rather confidently, therefore, that the $S_2O_5^{2-}$ bands shown in this earlier survey are caused by vibrations of the sulfate ion.

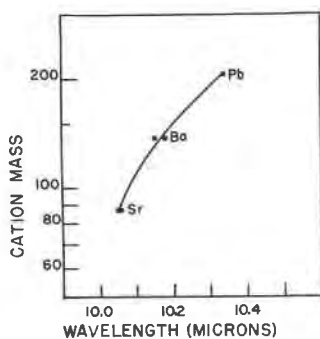


FIG. 3. Variation of the barite-group ν_1 sulfate absorption band with change in cation mass.

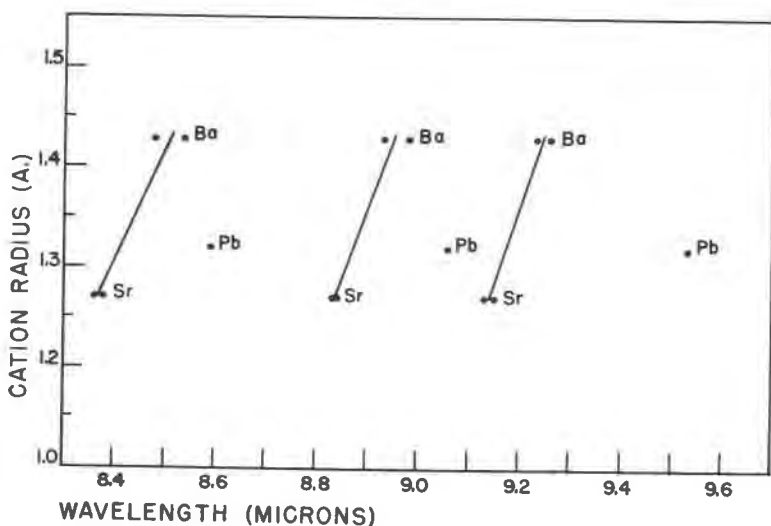


FIG. 4. Wavelength variation of the barite-group v_3 sulfate absorption bands with change in cation radius.

VIBRATIONAL CHARACTERISTICS OF MOLECULES WITH TETRAHEDRAL AND MODIFIED SYMMETRIES

Any molecule of high symmetry may react with its environment in a crystal in such a way that its normal or ideal configuration is modified to lower symmetry. For spectroscopic purposes, molecular point groups resulting from this interaction are referred to as subgroups of the molecule. As the deformational forces become weaker more symmetry elements may be added to the molecule, and its configuration becomes more symmetrical. Since molecular vibrational modes also conform to sym-

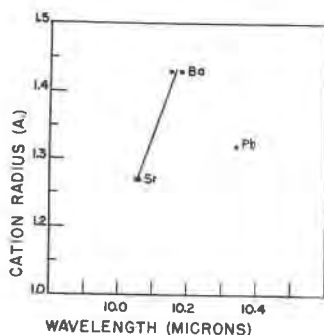


FIG. 5. Wavelength variation of the barite-group v_1 sulfate absorption band with change in cation radius.

TABLE 2. VIBRATIONS OF THE SO_4^{2-} ION AS A FUNCTION OF MOLECULAR SYMMETRY

Molecular Point Group	Number of Infrared Active Vibrational Modes			
	ν_3	ν_1	ν_4	ν_2
T_d	1	0	1	0
D_{2d}	2	0	2	0
C_{3v}	2	1	2	1
D_2	3	0	3	0
C_{2v}	3	1	3	1
C_2	3	1	3	2
C_s	3	1	3	2
C_1	3	1	3	2

metry properties, a simplification of the normal vibrations is brought about by increasing molecular symmetry. Hence, the maximum number of symmetry vibrations occur when the molecule either lacks or has low symmetry, and the minimum number occur when the molecule is in its highest symmetrical form.

Polyatomic molecules, such as the sulfate ion, SO_4^{2-} , perform complicated vibrational motions which are resolved into specific sets of vibrations or normal vibrational modes. Each normal mode is independent and vibrates with a given frequency. Since there are for non-linear molecules $3N-6$ normal modes of vibration, where N is the number of atoms in the molecule, the sulfate ion has nine possible vibrational modes. These occur as the ν_3 , ν_1 , ν_4 and ν_2 modes, listed in order of decreasing vibrational frequency.

