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FINAL REPORT

ON

INFRARED STUDIES OF CRYSTALS II

(Period 15 May 1954 to 30 March 1956)

BY

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I. PURPOSE OF THIS RESEARCH

The general purpose of this research was to complete certain phases of the investigations started in May 1951 under Contract DA-36-039 sc-5581 on the infra-red spectra and crystal structure of barium titanate, brucite, mica, diamond and gypsum.

II. ABSTRACT

This report gives an overall survey of the progress made between 15 May 1954 and 30 March 1956. Most of the factual data have already been reported in the 7 quarterly reports on this contract or in Technical Report No. 3 (dated June 1955) by Marvin Hass. The crystals studied will be dealt with in the following order:

A. Gypsum
B. Brucite
C. Micas
D. Barium Titanate
E. Diamond

since this order corresponds roughly to the relative priority and effort expended on these five separate problems. Details given in earlier quarterly or technical reports will not be repeated here, but references will be given to the appropriate report.

III. PUBLICATIONS AND LECTURES

During the period covered by this report the following publications have appeared dealing with work sponsored by this contract:

"The problem of Two Types of Diamond" by G.B.B.M. Sutherland, D. E. Blackwell, & W. G. Simeral Nature, 174 901 (1954)

"The Infrared Spectrum of Barium Titanate" by R. T. Mara, G.B.B.M. Sutherland & H. V. Tyrell Phys. Rev., 96 801(1954)

"Infrared and X-ray Analysis of Crystal Structure" by G.B.B.M. Sutherland Nuovo Cimento II X 635 (1955)

The following lectures were given dealing with certain aspects of the work:

"The Location of Hydrogen Atoms in Muscovite and Biotite" by C. Y. Pan Liang and G.B.B.M. Sutherland at the Ohio State Symposium on Spectroscopy and Molecular Structure on June 17, 1954 at Columbus, Ohio.

"Relation between X-ray Results and Infra-red Spectra of Large Molecules" by G.B.B.M. Sutherland at the Gordon Conference on Infra-red Spectra held on August 5, 1954 at Meriden, N. H.

"The Infra-red Spectrum of Gypsum" by M. Hass and G.B.B.M. Sutherland at the Diamond Conference held at Oxford, England on July 1, 1955.

The following note was accepted on March 16th for early publication in the Journal of the Optical Society Of America:

"Crystal Structure of Brucite and Portlandite in Relation to Infrared Absorption" by R. T. Mara and G.B.B.M. Sutherland. This note was reproduced in Quarterly Report No. 7 of March, 1956.

A manuscript has been submitted to the Royal Society of London for publication in the Proceedings entitled:

"The Infra-red Spectrum and Crystal Structure of Gypsum" by M. Hass and G.B.B.M. Sutherland

This manuscript is reproduced in full in the next section of this report.

IV. FACTUAL DATA

A. Gypsum

The results of the work on gypsum which were given in detail in Technical Report No. 3 have now been re-examined and prepared for publication. The following is a copy of the manuscript as submitted to the Royal Society of London.

"The Infra-Red Spectrum and Crystal Structure of Gypsum"

by

M. Hass and G. B. B. M. Sutherland, F.R.S.

ABSTRACT

Infra-red spectra of single crystals of gypsum ($CaSO_4 \cdot 2H_2O$) have been obtained between 450 and 3800 cm^{-1} by measurement of transmission and reflection of plane polarized radiation on three different crystal sections. Analysis of these observations, when combined with previous results on the Raman spectrum of gypsum, makes it possible to assign 16 out of the 18 internal fundamental modes of the two sulphate ions, and 10 of the 12 internal fundamental modes of the four water molecules in the unit cell.

Comparison of the spectra of the sulphate ions and water molecules in gypsum with those given by sulphate ions in solution and water molecules in the gaseous phase provides some information on the nature of the crystalline field.

If the intensities and the dichroism of the water bands are used to verify the orientations of the water molecules in the crystal (as determined by nuclear magnetic resonance) the results obtained are anomalous. The agreement between prediction and observation is satisfactory for the deformation mode of vibration but quite unsatisfactory for the two stretching modes. Possible causes of this anomaly are discussed.

Introduction

Although infra-red spectroscopy is one of the major physical methods of investigating molecular structure, comparatively little work has been done on crystals. The most obvious reason for this neglect is the outstanding success of X-ray diffraction in determining the positions of the atoms in a crystal lattice. However, there are other reasons why infra-red investigators have concentrated their attention on molecules in the gaseous or liquid state. An important one is that the experimental difficulties are very considerable. In order to obtain absorption spectra on which to base a structural analysis, it is essential to have sections of a single crystal (cut in certain specified directions relative to the crystal axes) which are sufficiently thin to allow the intensity of absorption to be measured accurately. In many cases this means that the thickness has to be less than 1μ. Although, in principle, the intensities of very strong absorption bands can be deduced from infra-red reflection spectra, the conversion of a reflection spectrum into an absorption spectrum is tedious and until very recently, this was only possible in a rigorous manner for isotropic crystals.

Even when the experimental problems have been overcome, the interpretation of crystalline spectra is not so straightforward as the interpretation of gaseous spectra. The selection rules for the absorption of infra-red radiation by a small molecule in the gaseous state depend only on the symmetry properties of the individual molecule; the corresponding rules for the same molecule in the crystalline state depend in addition on the symmetry of the crystal and on the number and positions of the molecules in the unit cell. In general this means that certain information about the structure of the crystal must have been determined previously by X-ray diffraction. At first sight it would seem, therefore, that infra-red analysis can only give confirmation of a structure already established by X-ray analysis and provide no new information. This is not so. The location of hydrogen atoms by X-ray diffraction is extremely difficult and is generally not attempted. Since vibrations involving the hydrogen atoms in a crystal are easily recognized in its infra-red spectrum, it is very desirable to know whether infra-red analysis can be used to fill this not unimportant gap in our knowledge of crystal structure. Even more important is the information which infra-red analysis should be able to give about the forces between the atoms in a crystal. X-ray analysis gives the mean positions of the atoms, but usually adds little to our knowledge of the crystalline force field; infra-red spectra arise from vibrations of the atoms about these mean positions, the frequencies of the vibrations being determined by the inter-atomic, inter-ionic and inter-molecular forces in the crystal lattice.

Gypsum ($CaSO_4 \cdot 2H_2O$) is a very suitable crystal for infra-red investigation since (a) exceptionally large single crystals occur in nature; (b) the positions of all of the heavy atoms have been determined by X-ray diffraction, while those of the hydrogen atoms have been established by nuclear magnetic resonance and (c) the Raman spectrum (which is very closely related to the infra-red spectrum) has been studied very extensively. It should, therefore, provide a suitable test of the feasibility of using infra-red spectroscopy to locate hydrogen atoms and to determine the orientation of water molecules in crystals. Furthermore, hydrogen bonding is supposed to exist between the sulphate ions and the water molecules and since hydrogen bonding to water is such an important factor in determining the structure of hydrated crystals, it is desirable to study its effect on the spectrum in a relatively simple case.

Although the infra-red spectrum of gypsum has been studied by several investigators, much of the information required for a satisfactory analysis had not been obtained, partly because the technique of obtaining high quality infra-red spectra has improved very markedly in recent years. We therefore undertook a complete re-examination of the spectrum (absorption and reflection) between 450 and 4000 cm^{-1} using polarised radiation.

Crystal Structure and Selection Rules

The crystal structure of gypsum has been determined by Wooster (1936) from X-ray diffraction measurements. The crystal belongs to the monoclinic system and the crystallographic unit cell has the following dimensions in Å. (assuming that Wooster used kX units in his paper):

$a = 10.49$ $b = 15.18$ $c = 6.52$ $\beta = 151°33'$

The positions of the atoms in this unit cell are shown in figure 1 which has been made from a photograph of a scale model. The calcium and sulphur atoms lie on C_2 axes parallel to the b axis of the unit cell. Each sulphur is surrounded by four oxygens in a tetrahedral arrangement. The oxygen atoms of the water molecules do not lie on any symmetry element, but two of the oxygens of neighboring sulphate groups lie within 2.71 Å of a water oxygen and the hydrogen atoms have been assumed to lie on these lines, forming hydrogen bonds between the sulphate ions and the water molecules. This would make the HOH angle in each water molecule 108°, a very reasonable value since spectroscopic investigations have established this angle as 104°31' in water vapor. Using proton magnetic resonance, Pake (1948) has been able to establish the directions of the lines joining the protons of each water molecule and also the distance between these protons. He finds this distance to be 1.58 Å, corresponding to an OH distance of 0.98 Å. This distance is somewhat larger than the value found spectroscopically in water vapor (0.96 Å) but an increase of this order would be expected in the formation of the hydrogen bond.

