INFRARED STUDY OF SULFOHALITE

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ABSTRACT

Sulfohalite $Na_6FCl(SO_4)_2$ is an anhydrous sulfate showing only a small number of infrared absorption bands in the wave number region between 4000 and 60 cm^{-1}. Sulfohalite was analysed mathematically by factor group analysis on the space group O_h^5 and by site group analysis on T_d of SO_4 ion. Force constants of the Urey-Bradley force field are calculated as K 6.45, H 0.70 and F 0.71 md/Å for the SO_4 ion of sulfohalite. And on the basis of the Urey-Bradley force field, normal vibrations were calculated. All the absorption bands of sulfohalite and also several anhydrous sulfates such as mascagnite, thenardite, glauberite, anhydrite, palmierite, anglesite, barite and celestite can be explained as combination bands. From the absorption bands of sulfohalite found in the far infrared region, the force constants of the octahedral FNa_6 and $ClNa_6$ ions were calculated as K 0.115, H 0.071 and F 0.250 md/Å and K 0.309, H 0.105 and F 0.104 md/Å, respectively and the interaction force constants between the FNa_6 and SO_4 ions and also the $ClNa_6$ and SO_4 ions were calculated as k 0.653 and 0.122 md/Å, respectively. The modes of these vibrations are the lattice vibration.

INTRODUCTION

Sulfohalite $Na_6FCl(SO_4)_2$ is an anhydrous sulfate with a peculiar isometric form but with symmetry somewhat out of balance. It contains ions of almost similar size including Na, F, Cl, S and O. In the structure, tetrahedral SO_4 ions are surrounded by 12 Na ions in the cubic face centered lattice, combined with octahedra of NaF and NaCl.

The SO_4 ion vibrates actively in infrared radiation and shows strong absorption bands, while both octahedra of NaF and NaCl, combined by ionic bonds show no absorption bands.

The infrared absorption of sulfohalite differs from that of mascagnite $(NH_4)_2SO_4$ that shows two kinds of infrared absorption bands, for the NH_4 ion and SO_4 ion. Sulfohalite is the anhydrous sulfate with the smallest number infrared absorption bands.

In the present paper the infrared absorption bands of sulfohalite in the wave number region between 4000 and 60 cm^{-1} are analyzed mathematically.

SULFOHALITE USED FOR THE STUDY

A crystal of sulfohalite from Searles Lake, California was used for the study. It was powdered in an agate mortar and a KBr disk was made by the usual method (Omori and Kerr, 1964) for infrared study in the wave number region between 4000 and 400 cm^{-1}. The infrared spectrum obtained by using a Perkin-Elmer Type 125 spectrophotometer with gratings is shown in Figure 1. The band between 900 and 400 cm^{-1} was also
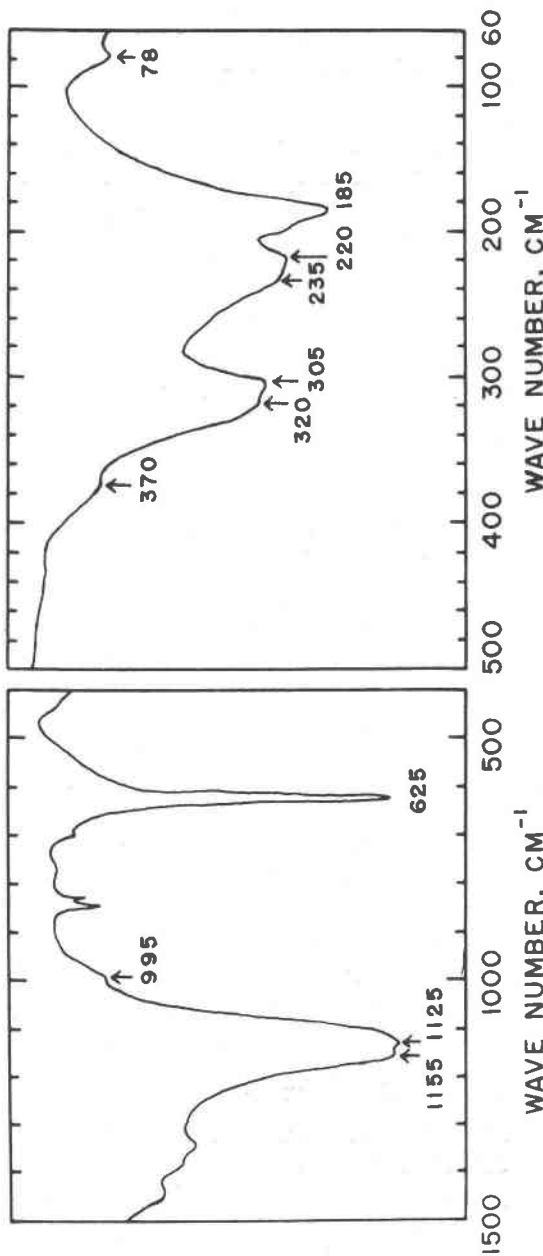
FIG. 1. Infrared absorption spectrum of sulfohalite from Searles Lake, California. Split weak bands at 850 and 830 cm⁻¹ and a weak band at 705 cm⁻¹ are the absorption bands of the CO_3 ion of a small amount of associated trona $Na_3H(CO_3)_2 \cdot 2H_2O$.