If during a symmetry operation one vibration of a particular mode is indistinguishable from a second, the vibrational frequencies will necessarily be identical, and the mode is then referred to as being doubly degenerate. Similarly, certain modes are endowed by their symmetry properties with triple degeneracy or non-degeneracy. Degenerate vibrations necessarily occur only for molecules having at least one rotation axis with more than two-fold symmetry, and triple degeneracy can occur only if a molecule possesses more than one three-fold axis and is therefore restricted to tetrahedral and octahedral molecules. The tetrahedral sulfate ion has two triply degenerate vibrations, ν_3 and ν_4 , one doubly degenerate vibration, ν_2 , and one non-degenerate vibration, ν_1 .

Among the possible molecular subgroups (Table 2) produced by variable external binding forces acting on the SO_4^{2-} ion, only subgroups D_{2d} and C_{3v} have degenerate vibration species. The ν_2 mode of subgroup C_{2v}

also appears degenerate though the group does not have the requisite symmetry property for degeneracy. Actually, ν_2 occurs as a single vibration because one of its two vibration species is infrared inactive.

The spectral activity of a molecule is also dependent on whether or not the vibration of the molecule produces a change in the dipole moment of the molecule. A vibration may be infrared active only if the centers of positive and negative charge in the molecule are separated during the vibrations of its positive and negative ions. In other words, if the vibrational motions of the participating atoms produce zero dipole moment in all vibrational positions, the vibrational mode will be inactive in the infrared.

Normally, degenerate modes of a molecule of low or no symmetry split observably into several components. In some cases, however, splitting is not resolved in the spectra, particularly those obtained in routine or survey studies, because of the low magnitude of the split or the low intensity of one component. This factor frequently accounts for the disparity in number of bands reported by various investigators. Such differences are usually restricted to modes having split components that vary only slightly in frequency.

Because symmetry imposes certain restrictions on the number of permissible vibrations, it is theoretically possible by determining the number of distinct vibrations to obtain information about the molecular symmetry. Furthermore, the molecular vibrations are significantly altered by changes of extramolecular environment that affect molecular symmetry. The question then arises whether site-symmetry considerations alone will reveal the nature of the spectrum. We have examined this problem and report our conclusions in the following sections.

MOLECULAR SYMMETRY, SITE SYMMETRY AND SPECTRAL CHARACTERISTICS

The fundamental frequencies of the sulfate ion are given by Herzberg (1945) as 1104 cm^{-1} (ν_3), 981 cm^{-1} (ν_1), 613 cm^{-1} (ν_4) and 451 cm^{-1} (ν_2), corresponding to absorption at approximately 9, 10, 16 and 22 μ respectively. When the symmetry of the SO_4^{2-} ion in a crystal is T_d , each of the triply degenerate vibrations, ν_3 and ν_4 , gives rise to one band. These are found near 9 and 16 μ . The ν_1 and ν_2 modes are totally symmetrical for this molecular configuration and are, therefore, infrared inactive. Nakamoto, *et al.* (1957), however, found weak absorption at 10 μ , although intrinsic symmetry was essentially unchanged from T_d , which they ascribed to coupling of molecular vibrations. Thus, when single bands are observed at 9 μ (ν_3) and 16 μ (ν_4) and no absorption appears at 22 μ (ν_2) the ion should have a well-defined highly symmetrical con-

figuration; absorption at $10\ \mu$ in this case may be either very weak or absent.

Effects of modified symmetry on vibrational frequencies of the sulfate ion have been demonstrated for coordination compounds containing strong metal-ligand bonds (Nakamoto, *et al.*, 1957). When functioning as a unidentate ligand the one strongly bonded oxygen of the SO_4^{2-} group is no longer symmetrically equivalent to the other three, and the effective symmetry of SO_4^{2-} is lowered to C_{3v} . When a bidentate bond is produced the symmetry is further reduced to C_{2v} . The activities of the vibrations increase observably with lowered symmetry and correlate very satisfactorily with the vibrational characteristics expected from theoretical considerations. The characterizing spectral differences for these two subgroups are given in Table 2 together with those for other possible molecular configurations of the sulfate ion.