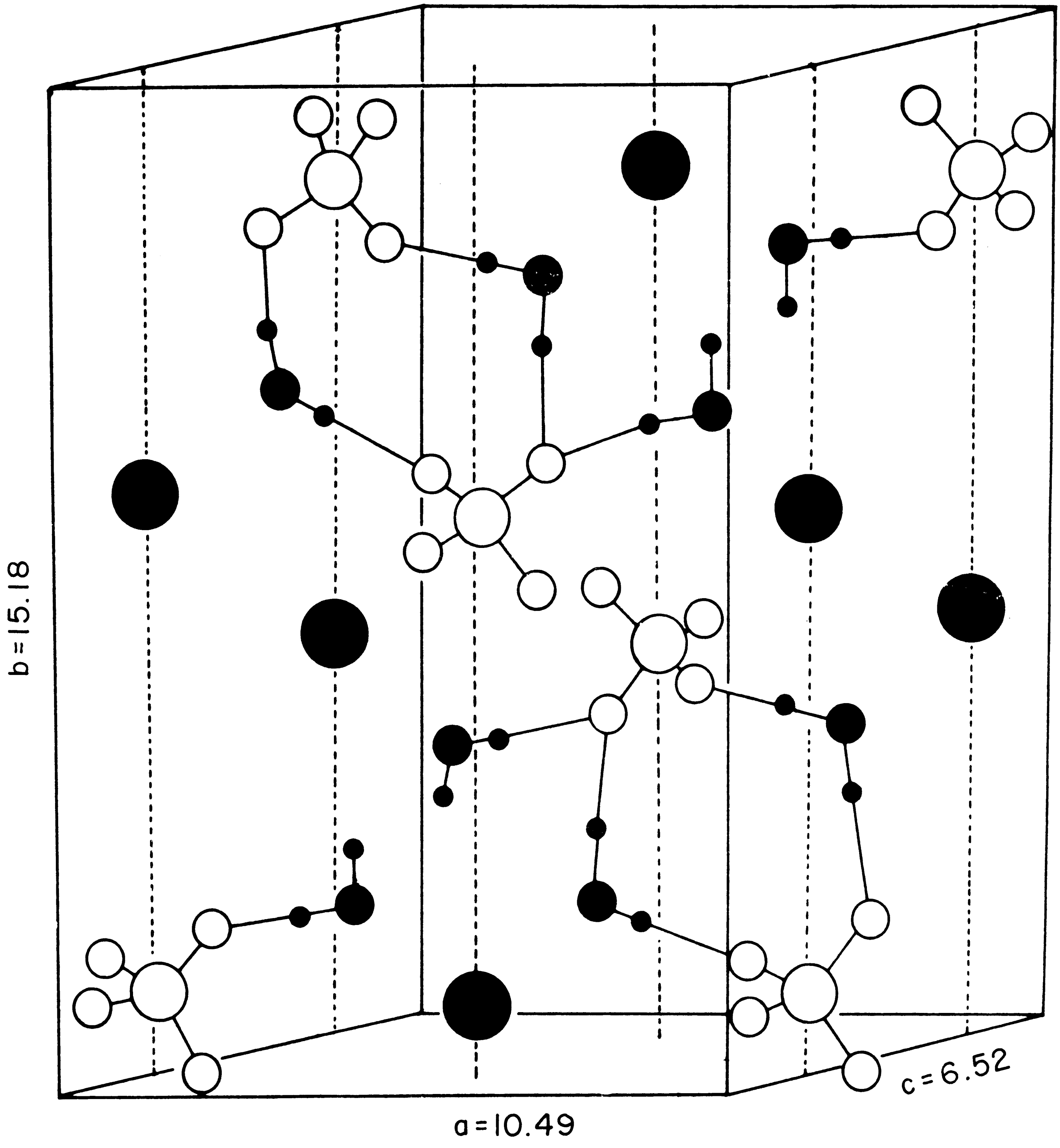


Fig. 1 The crystallographic unit cell of gypsum. The broken vertical lines indicate the C_2 axes. Calcium ions ●, sulphur atoms O, oxygen atoms of sulphate ion O, oxygen atoms of water molecules ●, hydrogen atoms • .

The gypsum crystal has a perfect principal cleavage parallel to the (010) face. It will be noticed that the water oxygens lie on planes parallel to the (010) plane, forming hydrogen bonds between similar adjacent layers of sulphate ions. The perfect cleavage presumably takes place between layers of sulphate ions which are not hydrogen bonded to one another.

The conventional crystallographic unit cell shown in figure 1 contains 4 "molecules" of $CaSO_4 \cdot 2H_2O$. However, the primitive or Bravais unit cell, from which selection rules are deduced (Bhagavantam and Venkatarayudu 1951) is defined as the smallest unit in which no two atoms become equivalent as a result of a simple translation. Since a simple translation will transform one of the "corner" sulphate ions in the crystallographic unit cell of figure 1 into one of the "central" sulphate ions, the Bravais unit cell must be smaller than the crystallographic unit cell. In this case, the Bravais unit cell is only half the size of the crystallographic unit cell and thus contains only two $CaSO_4 \cdot 2H_2O$ "molecules" or 24 atoms. The number of normal modes associated with the Bravais unit cell is therefore 72, of which 3 are purely translational. We are primarily interested in the internal modes of the two SO_4 ions and the four H_2O molecules and will confine our attention to the corresponding 30 normal vibrations, 18 of which are associated with the SO_4 ions and 12 with the H_2O molecules.

The space group for gypsum is conventionally described as C_{2h}^{6} (or C 2/c) and the selection rules can be obtained by considering the symmetry properties of the corresponding point group C_{2h}. The characters of the four symmetry species are given in table 1. Since there is a center of symmetry, the mutual exclusion rule holds and only nine sulphate fundamentals can be infra-red active. Similarly, only six water fundamentals can give rise to absorption. The

Table 1 Character Table and Symmetry Species for Gypsum

C_{2h}^{6}	E	$C_2(y)$	i	$C_2 \cdot i$	Activity		n	
					IR	Raman	SO_4	H_2O
A_g	1	1	1	1		α_{xx}, α_{yy} α_{zz}, α_{xz}	5	3
A_u	1	1	-1	-1	T_y		5	3
B_g	1	-1	1	-1		α_{xy}, α_{yz}	4	3
B_u	1	-1	-1	1	T_x,T_z		4	3
							18	12

n is the number of internal vibrations

IR denotes infrared active species

T_x, T_y, T_z denote translations in the Cartesian directions x, y, and z. The y direction is the same as the C_2 axis.

α_{xy}, α_{yz}, etc. denote the change in the polarizability tensor other fundamentals can only be Raman active. It should be observed that the eight infra-red active vibrations of the A_u class will have transition moments parallel to the C_2 axis, while the seven of the B_u class will have transition moments in planes perpendicular to the C_2 axis.

A clearer idea of the physical nature of these 15 infra-red active vibrations can be obtained by considering them to arise from the coupling of the normal modes of free sulphate ions or free water molecules using the viewpoint of the site method of Halford (Halford 1946, Winston and Halford 1949) and Hornig (1948). Thus each of the two sulphate ions in the unit cell has 9 fundamentals. These are coupled in such a way that only 9 of the resulting 18 modes are infra-red active. Similarly, each of the water molecules has 3 fundamentals and these couple to give 6 infra-red active modes. This is illustrated in figure 2 for either of the symmetrical modes of a water molecule (conventionally designated as ν_1, or ν_2). The arrows indicate the direction and phase of the change of electric moment for each water molecule. Similar diagrams can be made for the sulphate fundamentals, but it is simpler to represent the situation here by means of the correlation chart shown in table 2. The nine fundamentals of the free sulphate ion (which belongs to the tetrahedral point group T_d) only give rise to four distinct frequencies A (single), E (doubly degenerate), and F_2 (two, each triply degenerate). In the gypsum crystal,

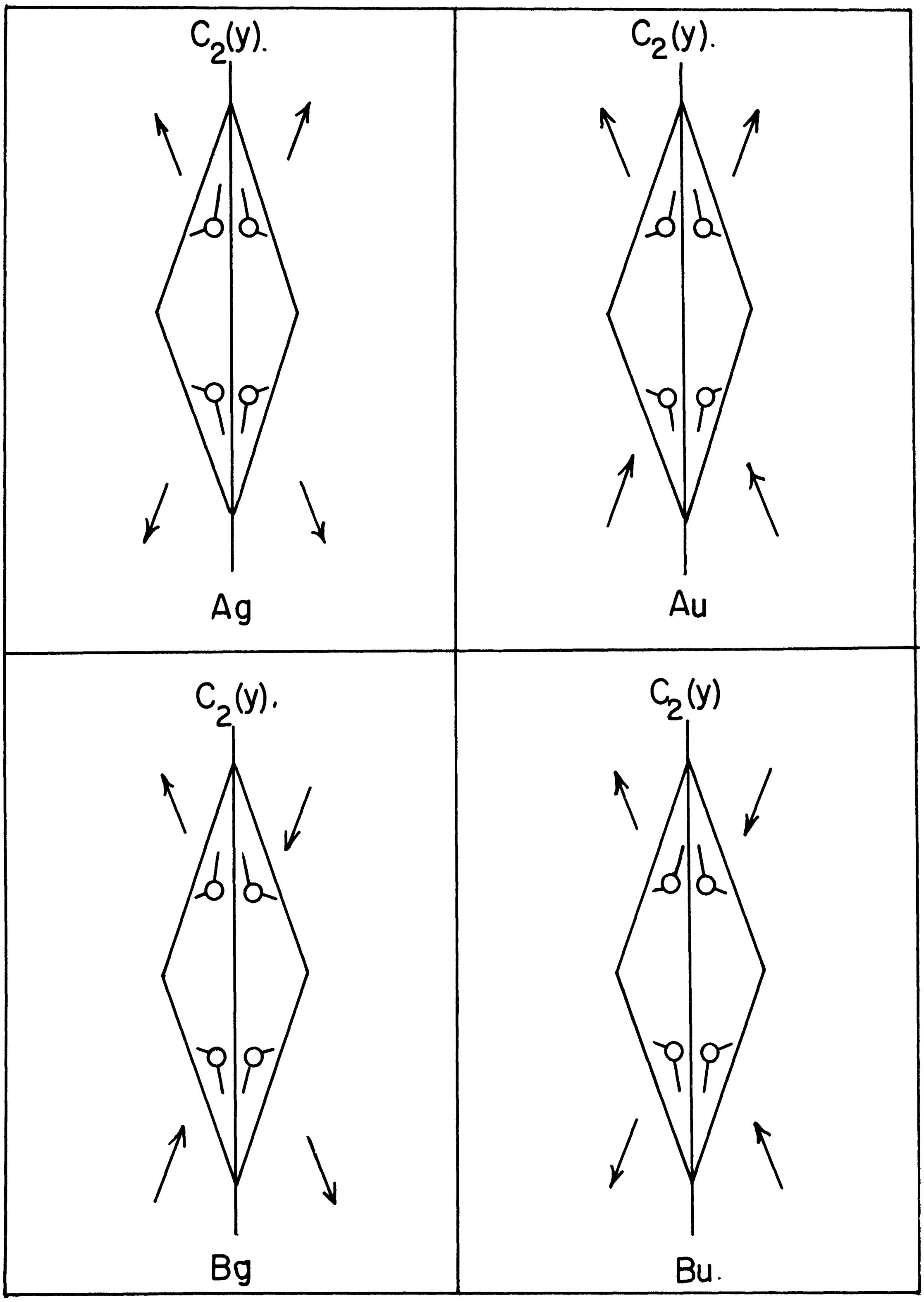
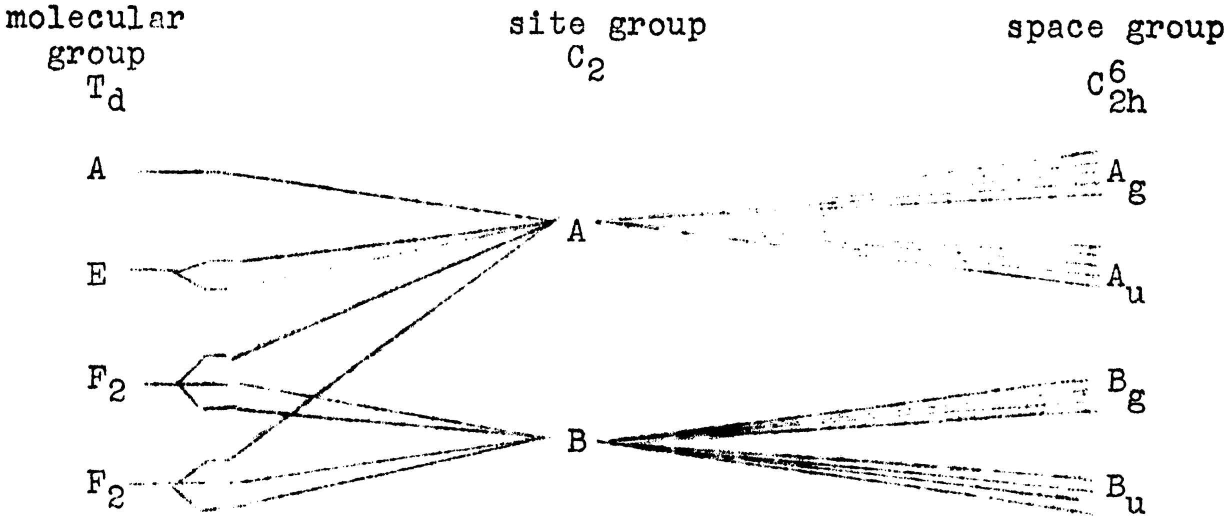