measured accurately by using the Hitachi Type EPI-ST spectro-photometer with a KBr prism.

For the far infrared spectrum the polyethylene plate method was used, with the plate covered by nujol mixed with a small amount of the powdered specimen (Omori, 1968). The far infrared spectrum in the wave number region between 500 and 60 cm^{-1} was obtained by using the spectrophotometer Hitachi Type FIS-1 with gratings. It is also shown in Figure 1 with the wave numbers of the absorption bands indicated on the spectrum. All wave numbers of the bands are compared in Table 1 be-tween sulfohalite and the free SO_4 ion.

TABLE 1. INFRARED ABSORPTION BANDS OF SULFOHALITE AND THE FREE SO_4 ION

Sulfohalite		Free SO_4 ion	
$\nu_{3b}(F_2)$	1155 cm^{-1}	$\nu_3(F_2)$	1104 cm^{-1}
$\nu_{3a}(F_2)$	1125		
$\nu_1 (A_1)$	995 (w)	$\nu_1(A_1)$	981 (R)
$\nu_4 (F_2)$	625	$\nu_4(F_2)$	613
$\nu_2 (E)$	—	$\nu_2(E)$	451 (R)
ν_0	370 (=2×185)		
ν_5	320		
ν_7	305		
ν_6	235		
ν_8	220		
ν_9	185		
ν_{10}	78		

FACTOR GROUP ANALYSIS OF SULFOHALITE OF
SPACE GROUP $O_h{}^5$

The crystal structure of sulfohalite has been determined by Watanabe (1934) and Pabst (1934). The space group was considered to be either $O_h{}^5$-$Fm3m$ or O^3-$F43$, cell dimensions given were $a_0 = 10.15$ Å (Watanabe) and $a_0 = 10.08$ Å (Pabst) and the unit cell contains four molecules of $Na_6F \cdot Cl(SO_4)_2$.

The Bravais unit cell, that is the smallest cell suitable to cover the entire unit cell by translations, contains one molecule of the formula as shown in Figure 2.

As shown in a review by Mitra and Gielisse (1964) a crystal composed of N cells with n atoms per cell has $3Nn$ normal modes of vibration. The $3Nn$ modes are classified in $3n$ branches, where $3n$-3 branches are optical branches and 3 branches are acoustic branches. If the numbers of the normal modes are $3n$-3, the numbers n are the numbers of atoms per Bravais unit cell. The symmetry classification of the vibration can be
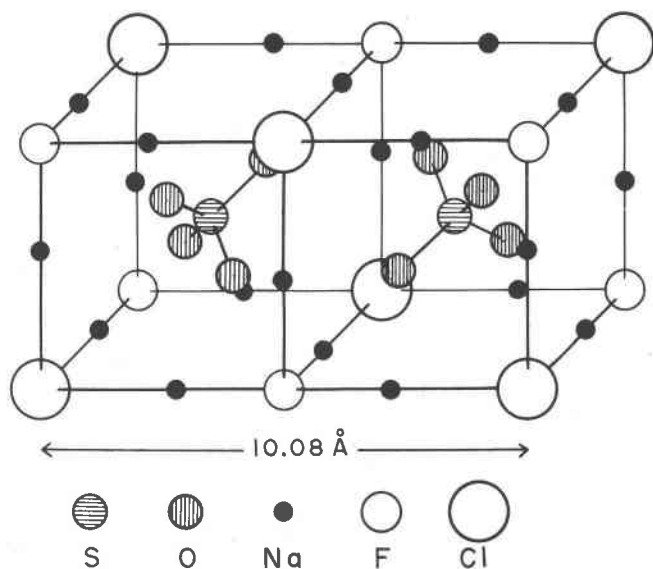
FIG. 2. Bravais unit cell of sulfohalite used
for the factor group analysis.

determined by the calculation of factor group analysis on the Bravais
unit cell.