The spectra in Figs. 1, 6, 7 and 8 give evidence of various molecular-configurational changes of the sulfate ion. The region of the infrared spectrum studied was, regrettably, restricted to wavelengths below $15\ \mu$; hence, only ν_3 and ν_1 were fully recorded. Supplemental data on ν_4 were, however, available from Moenke (1959) for many of these minerals and are included in Table 4.

It is clear from examination of the data in Tables 2 and 4 that the spectral characteristics of the vibrational modes may not always provide sufficient indication of molecular symmetry. For example, data on ν_3 and ν_1 for gypsum suggest C_{3v} symmetry for the sulfate ion, and Moenke's (1959) data on ν_4 are in accord; that is to say when ν_3 and ν_4 are doubly split and ν_1 is apparent, the ion, according to data in Table 2, should have C_{3v} symmetry. However, if the site symmetry, C_2 , of the SO_4^{2-} ion in gypsum (Strukturbericht IV, 1938) is considered, we find from inspection of Table 3 that the ion may have one of five possible configurations,

TABLE 3. POSSIBLE SITES FOR MOLECULAR POINT GROUPS
OF THE SULFATE ION

Molecular Point Group	Molecular Site Group
T_d	$C_1, C_8, C_2, C_3, C_{2v}, C_{3v}, D_2, D_{2d}, S_4, T, T_d$
D_{2d}	$C_1, C_8, C_2, C_{2v}, D_2, D_{2d}, S_4$
C_{3v}^*	C_1, C_3, C_2, C_{3v}
D_2	C_1, C_2, D_2
C_{2v}^*	C_1, C_2, C_{2v}
C_2^*	C_1, C_2
C_s^*	C_1, C_s
C_1^*	C_1

* Point groups to which a molecule with a dipole moment might belong.