Fig. 2 Symmetry species for the ν_1 and ν_2 fundamentals of water in gypsum.

the sulphate ions lie on sites of C_2 symmetry; if the inter-ionic forces giving rise to this reduction of symmetry are assumed to be weak compared to the inter-atomic forces in the ion, the effect of the crystalline field will be to perturb the internal vibrations slightly, thus removing the degeneracy and giving rise to nine separate frequencies. Five of these are of an A type (symmetric with respect to the C_2 axis) and four of a B type (anti-symmetric with respect to the C_2 axis). Finally, the nine separate fundamentals of the two sulphate ions in the unit cell will couple together to give 18 separate frequencies, falling into the four species of the C_{2h} group (A_g, A_u, B_g, B_u). This is shown in Tables 2 and 5.

Table 2 Correlation Chart for Sulphate Fundamentals



General Predictions

We are now in a position to predict to some degree those features of the infra-red spectrum of gypsum which arise from internal vibrations of the sulphate ions and the water molecules.

Sulphate Ion Absorption Bands

The four fundamental frequencies of the free sulphate ion (known from studies on the Raman spectrum in solution) have the following values (Kohlrausch 1943):

$\nu_1 = 981 \text{ cm}^{-1}$ A (1)
$\nu_2 = 451 \text{ cm}^{-1}$ E (2)
$\nu_3 = 1104 \text{ cm}^{-1}$ F_2 (3)
$\nu_4 = 613 \text{ cm}^{-1}$ F_2 (3)

where the figures in parentheses give the degree of degeneracy. Thus, in the infra-red spectrum of gypsum we may expect to find one band near 980 cm^{-1} polarized parallel to the C_2 axis, two bands near 450 cm^{-1} also polarized in that direction, three bands near 1100 cm^{-1}, one of which will be polarized parallel to the C_2 axis, while the other two will be polarized perpendicular to that axis, with a similar triplet near 610 cm^{-1}.

H_2O Absorption Bands

The three fundamental frequencies of the water molecule in the gaseous state are found at 3652 cm^{-1} (ν_1), 1595 cm^{-1} (ν_2) and 3756 cm^{-1} (ν_3). (Herzberg 1945) Near each of these values we may expect to find two absorption bands, one of which will be polarized along the C_2 axis and the other perpendicular to that axis.

Experimental

The reflection spectra were studied on a Perkin Elmer Model 12 C spectrometer using prisms of KBr, NaCl, CaF_2, and LiF. The effective spectrometer slit width near the reflection maxima varied from 5 cm^{-1} to 27 cm^{-1} as shown in Table 3.

Table 3 Effective Slit Widths for Reflection Spectra

Prism	range in cm^{-1}	slit width
KBr	450 - 750	5
	680 - 750	11
NaCl	900 - 1300	5
	1200 - 1250	9
CaF_2	1400 - 1900	16
LiF	2800 - 4000	27

On the high frequency sides of reflection bands, the reflecting power becomes very small (as low as 0.15%) but since it is important to know it accurately, the effective slit widths were increased in these regions to improve the signal-to-noise ratio. Since unusually large reflecting surfaces were available, it was possible to obtain the spectra by removing the plane mirror in the source chamber and replacing it with the sample. The average angle of incidence in this case is 13°. It can be shown (Robinson and Price 1953) that the error introduced by this small deviation from normal incidence is negligible in this case. The incident intensity was obtained by replacing the sample with a suitably masked aluminized plane mirror assumed to have 100% reflectivity. Plane polarized radiation was produced by a pile of six sheets of silver chloride, set so that the electric vector of the polarized radiation was perpendicular to the plane of incidence on the crystal face.

The transmission spectra from 660 cm^{-1} to 4000 cm^{-1} were obtained on a Perkin-Elmer Model 21 double-beam instrument equipped with a prism of NaCl and a pair of rotatable silver chloride polarizers. For the region between 450 cm^{-1} and 750 cm^{-1} the single beam Perkin-Elmer 12C was used with a KBr prism and a rotatable selenium polarizer.

Excellent large single crystals of gypsum (originally from Utah) were obtained from Ward's Natural Science Establishment, Rochester, N.Y. Three different crystal sections were prepared for reflection spectra viz. parallel to the (010), ($\bar{1}01$), and ($\bar{2}01$) planes. Each of these was at least 1.25 x 2 inc. in area. The (010) section, being parallel to the principal cleavage, is polished naturally and reflection spectra can be obtained from the cleavage face without further treatment. The other two faces were ground wet on a glass plate with American Optical Abrasive M303 and were then polished with rouge on a slightly moist cloth, stretched flat over a glass disc. It was possible to polish these faces sufficiently well so that newsprint could be read by reflection. A few cracks developed parallel to the principal cleavage but these covered only a very small fraction of the total surface area. It may be remarked that the reflecting power of these prepared surfaces was superior to that of the natural cleavage surface, and attempts to improve the latter by the usual method were unsuccessful.

Newman and Halford (1950) have emphasized the importance of selecting the orientation of a crystal surface relative to the incident radiation in such a way that plane polarized radiation may traverse it without suffering any change in polarization character, (e.g. plane to elliptical). In the monoclinic crystal gypsum, this means that with the crystal surface cut parallel to the C_2 axis, radiation incident normal to this surface should be plane polarized parallel to the C_2 axis, since with the electric vector perpendicular to the C_2 axis a change in polarization character may occur on traversing the crystal. Changes may also take place for radiation incident normal to the (010) plane (i.e. parallel to the C_2 axis). However, if in each of these last two cases, bands are observed which show <u>complete</u> polarization, then useful deductions can be made since no change in polarization character can have taken place. Observation of a partially polarized band in the last two cases means that an unambiguous interpretation of the results is not possible.

The Robinson-Price method (Robinson 1952, Robinson & Price 1953) of obtaining absorption spectra from reflection spectra has the advantage over other methods that the reflection spectrum need only be obtained at normal incidence instead of at two different angles of incidence. This is particularly important in investigations on anisotropic crystals. Starting from the reflection equation

$$R = \frac{N-1}{N+1} \qquad (1)$$

where R is the complex reflection coefficient and N is the complex index of refraction, the complex reflection coefficient may be written in terms of a modulus r and a phase angle Θ

$$R = re^{i\Theta} \qquad (2)$$

The square of the absolute value of the complex reflection coefficient, $|R|^2 = r^2$, is the observed reflecting power. The complex index of refraction is given by

$$N = n - ik \qquad (3)$$

in which n is the ordinary index of refraction and k is the extinction coefficient. The extinction coefficient k is related to the more familiar absorption coefficient α appearing in Lambert's law $T = e^{\alpha x}$ (where T is the fractional transmission and x is the sample thickness) by the relation

$$\alpha = \frac{4\pi k}{\lambda} \qquad (4)$$

where λ is the wavelength of the radiation. Substituting

(2) and (3) in (1) and solving for n and k we find

$$n = \frac{1 - r^2}{1 + r^2 - 2\,r\cos\theta} \qquad k = -\frac{2r\sin\theta}{1 + r^2 - 2r\cos\theta} \tag{5}$$

Consequently, if both r and θ are known at each frequency, then the optical constants n and k can be calculated. The value of r can be obtained directly from the reflection spectrum. The value of θ cannot be found directly from the reflection spectrum, but can be obtained indirectly because of the following considerations. Many complex quantities which occur in physics and engineering are functions of a frequency. If such complex quantities arise from linear systems (in our case this would imply that the reflection coefficient is independent of the intensity of the incident radiation), then the imaginary part can be found at every frequency if the real part is known as a function of the frequency. Conversely, except for an additive constant, the real part can be found at every frequency if the imaginary part is known as a function of the frequency.

Such relations were originally given by Kramers (1927) and Kronig (1926, 1942) to relate the real and imaginary parts of the complex index of refraction. They have also found use to relate the real and imaginary parts of complex impedances (Bode 1945), a complex dielectric constants (Frohlich 1949) and most recently in connection with scattering theory (von Kampen 1953 and Gell-Mann, et al, 1954).

The recent interest in connection with scattering theory has led to the search for more general proofs of the Kramers-Kronig dispersion formula.