Factor group analyses of a number of minerals have been reported.
Bhagavantam and Venkatarayudu (1939) have described the Raman
effect in relation to the crystal structure and have shown method of factor
analysis. Calculated results were shown for diamond, rock salt, calcite
and aragonite. Hass and Sutherland (1956) and Tsuboi (1958) have shown
the result for gypsum, Mitra (1961) has given the factor group analysis
of a crystal containing linear ions such as brucite and Iiishi, Shiro and
Umegaki (1968) have reported the results for corundum and calculated
the elastic constants.

The author has performed a factor group analysis of sulfohalite, space
group O_h^5. A character table of the irreducible representations of O_h
used in the calculation is shown in Table 2, where the order of group (g)
is 48.

The number of times (N_k) that a particular irreducible representation
(Γ_k) is contained in another representation (Γ) can be calculated by the
equation

$$N_k = \frac{1}{g} \sum_j h_j \chi_k(R) \chi_j{}'(R), \tag{1}$$

TABLE 2. FACTOR GROUP ANALYSIS OF SULFOHALITE OF THE SPACE GROUP O_h^5

O_h^5 (g=48)		I	$8C_3$	$6C_2$	$6C_4$	$3C_2''$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	Sulfohalite N	T	T'	R'	n	SO$_4$ ion N	T	T'	R'	n
	A_{1g}	1	1	1	1	1	1	1	1	1	1	2	0	1	0	1	1	0	0	0	1
	A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	0	0	0	0	0	0	0	0	0	0
	A_{2g}	1	1	-1	-1	1	1	1	-1	1	-1	0	0	0	0	0	0	0	0	0	0
	A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	1	0	0	0	1	1	0	0	0	1
	E_g	2	-1	0	0	2	2	0	-1	2	0	2	0	1	0	1	1	0	0	0	1
	E_u	2	-1	0	0	2	-2	0	1	-2	0	1	0	0	0	1	1	0	0	0	1
	F_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	2	0	1	1	0	1	0	0	1	0
	F_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	7	1	4	0	2	3	1	0	0	2
	F_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	4	0	2	0	2	3	0	1	0	2
	F_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	2	0	1	1	0	1	0	0	1	0
Sulfohalite	$U(p)$	18	6	2	4	6	2	4	0	6	10	54					30				
	$U(s)$	10	4	2	4	6	2	4	0	6	6										
	$U(s-v)$	2	2	0	0	2	0	2	0	0	2										
	(N)	54	0	-2	4	-6	-6	-4	0	6	10										
	(T)	3	0	-1	1	-1	-3	-1	0	1	1										
	(T')	27	0	-1	3	-5	-3	-3	0	5	5										
	(R')	6	0	0	0	-2	0	2	0	0	-2										
SO$_4$ ion	$U(p)$	10	4	0	0	2	0	2	0	0	6										
	$U(s)$	2	2	0	0	2	0	2	0	0	2										
	$U(s-v)$	2	2	0	0	2	0	2	0	0	2										
	(N)	30	0	0	0	-2	0	-2	0	0	6										
	(T')	3	0	1	-1	-1	3	-1	0	-1	1										
	(R')	6	0	0	0	-2	0	2	0	0	-2										

N: Number of the total degrees of freedom
T: Number of the translation
T': Number of the translational lattice vibration
R': Number of the rotational lattice vibration
n: Number of the intramolecular vibration of the SO$_4$ ion

where h_j is the number of group operations contained in the jth class, and $\chi_k(R)$ and $\chi_j'(R)$ are the characters of the group operation (R) in the representations Γ_k and Γ, respectively.

The group characters $\chi_j'(R)$ are obtained by the following equations. The group character $\chi_j'(N)$ of all unit cell modes in $3n$ Cartesian coordinates

$$\chi_j'(N) = U(p)(\pm 1 + 2 \cos \phi_R),$$

where $U(p)$ is the number of atoms remaining invariant under the symmetry operation (R) and ϕ_R is the angle of rotation corresponding to the symmetry operation (R). The signs plus and minus stand for proper and improper rotations, respectively.