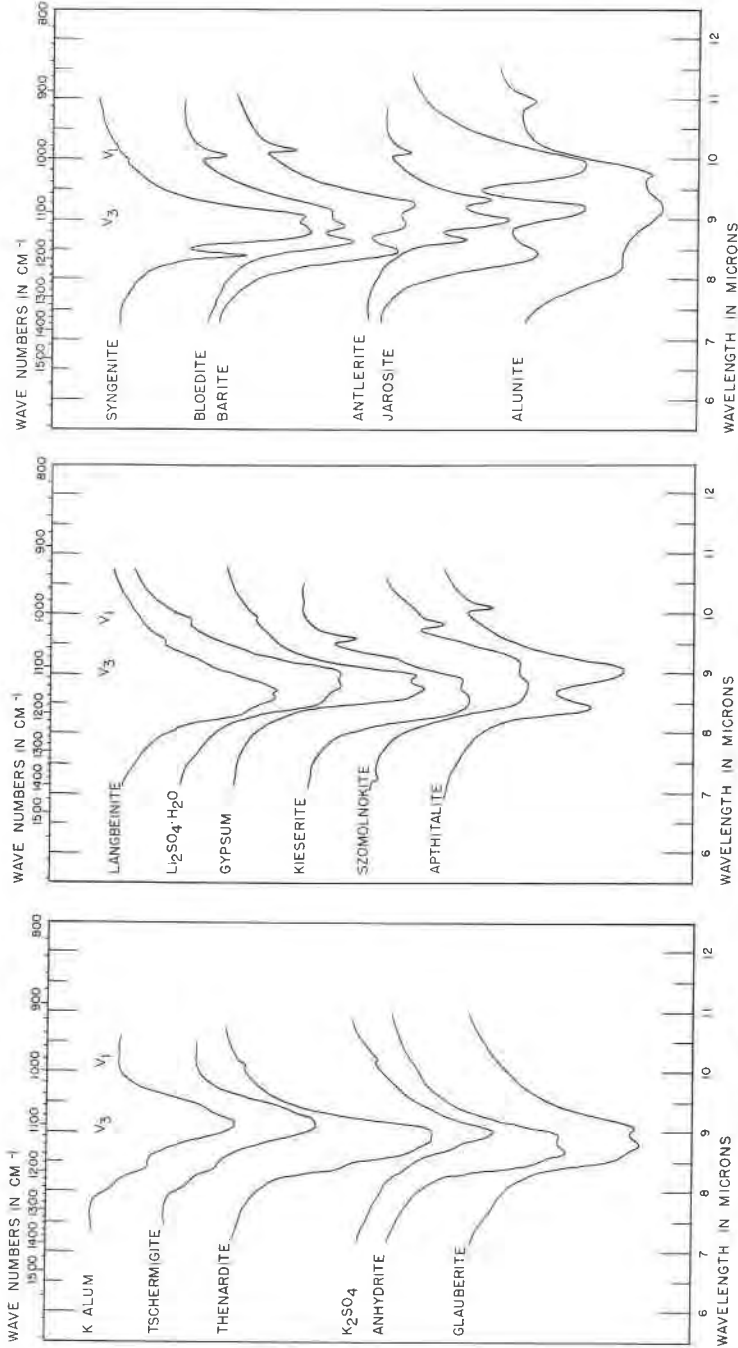


FIG. 6. Infrared absorption bands corresponding to the v_3 and v_1 vibration modes of sulfate minerals. Anhydrite and glauberite show doubly split bands characteristic of low molecular symmetry.

FIG. 7. Infrared absorption bands corresponding to the v_1 and doubly split v_3 vibration modes of sulfate minerals. bloedite, barite and antlerite. Jarosite and alunite contain non-equivalent molecules giving rise to multiple bands in the v_3 region.

TABLE 4. VIBRATIONAL DATA, SITE SYMMETRY AND POSSIBLE MOLECULAR SYMMETRIES OF SOME SULFATE MINERALS

Mineral	Number of Observed Absorption Bands			Site Symmetry	Suggested Molecular Symmetry ⁵
	ν_3	ν_1	ν_4^1		
thenardite	1	1 (vw)	2 ²	D_2	D_2 or D_{2d}
K-alum	1	—		C_3	C_{3v} , T_d
tschermigite	1	—		C_3	C_{3v} , T_d
apthitalite	2	1	1	C_{3v}	C_{3v}
anhydrite	2	0	3	C_{2v}	C_{2v}
gypsum ³	2	1 (vw)	2	C_2	C_2
kieserite	2	1		C_2^4	C_2 , D_2 , D_{2d}
glauberite	2	0	2	C_2 or C_1^4	all but T_d
$Li_2SO_4 \cdot H_2O$	2	1 (vw)		C_1	all but T_d
K_2SO_4 (arcanite)	1	1 (vw)		C_s	C_s , C_{2v} , C_{3v} , D_{2d} , T_d
barite	3	1		C_s	C_s or C_{2v}
antlerite	3	1		C_s^4	C_s or C_{2v}
syngenite	3	1 (vw)	3	C_1 or C_s^4	C_1 , C_s , C_2 or C_{2v}
langbeinite	2	1 (vw)	3	C_1	C_1 , C_s , C_2 or C_{2v}
bloedite	3	1	3	C_1^4	C_1 , C_s , C_2 or C_{2v}
jarosite	3	—		C_{3v}	non-equivalent molecules
alunite	3	1		C_{3v}	non-equivalent molecules

vw = very weak

¹ Data obtained from Moenke (1959).

² Moenke (1959) also shows 2 ν_3 bands.

³ Hass and Sutherland (1956) report 3 ν_3 , 1 ν_1 , 3 ν_4 and 2 ν_2 bands; their determination is used as the basis for selecting C_2 molecular symmetry.

⁴ Site symmetry determined by the method described by Halford (1946); all others obtained from Strukturbericht or Structure Reports.

⁵ Where more than one possibility is indicated, the molecular symmetry of choice, i.e., identical to site symmetry, is listed first.

T_d , D_{2d} , D_2 , C_{2v} or C_2 , but that it cannot have symmetry C_{3v} . If we attribute the 10 μ band to coupling of molecular vibrations rather than to a true ν_1 vibration, D_{2d} would be the symmetry choice. One cannot, however, discount the possibility that both ν_3 and ν_4 are incompletely resolved and, therefore, that the ion may have lower symmetry C_{2v} or C_2 . Hass and Sutherland (1956) have indeed determined this to be the case. From a detailed study of the spectrum of gypsum they found that both ν_3 and ν_4 have three component bands, the two closest ν_3 bands lying 11 cm^{-1} apart and the two closest ν_4 bands lying only 2 cm^{-1} apart. These pairs obviously could not be resolved without rigorous experimentation. One ν_1 and two ν_2 modes are also reported. The data of Hass and Suther-