In order to express the complex reflection coefficient $R = re^{i\theta}$ in terms of real and imaginary parts, it is convenient to consider the function

$$\ln \underline{R} = \ln r + i\theta \qquad (6)$$

In this case the value of θ is given by

$$\theta(\omega) = \frac{1}{\pi} \int_0^\infty \frac{d \ln r}{d\omega'} \ln \left| \frac{\omega + \omega'}{\omega - \omega'} \right| d\omega' \qquad (7)$$

Therefore if r or ln r is known as a function of the frequency, θ can be calculated at each frequency. Substitution of the value of θ in (5) yields the desired optical constants. The evaluation of the integral (7) is lengthy since r, the reflection coefficient, is a complicated function of the frequency which cannot be expressed analytically. For this reason we have carried out the integration numerically on a digital computer (MIDAC, the Michigan Digital Automatic Computer). The reflection spectrum was expressed in digital form by dividing it into 116 straight line segments over the region from 450 - 4000 cm^{-1}. A typical example of the results obtained is shown in figure 3 where a transmission spectrum, a reflection spectrum and the optical constants n and k derived from it are shown for the (010) face. The

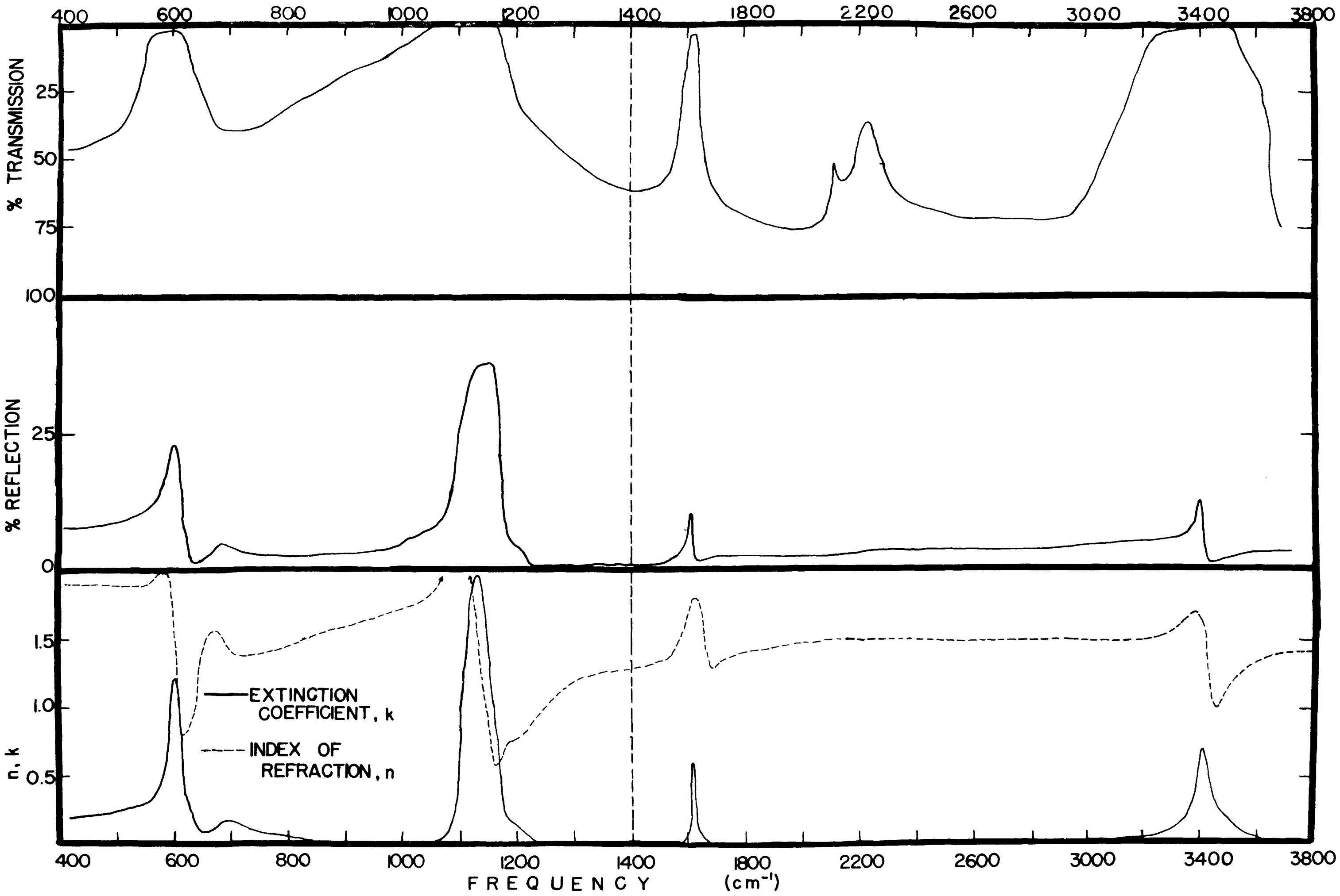


Fig. 3 Upper curve: Transmission spectrum of gypsum normal to (010) face.

Middle curve: reflection spectrum of gypsum normal to (010) face.

Lower curve: n and k deduced from middle curve.

advantages of the reflection method in defining the position and contour of very intense absorption bands are very obvious.

Results

The following spectra were obtained:

a) Transmission spectrum with plane polarized radiation incident normal to (010) face between 450 and 4000 cm^{-1}. The sample thickness was 15 microns. It was found that maximum dichroism was usually obtained when the electric vector made an angle φ with the a axis of either 9° or 99°; φ is measured clockwise from OA in the (010) plane. (figure 4). However, for a few bands φ was 19° and for a band at 2130 cm^{-1} it was 124°, (table 4).

b) Reflection spectra with plane polarized radiation incident normally on the (010), ($\bar{1}01$) and ($\bar{2}01$) faces. For the first face, φ was again varied and the directions of maximum dichroism found in (a) were verified for the most intense bands. For the ($\bar{1}01$) face, the electric vector was either parallel to the C_2 axis (giving the A_u bands) or in the (010) plane with φ = 33° (giving the B_u bands). For the ($\bar{2}01$) section the electric vector was either parallel to the C_2 axis (giving the A_u bands) or in the (010) plane with φ = 99° (giving the B_u bands.)

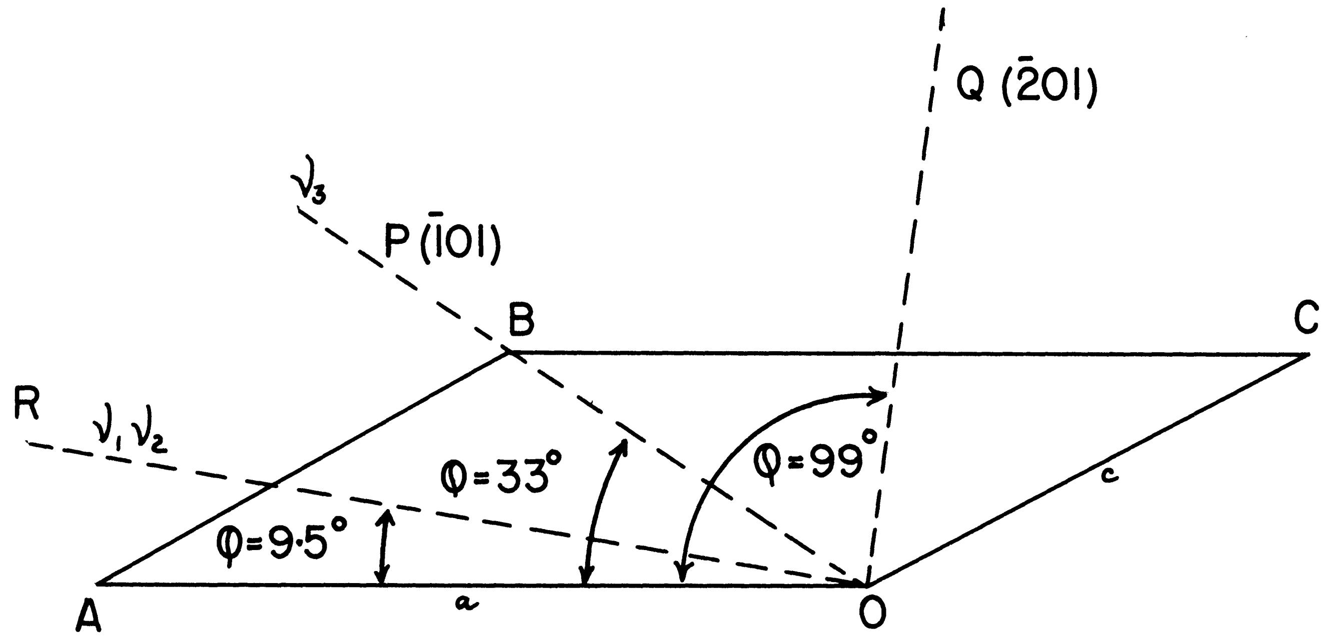


Fig. 4 OABC is the projection of the crystallographic unit cell on (010) plane. The intersections of the $(\bar{1}01)$ and $(\bar{2}01)$ planes with the (010) plane are OB and OQ respectively. The line OR is parallel to the projections on the (010) plane of the symmetry axes of the water molecules. The line OP, which is almost coincident with OB, is parallel to the projections on the (010) plane of lines joining the two hydrogen atoms in each water molecule.