The group character for the acoustic modes is

$$\chi_j'(T) = \pm 1 + 2 \cos \phi_R.$$

When $U(s)$ is the number of the structural groups remaining invariant under an operation (R), the group character of the translatory lattice modes

$$\chi_j'(T') = [U(s) - 1](\pm 1 + 2 \cos \phi_R).$$

Then, $U(s-v)$ is the number of the polyatomic groups remaining invariant under the operation (R), the group character of the rotatory lattice modes

$$\chi_j'(R') = [U(s - v)](1 \pm 2 \cos \phi_R),$$

where v is the number of the monatomic group and the signs plus and minus stand for proper and improper rotation, respectively.

The characters of sulfohalite and the SO_4 ion are shown in the fifth and sixth broad columns in Table 2, while the classified numbers of the modes of vibration are shown in the third and fourth broad rows in Table 2.

The total number of lattice vibrations is obtained as the sum of T' and R' and the number of the molecular vibrations is obtained from the subtraction

$$n = N - T - T' - R'.$$

Although the symmetry species F_{1u} belongs to the infrared active species, combinations exist between F_{1u} and F_{2g}, thus the numbers (n) of the molecular vibration of the SO_4 ion are found as two, and the numbers of the lattice vibration of sulfohalite are six from the sum of the numbers (T') in F_{1u} and F_{2g}. The numbers calculated are similar to the numbers of the band obtained on the infrared spectrum.

SITE GROUP ANALYSIS

In the classified description (Bragg, Laue, Hermann *et al.* 1935) of the space group, O_h^5 has a subgroup T_d, and O^3 has no subgroup T_d, thus the tetrahedral SO_4 ion contained in O_h^5 belongs to the site group T_d.

The total number of the normal modes of vibration of the SO_4 ion is calculated as nine $(3 \times 5 - 6 = 9)$. The nine degrees of freedom are classified as $A_1 + E + 2F_2$ by calculations using the character table of the irreducible representation of T_d and the equation (1). It is given from the calculation of the selection rules that the infrared active vibrational modes are $2F_2$.

When the SO_4 ion belongs to the point group C_{3v}, the total modes of vibration are $3A_1 + 3E$, where the infrared active modes are $3A_1 + 3E$. When it belongs to the point group C_{2v}, C_2 and S_4, the infrared active mode is $4A_1 + 2B_1 + 2B_2$, $5A + 4B$ and $3B + 2E$, respectively.

There are differences between the numbers of the infrared active modes of T_d, C_{3v}, C_{2v}, C_2 and S_4. Since the point group T_d belongs to the space group O_h^5, although there are two bands of ν_3 on the spectrum of

FACTOR GROUP   SITE GROUP
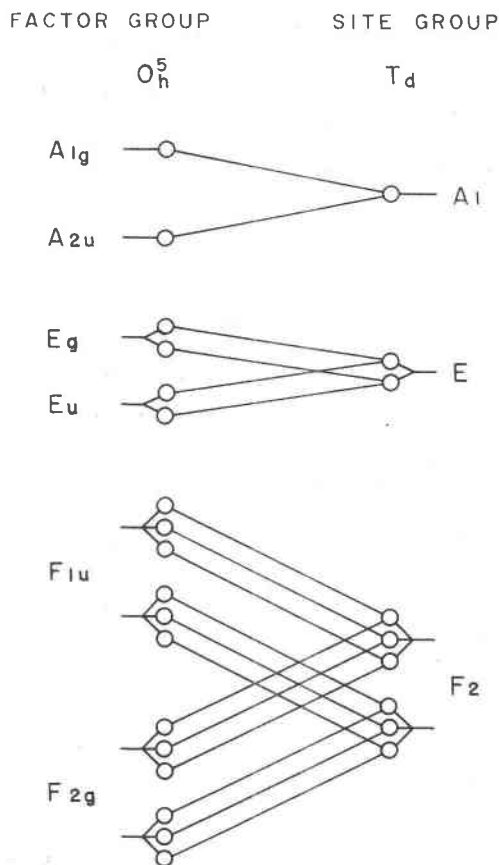
O_h^5 T_d

FIG. 3. Correlation chart of the normal modes of vibration of the SO_4 ion between O_h^5 and T_d.

sulfohalite, it may be considered that the tetrahedral SO_4 ion is in the site group T_d and the splitting of the stretching ν_3 band appears owing to the combinations of the vibrational modes. And F_{1u} and F_{2g} species in O_h^5 are correlated with the F_2 species in T_d from the correlation chart shown in Figure 3.