TABLE 5. ABSORPTION MAXIMA OF THE SO_4^{2-} ION
IN VARIOUS SULFATE MINERALS

Mineral	Locality	Absorption (in Microns and Cm^{-1})	
		ν_3	ν_1
potash alum	Esmeralda Co., Nev., 15768 ¹	9.15 1093	—
tschermigite	Dux, Czechoslovakia, 80401	9.14 1094	—
thenardite	Esmeralda Co., Nev., 95084	8.96 1116	10.09 991
K_2SO_4 (arcanite)	reagent	9.00 1111	10.19 981
anhydrite	Lyon Co., Nev., C4597	8.67, 8.94 1153, 1119	—
glauberite	Saline Valley, Calif., 87377	8.81, 9.08 1135, 1101	—
langbeinite	Carlsbad, N. M., R10389	8.60, 8.73 1163, 1145	9.04 1106
$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	reagent	8.81, 9.00 1135, 1111	9.90 1010
gypsum	Carrizalillo, Chile, 102749	8.76, 8.98 1142, 1114	9.96 1004
kieserite	Hallstatt, Austria, 96536	8.57, 8.88 1167, 1126	9.60 1042
szomolnokite	Dividend, Utah, 104303	8.80, 9.15 1136, 1093	9.84 1016
aphthitalite	Searles Lake, Calif., 105969	8.45, 9.06 1183, 1104	10.11 989
syngenite	Kalusz, Poland, R9779	8.41, 8.80, 9.05 1189, 1136, 1105	9.98 1002
bloedite	Stassfurt, Germany, R6166	8.64, 8.90, 9.10 1157, 1124, 1099	10.07 993

¹ U. S. National Museum number.

TABLE 5. (continued)

Mineral	Locality	Absorption (in Microns and Cm^{-1})	
		ν_3	ν_1
barite	Buck Creek, N. C., 18160	8.48, 8.93, 9.23 1179, 1120, 1083	10.15 985
antlerite	Chuquicamata, Chile, 97739	8.68, 9.00, 9.34 1152, 1111, 1071	10.13 987
jarosite	Chuquicamata, Chile, 105778	8.44, 9.20, 9.94 1185, 1087, 1006	?
alunite	Death Valley, Calif., 87529	8.30, 9.20, 9.74 1205, 1087, 1027	10.98 (?) 911

land (1956), therefore, provide evidence of molecular symmetry C_2 which is identical to the site symmetry of the molecule.

As another example, data presented here on ν_3 and ν_1 for thenardite suggest T_d molecular symmetry whereas data by Moenke (1959) point to D_{2d} or C_{3v} symmetry. The site symmetry for thenardite, D_2 (Strukturbericht II, 1927), allows a choice of D_2 , D_{2d} or T_d molecular symmetry, but C_{3v} symmetry is not allowed. Since one cannot be certain that ν_3 and ν_4 are not triply separable, the true molecular symmetry is not discernible from the data at hand. Other examples are evident from the data presented in Table 4.

Failure to identify the symmetry of the molecule from spectral considerations alone is caused largely by the uncertainty of whether the vibrational modes are completely resolved. Although it is probable that molecular symmetry conforms closely to site symmetry, this cannot be regarded as established from the data at hand. To obtain the agreement between site symmetry and suggested molecular symmetry in Table 4 it was necessary in some cases to assume that the spectra are incompletely resolved. An extension of the spectra to include ν_4 and ν_2 and work at higher resolution might resolve this question.

NON-EQUIVALENT MOLECULAR SITES IN SULFATES

Infrared criteria for the presence of non-equivalent ions in the unit cell have been established in a previous paper on carbonate minerals (Adler and Kerr, 1963b). Since a polyatomic molecule having N atoms can have no more than $3N-6$ normal modes of vibration, the fundamental spec-

trum for any CO_3^{2-} ion is limited to six vibrational modes. For the same reason, SO_4^{2-} ions cannot have more than nine fundamental vibrational frequencies. These fundamental vibrations are basically symmetric or asymmetric with respect to certain symmetry elements and are grouped accordingly into distinguishable species such as ν_1 , ν_2 , etc. Any component vibration of a mode may undergo position transformation with respect to a particular symmetry operation, and under proper symmetry conditions will become degenerate. Molecular symmetry limits the number of vibrational components for each species. Thus, as already indicated for the sulfate ion, ν_3 can have no more than three components, ν_1 no more than one and so on.