Table 4 Observed Frequencies, Intensities, and Dichroism of $CaSO_4 \cdot 2H_2O$ Absorption Bands

assignment	species	direction[a] (in deg.)	method[b]	frequency (cm^{-1})	intensity[c] (cm^{-1})	width[d] (cm^{-1})
$\nu_{R'}(H_2O)$	B_u	99	Re	450		vb
$\nu_{R''}(H_2O)$	A_u		Re	580		b
ν_4 (SO_4)	A_u		Re	602	30	17
ν_4 (SO_4)	B_u	9	Re	604	30	20
ν_4 (SO_4)	B_u	99	Re	672	35	16
ν_1 (SO_4)	A_u		Re	1000		
ν_3 (SO_4)	B_u	9	Re	1118	120	32
ν_3 (SO_4)	A_u		Re	1131	100	34
ν_3 (SO_4)	B_u	99	Re	1142	130	27
$\nu_4+\nu_4$ (SO_4)	B_u	9	Re	1205		
ν_2 (H_2O)	B_u	9	Re	1623	12	16
ν_2 (H_2O)	A_u		Re	1685	6.5	25
$\nu_3+\nu_1$ (SO_4)	B_u	19	Tr	2112		
$\nu_3+\nu_1$ (SO_4)	B_u	124	Tr	2130		
$\nu_{R''}+\nu_2$ (H_2O)	B_u	9	Tr	2198		
$\nu_{R''}+\nu_1$ (H_2O)	B_u	9	Tr	2235		
$\nu_2+\nu_2$ (H_2O)	B_u	19	Tr	3248		
$\nu_2+\nu_2$ (H_2O)	B_u	19	Tr	3350		
ν_1 (H_2O)	B_u	19	Re	3410	42	49
ν_1 (H_2O)	A_u		Re	3430	8	b
ν_3 (H_2O)	B_u		Re	3490	2	
(H_2O)	B_u	unp[e]	Tr	3495		
ν_3 (H_2O)	A_u		Re	3537	60	67
(H_2O)	B_u	19	Tr	3560		

Table 4 (continued)

[a] Direction of transition moment in (010) plane

[b] Re = data derived from reflection measurements

Tr = data derived from transmission measurements

[c] Where numerical values are given, the number is the integrated intensity defined as $K = \int k d\nu$ where k is the extinction coefficient and ν is the frequency in cm^{-1}

[d] vb = very broad   b = broad

[e] unp = unpolarized. This band is anomalous and is discussed further in the text

The transmission spectrum is shown in figure 5 for values of φ = 9° and 99°. These are all B_u bands. The absorption spectra derived from the reflection spectra are shown in figures 6 and 7. The upper halves of these two figures show the A_u bands as obtained from the $(\bar{1}01)$ face (450 to 1200 cm^{-1}) and the $(\bar{2}01)$ face (1400 to 3700 cm^{-1}). Apart from some small differences in intensity, virtually the same spectrum of the A_u bands was obtained from the $(\bar{2}01)$ face in the lower frequency range and the $(\bar{1}01)$ face in the higher frequency range. The lower halves of figures 6 and 7 show the B_u bands as obtained from the (010) face for φ = 9° and φ = 99° with two minor exceptions due to the imperfection of the (010) surface. The curve for the region 450 to 750 cm^{-1} with φ = 99° is actually that obtained from the $(\bar{2}01)$ face while the curve for the region 1000 to 1200 cm^{-1} with φ = 9° is actually that obtained from the $(\bar{1}01)$ face and therefore corresponds to φ = 33°. The combined results of all the observations are given in table 4 where the intensity values have been averaged in cases where independent measurements were made of the intensity of a band from two different sections.

A few observations were made on the transmission spectrum at liquid nitrogen temperatures. The bands near 450 cm^{-1} and 600 cm^{-1} became considerably weaker, and the latter much narrower. A similar sharpening was observed for the bands between 3200 and 3700 cm^{-1} so that shoulders on the

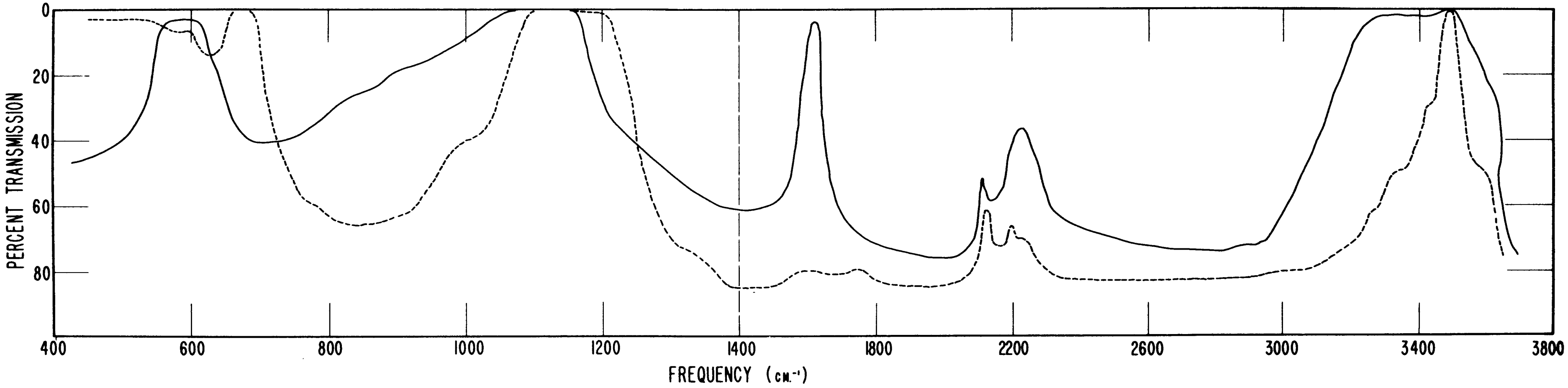


Fig. 5 Transmission spectrum of gypsum normal to the (010) face:

———————— indicates electric vector set at ϕ = 9°;

------------- indicates electric vector set at ϕ = 99°.

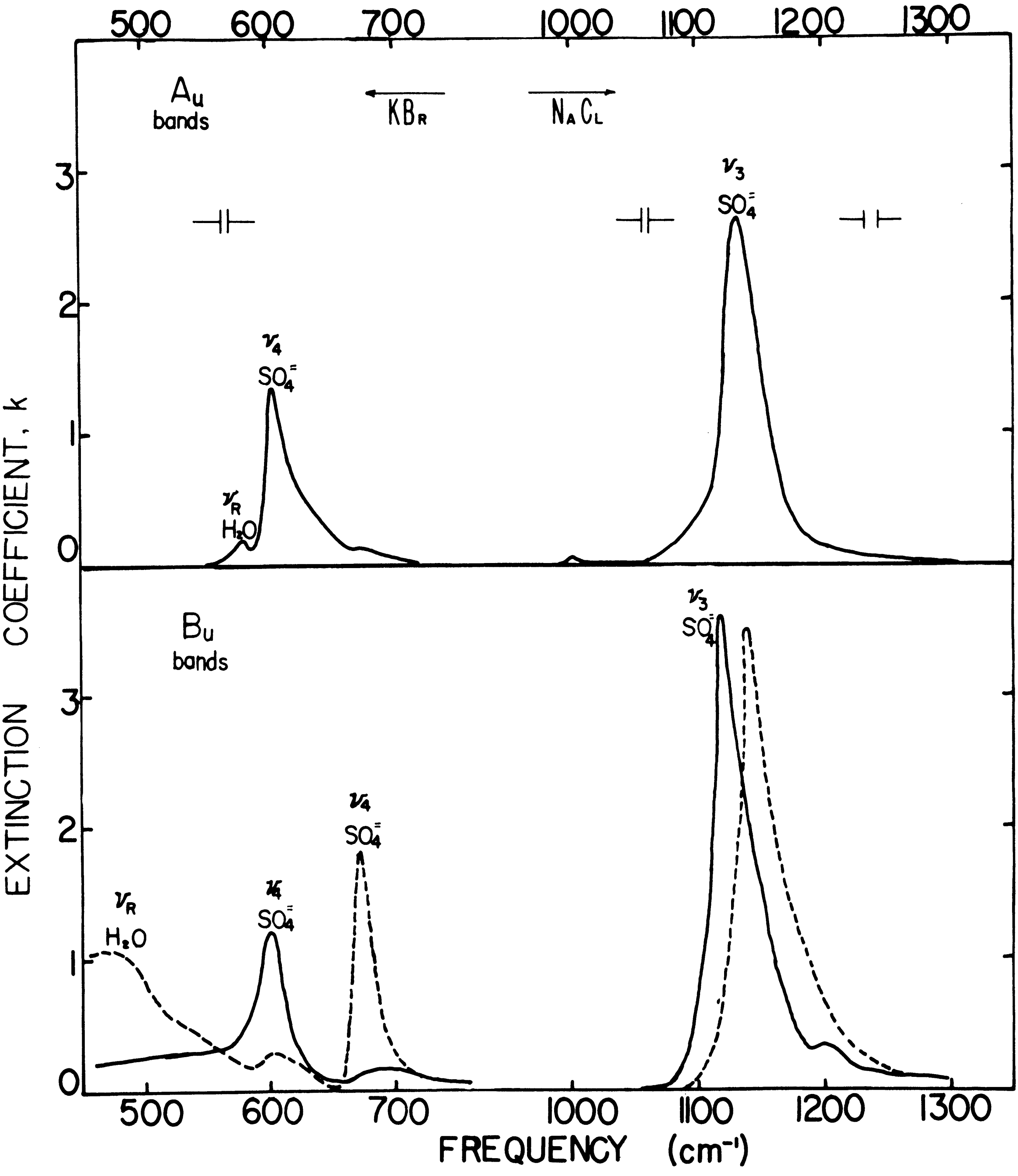


Fig. 6 Absorption spectrum of gypsum derived from reflection spectra in the range 450 to 1200 cm^{-1}. For the B_u bands, ________ indicates electric vector set at $\varphi = 9°$, while -------- indicates electric vector set at $\varphi = 99°$.