Molecular vibrations of the SO_4 ion appear partially in the crystal lattice, while the lattice vibrations can propagate through the entire crystal lattice. Combinations of these two kinds of vibration cause the splitting of the band and it is considered that the force constants of the SO_4 ion of sulfohalite differ somewhat from these of the free SO_4 ion.

Force Constants of the Tetrahedral SO₄
Ion of Sulfohalite

Urey and Bradley (1931) have calculated the vibrational frequencies of tetrahedral molecules such as the CCl_4, $SnCl_4$, CBr_4, $SnBr_4$, ClO_4 and SO_4 ions under an assumption that the restoring forces can be best chosen as harmonic restoring forces along the directions of the chemical bonds and perpendicular to them. There are two possible cases of forming the SO_4 ion from S^{6+} and $4O^{2-}$ and from S^{2+} and $4O^{1-}$, and in the latter case the SO_4 ion is believed to be tetrahedral, but the actual ion may be a combination of both of these and perhaps of other configurations. It was also reported that the inverse repulsive force is in need of the additional term of the electronic charge.

Shimanouti (1949) has calculated the normal modes of vibration as treated by the Urey-Bradley force field, and Decius (1948) has reported a useful tabulation of general formulae for inverse kinetic energy matrix elements in an acyclic molecule. Recently Colthup, Daly and Wiberley (1964) reported a systematic method to calculate the normal modes of vibration of the molecule and described in detail an example, $CHCl_3$.

The author has calculated the force constants of the Urey-Bradley force field for the SO_4 ion of sulfohalite from the GF matrices using Decius' table of the kinetic energy matrix. The force constants obtained are K(S–O) 6.45, H(O–S–O) 0.70 and F(O $\cdots$ O) 0.71 md/ Å. The force constants of the free SO_4 ion are already reported as K 6.01, H 0.43 and F 0.76 md/ Å.

From the comparison of the force constants of the SO_4 ion between sulfohalite and the free SO_4 ion, it is known that the stretching force constant (K) and the bending force constant (H) of sulfohalite are larger and the repulsive force constant (F) is smaller than the force constant of the free SO_4 ion.

By using the force constants the wave numbers of the normal vibrations were calculated as ν_1 995, ν_3 1142 and ν_4 625 cm^{-1}, all of which are near similar to the wave numbers measured.

Combination Bands of Sulfohalite

Combination bands appear because of the direct interactions between the infrared radiation and the phonons in the crystal lattice. And a phonon is absorbed and through the state where the normal mode of vibration is excited, two phonons are created. The combination bands exist where a phonon is absorbed and two or more phonons are emitted.

The infrared absorption bands of sulfohalite are attributed to the combination bands. The summation of each band is examined and the results obtained shown below.

The ν_{3b} band (1155 cm^{-1}):

$$\left.\begin{array}{l} \nu_4 + \nu_5 + \nu_8 = 1165 \text{ cm}^{-1} \\ \nu_4 + \nu_7 + \nu_8 = 1140 \\ \nu_4 + \nu_6 + \nu_8 + \nu_{10} = 1158 \\ \nu_5 + \nu_7 + \nu_6 + \nu_8 + \nu_{10} = 1158 \end{array}\right\} \text{Mean 1155 cm}^{-1}$$

Since $\nu_4 = \nu_5 + \nu_7$,

$$\nu_{3b} = \tfrac{1}{4}\left[5(\nu_5 + \nu_7) + 2(\nu_6 + 2\nu_8 + \nu_{10})\right].$$

The ν_{3a} band (1125 cm^{-1}):

$$\left.\begin{array}{l} \nu_4 + \nu_5 + \nu_9 = 1130 \text{ cm}^{-1} \\ \nu_4 + \nu_7 + \nu_9 = 1115 \\ \nu_4 + \nu_6 + \nu_9 + \nu_{10} = 1123 \\ \nu_5 + \nu_7 + \nu_6 + \nu_9 + \nu_{10} = 1123 \end{array}\right\} \text{Mean 1123 cm}^{-1}$$

Since $\nu_4 = \nu_5 + \nu_7$,

$$\nu_{3a} = \tfrac{1}{4}\left[5(\nu_5 + \nu_7) + 2(\nu_6 + 2\nu_9 + \nu_{10})\right].$$

The splitting of ν_{3b} and ν_{3a} of F_2 mode is due to the variation between the absorption band ν_8 and ν_9.