Because the vibrational behavior of the molecule must be in accord with site symmetry, any enrichment of the spectrum beyond the limitations imposed by site symmetry may be an indication of the existence of non-equivalent ions in the crystal. Such ions may have similar site symmetries but differ necessarily with respect to internal internuclear forces. These intrinsic differences may be brought about in minerals by changes in the molecular surroundings, *e.g.* by substitution of intermolecular cations of different radii or electronic properties.

For all of the sulfate minerals already considered there are never more vibrational components than allowed by the site symmetry. However, when considerations similar to the foregoing are applied to alunite and jarosite we find that the number of vibrational components identifiable with ν_3 , namely three, exceeds the maximum number permitted by the C_{3v} site symmetry of the sulfate ion, namely two (Tables 2 and 4). Since the molecule cannot have lower symmetry than the site, this enrichment points to the existence in the crystals of each mineral of at least two molecules that are not equivalent. This interpretation is in accord with Hendrick's (1937) identification of two sets of sulfate ions with different orientations. Observation of more bands than necessary to satisfy site-symmetry requirements, therefore, is a very effective method for determining whether non-equivalent functional ions populate the unit cell, and because of the simplicity of its application may be of considerable value as an adjunct to *x*-ray structure studies.

It should be pointed out that other mechanisms of spectral enrichment exist. Hornig (1948), for example, has cautioned that combination bands may cause apparent violations of selection rules for internal vibrations and that the intensity of these combination frequencies may be considerable. In some cases a forbidden fundamental may be represented by a combination band in the vicinity of the fundamental. Coupling of molecular motions is also a cause of spectral enrichment.

Although these alternative possibilities cannot be overlooked, only two

of the eighteen sulfate minerals studied show evidence of multiplicities exceeding the number expected on the basis of symmetry considerations, and in both cases the enrichment is compatible with structural evidence of the presence of non-equivalent functional groups. We may conclude from this that other contributive mechanisms are unimportant. Our studies of carbonate minerals have also led to this conclusion (Adler and Kerr, 1963b).

REFERENCES

- ADLER, H. H. AND P. F. KERR (1963a) Infrared absorption frequency trends for anhydrous normal carbonates. *Am. Mineral.* **48**, 124-137.
- AND P. F. KERR (1963b) Infrared spectra, symmetry and structure relations of some carbonate minerals. *Am. Mineral.* **48**, 839-853.
- HALFORD, R. S. (1946) Motions of molecules in condensed systems: 1. Selection rules, relative intensities, and orientation effects for Raman and infrared spectra. *Jour. Chem. Phys.* **14**, 8-15.
- HAAS, M. AND G. B. B. M. SUTHERLAND (1956) The infra-red spectrum and crystal structure of gypsum. *Proc. Royal Soc. London A-236*, 427-445.
- HENDRICKS, S. B. (1937) The crystal structure of alunite and the jarosites. *Am. Mineral.* **22**, 773-784.
- HERZBERG, G. (1945) *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules*. D. Van Nostrand Co., Inc., New York.
- HORNIG, D. F. (1948) The vibrational spectra of molecules and complex ions in crystals. I. General theory. *Jour. Chem. Phys.* **16**, 1063-1076.
- MELOCHE, V. W. AND G. E. KALBUS (1958) Anomalies in the infra-red spectra of inorganic compounds prepared by the potassium bromide pellet technique. *Jour. Inorg. Nucl. Chem.* **6**, 104-111.
- MOENKE, H. (1959) Ultrarot-spektralphotometrische Bestimmung der gesteinsbildenen Salzmineralien. *Jenaer Jahrbuch* **2**, 361-395.
- NAKAMOTO, K., J. FUJITA, S. TANAKA AND M. KOBAYASHI (1957) Infrared spectra of metallic complexes. IV. Comparison of the infrared spectra of unidentate and bidentate metallic complexes. *Jour. Am. Chem. Soc.* **79**, 4904-4908.
- OMORI, K. AND P. F. KERR (1963) Infrared studies of saline sulfate minerals. *Geol. Soc. Am. Bull.* **74**, 709-734.
- WEIR, C. E. AND E. R. LIPPINCOTT (1961) Infrared studies of aragonite, calcite, and vaterite type structures in the borates, carbonates, and nitrates. *Jour. Research NBS*, **65A**, 173-183.

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