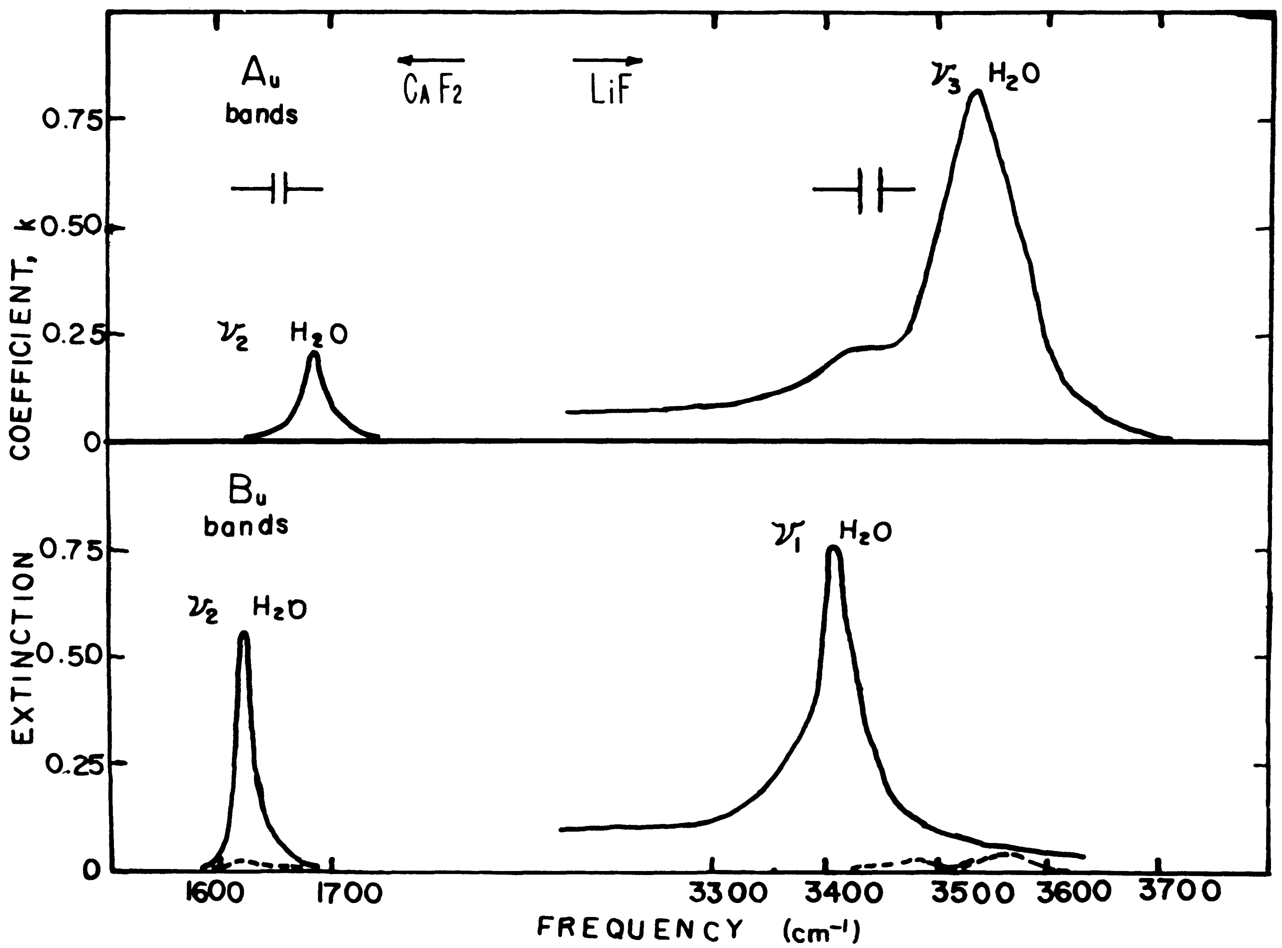


Fig. 7 Absorption spectrum of gypsum derived from reflection spectra in the range 1400 to 3800 cm^{-1}. For the B_u bands ________________ indicates electric vector set at $\varphi = 9°$ and ---------------- indicates electric vector set at $\varphi = 99°$.

broken line curve of figure 5 became well defined maxima in most cases. The same effect has been noticed in the low temperature Raman spectrum of gypsum by Stekhanov (1953).

It will be seen that in general the results are in satisfactory agreement with the predictions made earlier. Thus the ν_1 frequency of the SO_4 ion is found at 1000 cm^{-1} (i.e. near 981 cm^{-1}) and shows A_u character. The ν_2 frequency of SO_4 was predicted to give two A_u bands near 450 cm^{-1}. No A_u bands were observed near 450 cm^{-1} but these bands (like the ν_1 band) will be very weak and so could easily be missed or lie just outside the range of observation. The ν_3 frequency, expected near 1104 cm^{-1}, shows three components, two of which (at 1118 cm^{-1} and 1142 cm^{-1}) show B_u character, while the third (at 1131 cm^{-1}) shows A_u character exactly as predicted. The same is true of the ν_4 frequency which gives a similar triplet with components at 604 cm^{-1}, 672 cm^{-1} (both B_u) and 602 cm^{-1}(A_u).

In the case of the H_2O frequencies, each band should show two components, one having A_u character and the other B_u character. A pair of such bands appearing at 1623 cm^{-1} (B_u) and 1685 (A_u) can be immediately assigned to ν_2, which lies close to 1600 cm^{-1} in the gaseous state. The A_u components of ν_1 and ν_3 are presumably to be identified respectively with the A_u bands found at 3430 cm^{-1} and 3537 cm^{-1}. The corresponding B_u components are harder to identify, since there are several B_u bands in this region, The strongest lies at 3410 cm^{-1}, a value which would make it appear to be the other component of ν_1. The B_u component of ν_3 must then be assigned to one or other of the weak bands at 3490 cm^{-1} and 3560 cm^{-1}. The former seems preferable since the band at 3560 cm^{-1} is so much weaker in the transmission spectrum. It should be remarked that there is an unpolarized peak in the transmission spectrum at 3495 cm^{-1} which is anomalous since it appears only very weakly in the reflection spectrum and is not reported in the powder spectrum of gypsum (Pain, Duval and Lecomte 1953).

In addition to the bands just discussed, there are three bands in the reflection spectrum at 450 cm^{-1} (B_u) 580 cm^{-1} (A_u) and 1205 cm^{-1} (B_u) which have to be assigned. The first two of these bands would appear to be associated with a hindered rotation of the water molecules i.e. rotary lattice mode. It will be noticed that the 450 cm^{-1} band is extremely broad (a well-known characteristic of water bands in the condensed state) while the 580 cm^{-1} band lies very close to Raman lines at 565 cm^{-1} and 588 cm^{-1}, which Krishnan (1945) has assigned to external vibrations of the water molecules because of their resemblance to bands found in water (500 cm^{-1}) and ice (600 cm^{-1}). Although the 450 cm^{-1} band has the correct value for association with ν_2 of the SO_4 ion, its dichroism intensity and width preclude this assignment. The other band in the reflection spectrum at 1205 cm^{-1} is presumably a combination of the SO_4 pair of bands near

600 cm^{-1}. A group of weak bands found in the transmission spectrum between 2100 and 2250 cm^{-1} are partly due to similar overtones and combinations of the ν_1 and ν_2 frequencies of the sulphate ion, but the broader part of this absorption is probably due to the water molecules, since liquid water has a well known band in this region. Probable assignments for the weak bands observed in transmission are indicated in table 4.

Discussion

The Sulphate Ions. Our assignment of 16 of the 18 fundamental vibrations of the SO_4 ion in gypsum is given in table 5 which includes the assignments of the Raman (G) frequencies by Rousset and Lochet (1945). The only fundamentals which still have to be observed are the two weakly infrared active components of ν_2. Comparison of the values of these frequencies with the corresponding values for the SO_4 ion in solution (given in the first column of table 5) shows that all the component frequencies of ν_1 and ν_3 are higher in the crystal than in solution, whereas for ν_2 and ν_4 the removal of degeneracy and interactions within the unit cell have given rise to a distribution of frequencies on each side of the unperturbed frequency. Since the values of ν_1 and ν_3 are controlled principally by the stretching force constant of the S - O band, we conclude that this force constant is slightly higher when the SO_4 ion is in a

Table 5

Sulphate Ion Fundamentals

SOLUTION			GYPSUM	K
981	ν_1	A_G	1006	
		A_U	1000	(...)
451	ν_2	A_G	492	
		A_U	...	
		A_G	413	
		A_U	...	
1104	ν_3	A_G	1144	
		A_U	1131	(100)
		B_G	1138	
		B_U	1142	(130)
		B_G	1117	
		B_U	1118	(120)
613	ν_4	A_G	621	
		A_U	602	(30)
		B_G	669	
		B_U	672	(35)
		B_G	623.5	
		B_U	604	(30)

gypsum crystal than when it is in solution.

The removal of degeneracy is quite complete in ν_2, ν_3, and ν_4 and the magnitude of the splittings observed in each case are of some interest. In ν_2, the splitting of the Raman frequencies is 79 cm^{-1} and since the infra-red components are unknown, this represents a minimum value. The size of this splitting has made Rousset and Lochet (1945) suggest that the SO_4 ion is no longer tetrahedral in gypsum but is distorted to some lower symmetry class. Since two of the oxygen atoms in the sulphate ions are probably hydrogen-bonded to water molecules, whereas the other two are free this does not seem unreasonable, although no X-ray evidence exists as yet against the tetrahedral structure. The higher frequency (492 cm^{-1}) may be associated mainly with motions of the SO_2 part of the sulphate ion which is hydrogen bonded and therefore resists deformation more strongly. The lower frequency (413 cm^{-1}) would then be associated mainly with a deformation motion of the SO_2 part of the ion which is free. In this connection, it is interesting to note that the maximum splitting in ν_4 (70 cm^{-1}) which is also a deformation mode is of the same order of magnitude as in ν_2 whereas in ν_3 (a stretching mode) it is much less (27 cm^{-1}). Next we may consider the splitting between two associated component vibrations, one of which is Raman active while the other is infra-red active. The magnitude of this quantity will depend upon the interaction of the two sulphate ions in the unit cell, for that particular mode of vibration. For ν_1 the splitting is 6cm^{-1} and the interaction must be quite small; for the A_u components of ν_3 and ν_4, we find respectively 13 cm^{-1} and 19 cm^{-1} so the interactions are considerably larger in these two cases. The corresponding splittings in the two B_u components of ν_3 are 4 cm^{-1} and 1 cm^{-1} and in one of the B_u components of ν_4 the separation is 3 cm^{-1}. Thus for these modes of vibration the interaction must be even smaller than it is in the case of ν_1. For the remaining B_u components of ν_4 the splitting is 19.5 cm^{-1}, indicating a very appreciable interaction.

Finally, the orientation of the transition moments for the B_u vibrations given in table 4 may throw further light on the nature of crystalline field to which the sulphate ions in gypsum are subjected. The two B_u components of ν_3 and ν_4 were each found to be nearly completely polarized along directions corresponding to $\varphi = 9°$ and $\varphi = 99°$. It is probably significant that there is a chain of $-Ca-SO_4-Ca-SO_4-$ ions located on a line corresponding to $\varphi = 99°$.