The summation of band ν_3 (981 cm^{-1}) of the free SO_4 ion

$$\nu_3 = 2\nu_5 + \nu_8 + \nu_9 + \nu_{10} = 1104 \text{ cm}^{-1}.$$

Variations of the bands between ν_5 and ν_7, between ν_6 and ν_8 and between ν_8 and ν_9 are considered to originate the band variations between ν_{3b}, ν_{3a} and ν_3.

The ν_4 band (625 cm^{-1}):

$$\nu_4 = \nu_5 + \nu_7 = 625 \text{ cm}^{-1}$$

The summation of ν_4 band (613 cm^{-1}) for the free SO_4 ion

$$\nu_4 = 2(\nu_8 + \nu_{10}) = 596 \text{ cm}^{-1}.$$

The ν_4 band of sulfohalite is due to the variation between ν_5 and ν_6, where $\nu_7 = \nu_8 + \nu_{10}$.

The ν_1 band (995 cm^{-1}):
This is an apparent band in the infrared spectrum.

$$\nu_1 = \nu_4 + \nu_0 = 995 \text{ cm}^{-1}$$

The ν_1 band (981 cm^{-1}) of the free SO_4 ion has the following combination.

$$\nu_1 = 2\nu_0 + \nu_8 = 980 \text{ cm}^{-1}$$

And ν_2 band (450 cm^{-1}) of the free SO$_4$ ion is the combination band as

$$\nu_2 = \nu_0 + \nu_{10} = 448 \text{ cm}^{-1}.$$

The ν_0 band (370 cm^{-1}) is an overtone of the ν_9 band,

$$\nu_0 = 2\nu_9 = 370 \text{ cm}^{-1}.$$

And the differences between ν_5 and ν_7 and between ν_6 and ν_8 are similar.

$$\nu_5 - \nu_7 = 15 \text{ cm}^{-1}$$
$$\nu_6 - \nu_8 = 15$$

Similar combinations of bands are also found in other anhydrous sulfates. The examples are shown in Table 3, where all the wave numbers of absorption bands have been measured by the author on the spectra shown in Figure 4. The inner molecular vibrations vibrate partially in the crystal lattice and vibrate in harmony with the vibrations in the far infrared region, which propagate in the entire crystal lattice. The splitting of the absorption bands and the vibration of the wave number are attributed to the different combinations of the characteristic phonons.

Absorption Bands in the Far Infrared Region

Although seven absorption bands are found in the far infrared region of the spectrum of sulfohalite, the ν_0 band at 370 cm^{-1} seems to be an overtone of the ν_9 band at 185 cm^{-1}.

The octahedral ions, FNa$_6$ and ClNa$_6$, are found in the crystal structure of sulfohalite. The force constants, K, H and F, of the octahedral ions were calculated by using the GF matrices. The force constants obtained and the wave numbers calculated are shown below.

Octahedral FNa$_6$ ion: K = 0.115, H = 0.071 and F = 0.250 md/Å

Wave numbers measured 320(ν_5) and 235(ν_6)

Wave numbers calculated 321   242

Octahedral ClNa$_6$ ion: K = 0.309, H = 0.105 and F = 0.104 md/Å

Wave numbers measured 305(ν_7) and 220(ν_8)

Wave numbers calculated 305   202.

Then, the force constant k of the interaction between the (F,Cl)Na$_6$ and SO$_4$ ions was calculated by using the following equation

$$\lambda = \frac{4}{3} k \left[2\mu_{((\text{F,Cl})\text{Na}_6)} + \mu_{(\text{SO}_4)} \right],$$

1. Mascagnite

(ν_1) 970 (w) $450+220\times2+80=970$ cm^{-1}
(ν_2) 450 (w) $220\times2=440$
        $380+80=460$

2. Sulfohalite

(ν_3) 1155 . . . $625+320+220=1165$
          $625+305+220=1140$
          $625+235+220+78=1158$
          $320+305+235+220+78=1158$
    1125 . . . $625+320+185=1130$
          $625+305+185=1115$
          $625+235+185+78=1123$
          $320+305+235+185+78=1123$
(ν_1) 995 (w) $625+370=995$
(ν_4) 625 . . . $320+305=625$
    370 . . . $185\times2=370$

3. Thenardite

(ν_3) 1155(sh) $1010+145=1155$
    1120 . . . $617+180\times2+145=1122$
(ν_1) 1010 . . . $617+180+145+75=1017$
(ν_4) 633 . . . $450+180=630$
    617 . . . $180+145\times2+75\times2=620$
(ν_2) 450 . . . $145\times2+75\times2=440$
    145 . . . $75\times2=150$