The Water Molecule. Our assignment of 10 of the 12 internal fundamental frequencies of the water molecules in gypsum is given in table 6, which includes the assignments of Cabannes, Couture, and Mathieu (1953) for the Raman active components

Table 6

Water Fundamentals

VAPOUR			GYPSUM	K
3657.1	ν_1	A_G	3404.5	
		A_U	3430	(8)
		B_G	3402.5	
		B_U	3410	(42)
1595	ν_2	A_G	...	
		A_U	1685	(6.5)
		B_G	...	
		B_U	1623	(12)
3755.8	ν_3	A_G	3496.5	
		A_U	3537	(60)
		B_G	3498	
		B_U	3490	(2)

of ν_1 and ν_3, together with the assignments of the infrared active components of ν_1, ν_2 and ν_3 made in the preceding section. These authors also assign a weak but sharp line at 1632 cm^{-1} to the ν_2 mode of water. This frequency had previously been reported by Krishnan (1945) who had incorrectly assigned it to the sulphate ion. Using the 5461 Å line of mercury, Aynard (1940) has reported a very weak band at 1660 cm^{-1} and has assigned it to ν_2 without specifying whether it is A_g or B_g. From their numerical values, we very tentatively assign 1632 cm^{-1} as the B_g component and 1660 cm^{-1} as the A_g component of ν_2.

It will be noticed that for ν_1 and ν_3 all of the component frequencies in the crystalline state have considerably lower values than ν_1 and ν_3 in the gaseous state, while the opposite is true for ν_2. This is in agreement with the general observation that hydrogen bonding lowers the numerical values of valency vibrations and increases the values of deformation frequencies. The magnitude of the change in the stretching frequencies is however markedly less than would be predicted from empirical rules on this phenomenon (Rundle and Parasol 1952; Lord and Merrifield 1953). The average increase in the deformation frequency ν_2 is somewhat less than that observed between water vapour and ice, although the O - O distance in gypsum (2.70 Å) is smaller than that in ice (2.76 Å).

Since none of the fundamental vibrations of the water molecule is degenerate, the splitting of each into four components is due to interaction between the four molecules in the unit cell. The maximum value of this splitting is 27 cm^{-1} for ν_1, 62 cm^{-1} for ν_2, and 47 cm^{-1} for ν_3. In general these values are considerably larger than the corresponding ones for the sulphate ion, even when expressed as a percentage of the unperturbed value of the frequency. This is understandable since the neighboring water molecules are coupled together rather strongly through hydrogen bonding to the same oxygen atom of a sulphate ion, whereas the two sulphate ions in the unit cell have no such direct coupling. A detailed study of this phenomenon should throw considerable light on inter-atomic forces in the crystalline state.

The intensities of the water bands in gypsum are of considerable interest. In water vapour ν_1 is very much weaker than ν_3, whereas in gypsum, ν_1 has an intensity quite comparable to ν_3. A similar alteration in the relative intensities of these two bands is found in the Raman spectrum (Krishnan 1945, Cabannes, Couture and Mathieu 1953) where ν_1 and ν_3 are again of comparable intensity in gypsum whereas in water vapour ν_1 is much more intense than ν_3. This indicates that the charge distribution on the vibrating water molecule in gypsum is far different from that in the free molecule, and/or that the form of the vibration may be very different in the two cases. The next question is whether the positions of the hydrogen atoms as given by nuclear magnetic resonance can be confirmed by infra-red analysis, and in particular, from our measurements on the intensities of the A_u and B_u components of each of the three fundamentals. Let ψ denote the angle between the direction of the C_2 axis and that of the transition moment associated with the particular fundamental under consideration. This is illustrated for ν_1 and ν_2 in figure 8 where $\psi = 52.7°$. It follows that $\cot^2 \psi$ should be equal to the observed value of K_{A_u}/K_{B_u} when K is the integrated intensity defined in table 4. The comparison of predicted and observed values is given in table 7.

Table 7 Predicted and Observed Values for $\cot^2 \psi$ and φ

fundamental frequencies of H_2O	$\cot^2 \psi$ predicted	observed	φ (in degrees) predicted	observed
ν_1	0.61	0.2	9.5	19
ν_2	0.61	0.54	9.5	9
ν_3	1.40	30	33.0	--

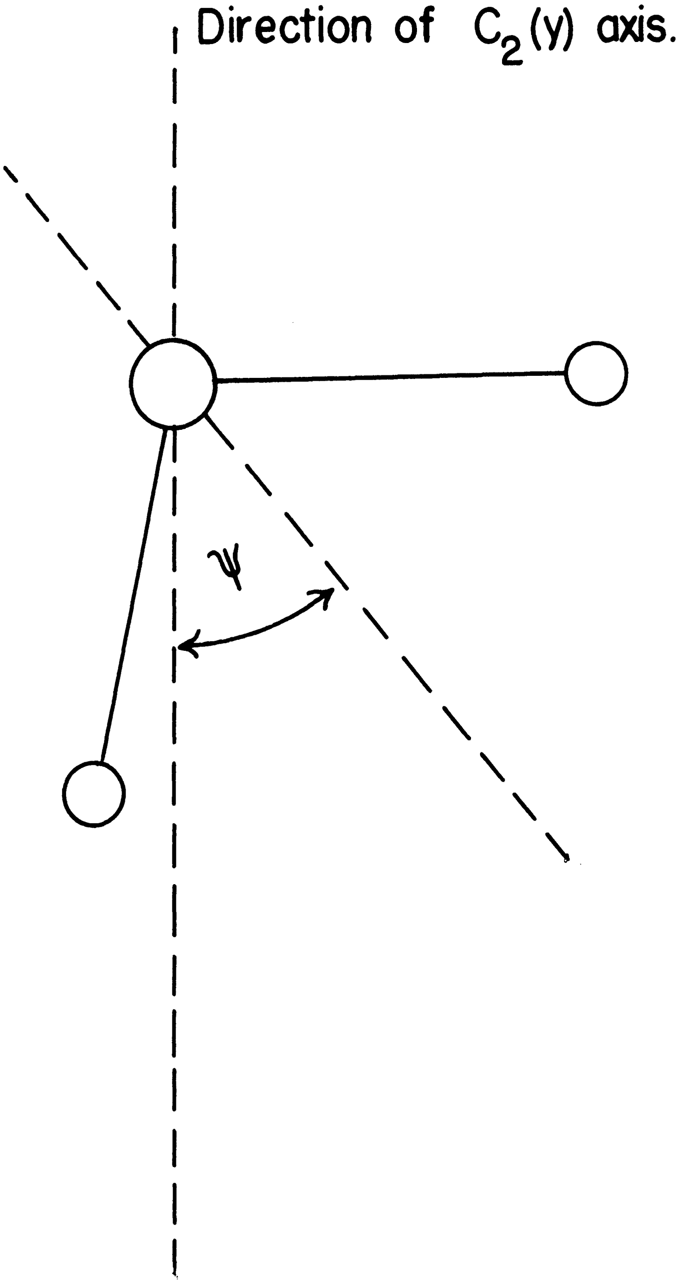


Fig. 8 The angle ψ is defined as the acute angle between the symmetry axis of any water molecule and a line parallel to the C_2 axis passing through the oxygen of that water molecule.

It will be seen that for ν_2 the agreement is quite satisfactory, considering the experimental error in measuring intensities of weak reflection bands. The agreement is very poor for ν_1 and definitely outside experimental error while the values for ν_3 differ by more than a factor of twenty. Before discussing reasons for these apparent discrepancies, it is illuminating to examine the results of polarization measurements on the B_u bands. The projections of certain directions in the water molecules on the (010) plane are shown in figure 4. The H - H lines are found to correspond to $\varphi = 32°57'$ while the symmetry axes of the water molecules lie parallel to $\varphi = 9.5°$. One might therefore anticipate that for ν_1 and ν_2 maximum dichroism in the B_u components would be found along $\varphi = 9.5°$ while for ν_3 the corresponding value of φ would be 33°. The observed values are compared with these predictions in table 7. Again the agreement is excellent for ν_2 but very poor for ν_1.

There would seem to be two possible reasons for discrepancies in table 7. The first is that we have assumed what is conventionally known as the "oriented gas model" (Pimentel, McClellan, Person and Schnepp 1955) for the water molecules in gypsum, i.e., we have ignored the effects of the crystalline field on the vibrations. However, if this were the correct interpretation of our results, the agreement found for ν_2 must be attributed to chance, since any crystalline field which affects ν_1 would be expected to affect ν_2 in a rather similar manner. If the agreement obtained for ν_2 is not accidental, then reasons must be found for the anomalous results associated with ν_1 and ν_3. One explanation is that while ν_2 is a truly separable frequency (in that it has a sharp, narrow contour and there are no weaker bands found alongside it), the ν_1 and ν_3 bands are much broader and have a number of companion bands, which can only be explained as coming from combinations with lower lattice vibrations, probably due to hindered rotation and translation of the water molecule (Webber 1954). A large number of such low frequencies have been found in the Raman spectrum and combinations with them could easily produce very marked anomalies in intensity and in direction of polarization. It should also be noted that in the free molecule ν_1 and ν_3 cannot interact since they belong to different species. However, in gypsum certain of the components of ν_1 and ν_3 have the same symmetry character and the difference between the mean values of these frequencies is only about 100 cm^{-1}. It is possible, therefore, that ν_1 and ν_3 become mixed vibrations in gypsum, making the application of the oriented gas model inadmissable for this pair of vibrations.

It is important to note that Cabannes, Couture and Mathieu (1953) were also forced to conclude that the positions of the hydrogen atoms in the gypsum could not be determined from the vibration spectra of single crystals, in this case, investigated by Raman scattering. They attributed the anomalies they found in the Raman spectrum to the "perturbation" of the water molecule in gypsum. It is clear that the location of hydrogen atoms in crystals by infra-red or Raman spectra presents many difficult problems, and it seems likely that it will be more profitable in the immediate future to use neutron diffraction or nuclear magnetic resonance to solve the location problem and the spectroscopic data on hydrogen vibrations to provide information on crystalline force fields. In order to elucidate effects due to combination of molecular fundamentals with lattice vibrations, it will be advisable to obtain spectra at very low temperatures.

The authors wish to thank Professors D. L. Wood and T. Venkatarayudu for helpful discussions, and the staff of the MIDAC Computation group of the Willow Run Research Center for valuable aid in the early stages of the computational work. Some financial support for the later stages of this research from the U. S. Army Signal Corps under Contract DA-36-030-sc-56736 is gratefully acknowledged.

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B. Brucite

One of the important problems left unsolved when the first contract (DA-36-039 sc-5581) terminated in May 1954 was the structure of brucite. There appeared to be a direct contradiction between the results of infra-red and X-ray analysis on the size of the unit cell and on the positions of the hydrogen atoms. This conflict has now been resolved. It seems certain that the original conclusions of the X-ray analysts were correct and that unexpectedly low frequency vibrations of the hydrogen atoms combining with the stretching vibrations of the OH ions are responsible for the unusual fine structure found in the infra-red spectrum of brucite. This was conclusively proved by the low temperature work done by Dr. R. T. Mara in the summer of 1955. The situation at the termination of this contract is given in Quarterly Report No. 7 of March 1956, in which the manuscript referred to in section III of this report, p. 3 has been reproduced.

C. Micas

When Contract DA-36-039 sc-5581 terminated in May 1954, the problem of the orientation of the OH groups in muscovite and biotite had not been completely resolved. In each case it was possible from measurements on infra-red dichroism to give the absolute value of the angle which any OH bond made with the crystallographic axis, but not the sign of the angle. By making up models and considering the physical environment of the hydrogen atom, it has been possible to settle the signs in the case of muscovite. Biotite presents a much more difficult problem, since the exact locations of the Fe and Mg ions are unknown. There seems to be no way round this difficulty (cf Quarterly Report No. 2, December 1954).

A second problem has arisen in connection with biotite. We had assumed that the specimen of biotite examined by us belonged to the space group C_{2h}^{4}, but had no direct proof of this. Professor A. A. Levinson, of Ohio State University, very kindly examined the particular crystal we had used for infra-red work by X-ray diffraction, and reported to us that this biotite crystal had a one-layer monoclinic structure and the space group appeared to be C_s^3-C_m, on the basis of the standard work done by Hendricks and Jefferson (J. Min. Soc. Am. 24, 729 (1939)). We therefore set about re-interpreting our observations on the basis of a C_s^3 - C_m space group. It turned out that this was not possible, at least with respect to the 2.83µ absorption band (cf. Quarterly Report No. 3, March 1955). A closer study of the work of Hendricks and Jefferson reveals that atomic coordinates were not determined experimentally, and this throws some doubt on their assignment of the space group as $C_s^3 - C_m$. Even if this is the correct space group for X-ray analysis, it has to be remembered that isomorphous replacement of ions which may cause very little difference in an X-ray pattern could give rise to different selection rules (i.e., effectively a different space group) for infrared absorption (see Quarterly Report No. 4, June 1955.) Another possibility is that the anomalies in the spectrum of biotite are due to combinations with low frequency liberational motions of the OH groups. If this were the case, then temperature effects similar to those found in brucite should be observable in biotite. The spectrum of biotite has been examined between 2500 and 4500 cm^{-1} at liquid nitrogen temperatures and also at 450° C (Quarterly Report No. 1, Sept. 1954). The 2.83μ band showed no diminution in intensity at liquid nitrogen temperatures. It therefore cannot be a difference frequency. The temperature studies just referred to indicate that low frequency combination bands do exist, but are separated from the 2.72μ band by at least 500-600 cm^{-1}.

Some preliminary studies were made on the bands in muscovite and biotite in the 2.8μ region under high resolving power (about 1 cm^{-1}) using a grating spectrometer (Quarterly Report No. 4, June 1955). The purpose was to see whether any fine structure of these bands existed which had been missed in our work with a prism spectrometer, where the resolving power was about 8.0 cm^{-1}. The effect was merely to spread out each of the bands into a wide region of absorption. Although there were indications of some structure in these regions, no definite new maxima were observed, and further work is required to determine the contours of these bands accurately, before it can be decided to what extent they are composite.

In order to complete our survey of the spectra of various forms of mica, observations were made in the region between 300 and 100 cm^{-1} of the absorption bands of muscovite, biotite, phlogopite (natural and synthetic), lepidolite, and zinnwaldite. There is no common feature in these spectra, the nearest approach being a band near 150 cm^{-1} in biotite, zinnwaldite, and phlogopite (both natural and synthetic). In muscovite and lepidolite the nearest bands to this are at 166 cm^{-1} and 170 cm^{-1} respectively. It seems most probable that these absorption bands are associated with the linked SiO_4 groups common to all micas.

D. Barium Titanate

During the period covered by this report some work has been done by Mr. H. Diamond (1) on the effect of temperature on the infra-red spectrum of barium titanate and of strontium titanate, and (2) on the spectra of single crystals of barium titanate using polarized radiation.

(Quarterly Reports 1, 2, and 3 of September 1954, December 1954, and March 1955 respectively.)

Since barium titanate passes from the tetragonal (ferro-electric) form to the cubic form at the Curie temperature of 120°C, the spectrum of powdered barium titanate in a KBr disc was observed at a temperature of about 170°C. The only effect was an increase in absorption on the long wave side of the band which has a maximum near 500 cm^{-1} (cf. Final Report of October 1954 or Mara, Sutherland and Tyrell Phys. Rev. 96, 801, 1954). In order to see whether this was a pure temperature effect or was connected with the transition from the tetragonal to the cubic form, the spectrum of strontium titanate was also observed at 180°C, since there is no transition in this case over a Curie point. A similar (although less marked) effect was found in the corresponding band of strontium titanate. It seems, therefore, that no major changes occur in the 500 cm^{-1} absorption band of barium titanate, as this material passes through the Curie temperature, although very careful studies a few degrees above and below the Curie point should be made to verify this conclusion.

Since this work was done, a report has appeared from the Insulation Research Laboratory of M.I.T. (Progress Report No. XVIII Dec. 1955, p. 17) on the effect of temperature on the infra-red spectrum of a single crystal (1.5μ thick) of barium titanate between -190° and +130°C. In going from room temperature to +130°C, J. T. Last found that the band maximum shifted from 505 cm^{-1} to 495 cm^{-1}. This shift to longer wave lengths confirms our observation that the wing of the band moves to longer wavelengths. We were not able to observe the shift of the band maximum because the absorbing crystals were too thick (up to 75μ). It should be remarked that much greater changes were found by Last in going to the rhombohedral form of barium titanate, which he observed at -190°C. Under these conditions the band shows a beautiful doublet structure. Thus in looking for changes in the infra-red spectrum related to changes in ferroelectric properties, it should be remembered that changes due to crystal form may be very marked, irrespective of any effects arising from the ferroelectric state.

The work on single crystal barium titanate was carried out on a specimen about 100μ thick. This made it impossible to determine the position of the strong band (centered near 500 cm^{-1}). One could only observe the short wave edge of this band on which there appeared a subsidiary maximum near 1230 cm^{-1} and a shoulder near 1000 cm^{-1}. Observations were made with the electric vector parallel and perpendicular to the c (or polar) axis. No detectable difference was observed. It should be remarked that Last (in the work referred to in the preceding paragraph) using a much thinner single crystal, found a shift of 20 cm^{-1} in the position of the band maximum between these two directions of the electric vector, the higher frequency being associated with absorption parallel to the c axis. It would be very interesting to have Last's experiment repeated above the Curie point.

It should be added that on raising the temperature to 180°C the absorption edge of the 500 cm^{-1} band was found to increase in intensity; the subsidiary maximum at 1230 cm^{-1} became less marked and the shoulder at 1000 cm^{-1} disappeared.

Unfortunately, lack of time has prevented further observations on barium titanate.

E. Diamond

No new experimental work has been done on diamond. Some progress has been made in the preparation of the material in Technical Report No. 1 for publication and reprints of this work will be sent to the Signal Corps as soon as it is published.

V. MAJOR CONCLUSIONS AND RECOMMENDATIONS

A. GYPSUM

It has been possible to assign 26 of the 30 fundamental modes of the sulphate ions and water molecules in gypsum. The values of these frequencies can be used to give information on the crystalline field in gypsum. Location of the hydrogen atoms in gypsum by infra-red analysis leads to inconsistent results. This is probably due to the interaction of the internal and external frequencies of the water molecules, but other factors may also be operative.

B. BRUCITE

The anomalies found in the infra-red spectrum of brucite, which at first sight appeared to indicate a larger unit cell than that found by X-ray methods, can now be explained qualitatively as arising from combination of librational motions of the OH ions with their stretching vibrations. Further theoretical work is required on this problem.

C. MICAS

The hydrogen atoms of the OH ions in muscovite can be located with a considerable degree of confidence. The same is not true of biotite, although it is certain that the positions are very different from those found in muscovite. Infra-red analysis may be a very fruitful field of research in the study of the structure of micas.

D. BARIUM TITANATE

Only minor changes occur in the infra-red spectrum of barium titanate when it passes through the Curie point. It does not appear that infra-red analysis offers a very promising approach to the explanation of the ferroelectric properties of this material because of severe technical problems. However, if polarized spectra can be obtained of thin single crystals over a wide range of temperatures, then it may be possible to gain more insight into the molecular basis for the ferroelectric properties of this compound.

E. DIAMOND

Our earlier conclusion that type I diamonds are much more imperfect than type II diamonds has been reinforced by work of many different sorts from various laboratories. Infra-red analysis should continue to be a very valuable tool in the study of imperfections in the diamond lattice.

VI. PERSONNEL

The following people have been engaged on the work described in this report:

Prof. G.B.B.M. Sutherland, Principal Investigator (Part Time)

Prof. D. L. Wood (Part Time)

Dr. C. Y. Pan Liang (Full Time May 1954-Feb. 1955)

Dr. R. T. Mara (Full Time June-Aug. 1955)

Dr. M. Hass (Part Time)

Mr. D. DeGraaf (Part Time)

Mr. A. Dockrill (Technician, Part Time)