4. Glauberite

(ν_3) 1140 . . . $995+135=1130$
    1105 . . . $645+464=1109$
        $630+475=1105$
(ν_1) 995 . . . $475+288+230=993$
(ν_4) 645 . . . $464+186=650$
        $288+230+135=653$
    609 . . . $288+186+135=609$
(ν_2) 475 . . . $288+186=474$
    464 (w) $230\times2=460$

5. Anhydrite

(ν_3) 1190(sh) $595\times2=1190$
        $675+510=1185$
        $675+283+238=1196$
        $612+283+191+105=1191$
    1153 . . . $675+283+191=1149$
        $675+191+173+120=1159$
        $612+238+191+105=1146$
        $595+283+173+105=1156$
        $595+238+173+140=1146$
    1119 . . . $675+191+140+120=1126$
        $612+238+140+120=1110$
        $595+283+238=1116$
        $595+283+140+105=1123$
        $595+238+173+120=1126$
(ν_4) 675 . . . $510+173=683$
        $238+191+140+105=674$
        $238+173+140+120=671$
    612 . . . $510+105=615$
        $283+191+140=614$

Right column

    595 . . . $283+191+120=594$
        $283+173+140=596$
(ν_2) 510 . . . $191+173+140=504$
    283 . . . $173+105=278$
        $140\times2=280$
    238 . . . $140+105=245$
        $120\times2=240$

6. Palmierite

(ν_3) 1190 . . . $990+190=1180$
        $650+343+190=1183$
        $615+295+166+105=1181$
    1140 . . . $650+295+190=1135$
        $615+343+190=1148$
    1105 . . . $650+343+105=1098$
        $635+475=1110$
        $615+295+190=1100$
(ν_1) 990 . . . $650+343=993$
        $343+295+190+166=994$
(ν_4) 650 (w) $295+190+166=651$
    635(sh) $343+295=638$
    615 . . . $343+166+105=614$
(ν_2) 475 . . . $295+190=483$
    445 . . . $343+105=448$
    295 . . . $190+105=295$

7. Anglesite

(ν_3) 1105 . . . $592+185+150+104+73=1109$
        $960+150=1110$
    1165 . . . $960+185=1145$
    1045 . . . $592+185+150+120=1047$
(ν_1) 960 . . . $620+150+120+73=963$
        $592+150+120+104=966$
(ν_4) 620 . . . $185+150+120+104+73=632$

8. Barite

(ν_3) 1120 . . . $608+198+167+142=1115$
        $980+142=1122$
    1180 . . . $980+198=1178$
    1080 . . . $633+167+142+125=1087$
        $608+198+142+125=1073$
(ν_1) 980 . . . $633+198+142=973$
        $608+198+167=973$
        $608+142+125+100=975$
(ν_4) 633 . . . $198+167+142+125=632$
    608 . . . $198+167+142+100=607$

9. Celestite

(ν_3) 1130 . . . $610+212+170+132=1124$
        $990+132=1122$
    1195 . . . $990+212=1202$
    1095 . . . $639+212+132+120=1103$
        $610+212+147+120=1089$
(ν_1) 990 . . . $639+212+147=998$
        $610+212+170=992$
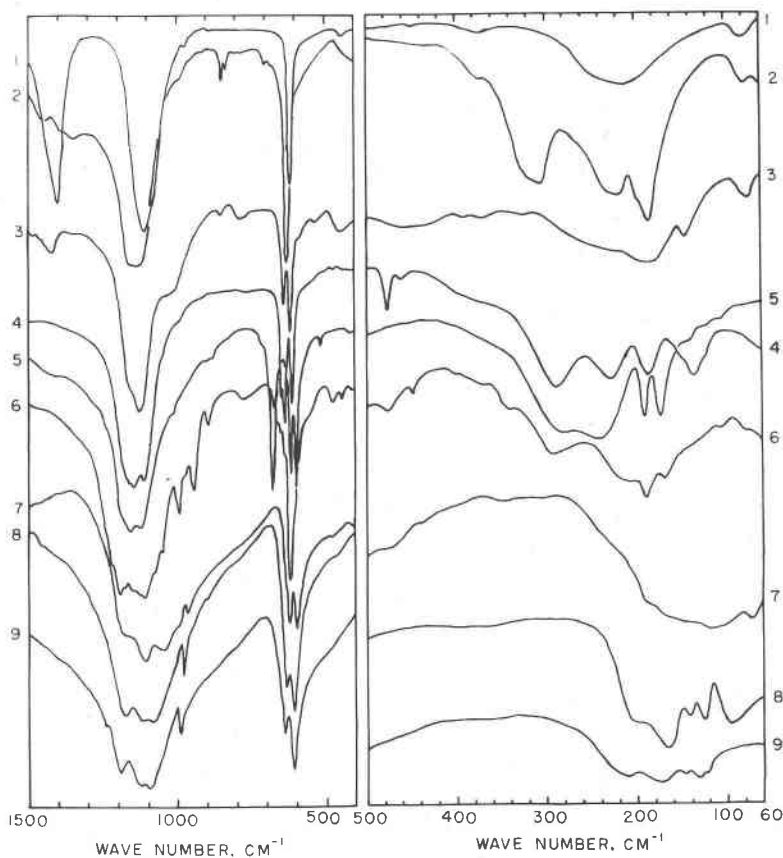(ν_4) 639 . . . $212+170+132+120=634$
    610 . . . $212+147+132+120=611$

Fig. 4. Infrared absorption spectra of the anhydrous sulfates in the wave number region between 1500 and 60 cm⁻¹. 1. Mascagnite, Larderello, Tuscany, Italy, 2. Sulfohalite, Searles Lake, Calif., 3. Thenardite, Borax Lake, Lake Co., Calif., 4. Glauberite, San Bernardino Co., Calif., 5. Anhydrite, Roundhouse, Nev., 6. Palmierite, Vesuvius, Italy, 7. Anglesite, Los Lamentos, Chihuahua, Mexico, 8. Barite, Tazewell Co., Va., and 9. Celestite, Strontian Island, Lake Erie.

where $\mu_{((F,Cl)Na_6)}$ is the reciprocal mass of either FNa_6 or $ClNa_6$ ion and $\mu_{(SO_4)}$ is the reciprocal mass of the SO_4 ion. The interaction force constants obtained are k 0.653 md/ Å for the FNa_6 and SO_4 ions from the absorption band at 185 cm⁻¹(ν_9) and k 0.122 md/ Å for the $ClNa_6$ and SO_4 ions from the absorption band at 78 cm⁻¹(ν_{10}). The modes of these vibrations are the lattice vibration.

CONCLUSIONS

Infrared and the far infrared absorption spectra of sulfohalite $Na_6FCl(SO_4)_2$ were studied and in addition mascagnite $(NH_4)_2SO_4$,

thenardite Na_2SO_4, glauberite $Na_2Ca(SO_4)_2$, anhydrite $CaSO_4$, palmierite $(K,Na)_2Pb(SO_4)_2$, anglesite $PbSO_4$, barite $BaSO_4$ and celestite $SrSO_4$ in the wave number region between 4000 and 60 cm^{-1}.

The single sulfate that contains one ion of SO_4 in its chemical formula is orthorhombic dipyramidal, while the double sulfate that contains two ions of SO_4 in its chemical formula is either monoclinic prismatic or rhombohedral scalenohedral. Sulfate containing hologens such as sulfohalite is isometric, such as schairerite is rhombohedral or such as chlorothionite is orthorhombic.

Among the anhydrous sulfates sulfohalite shows a small number of infrared absorption band from 4000 cm^{-1} to 60 cm^{-1}. Though the absorption of mascagnite is also the small number, the bands of the SO_4 ion are accompanied by the bands of NH_4 ion.

Factor group analysis of sulfohalite for O_h^5 is shown in Table 2. Site group analysis of the SO_4 ion of T_d shows that the infrared active modes are two F_2 shown in Figure 3.

Force constants of the Urey-Bradley force field are calculated $K(S-O)$ 6.45, $H(O-S-O)$ 0.70 and $F(O \cdots O)$ 0.71 md/ Å for the SO_4 ion of sulfohalite. The stretching force constant (K) and the bending force constant (H) of sulfohalite are larger and the repulsive force constant (F) is smaller than those of the free SO_4 ion.

From the analyses of the absorption bands in the far infrared region the force constants K 0.115, H 0.071 and F 0.250 md/ Å for the octahedral FNa_6 ion and K 0.309, H 0.105 and F 0.104 md/ Å for the octahedral $ClNa_6$ ion were obtained. And the interaction force constants k 0.653 and 0.122 md/ Å were calculated for the FNa_6 and SO_4 ions and the $ClNa_6$ and SO_4 ions, respectively. The mode of these vibrations is the lattice vibration.

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