INFRARED DIFFRACTION AND THE FAR INFRARED SPECTRA OF ANHYDROUS SULFATES

KEIICHI OMORI

*Institute of Mineralogy, Petrology and Economic Geology,
Faculty of Science, Tohoku University, Sendai*

ABSTRACT

A phenomenon analogous to X-ray diffraction and described as infrared diffraction has been obtained by mathematical analysis, between the absorption bands of the SO_4 molecule in solution, and those of crystals of anglesite, barite, celestite, and anhydrite. The absorption bands of the fundamental vibrational mode are discussed for each mineral. From the results, it has been concluded that relationships showing wave motions exist between the bands of the spectrum. Infrared spectra are calculated by using the damped equation in the wave number region from 2000 to 100 cm^{-1} . The features of the calculated spectra are similar to those of the spectrum obtained by using infrared spectrophotometers.

Introduction

Infrared spectra of anhydrous sulfates have been studied by Moenke (1962), Omori and Kerr (1963 and 1964), and Adler and Kerr (1965), while the absorption bands of barite have been discussed by Ramdes (1954) and Spencer (1959).

From these studies several characteristic features of the absorption bands have become better understood, but some fundamental properties remain to be explained. Frequencies of the fundamental vibrational modes of the SO_4 molecule differ between those observed for crystal powders of sulfates and those observed in solution. The differences between these states have not yet been discussed. They can be interpreted clearly by the phenomenon designated infrared

diffraction as given in this paper.

Also, far infrared spectra of anhydrous sulfates have not yet been studied, although recently, Angino has discussed the far infrared spectra of carbonates (1967) and referred to the spectra of plagioclase feldspars (1967a). Likewise, Omori (1968) has studied the far infrared spectrum of quartz, with a discussion of the relative wave motion, and compared the calculated spectrum with the observed spectrum in the region from 2000 to 100 cm^{-1} . Similar relations have been found in the anhydrous sulfates. The calculated spectra are compared in the present paper. Thus, infrared spectra can be interpreted in terms of wave motion.

Anhydrous sulfates used for the study

Four anhydrous sulfates have been used for this study: anglesite (PbSO_4) from Los Lamentos, Chihuahua in Mexico, barite (BaSO_4) from Tazewell Co., Va., celestite (SrSO_4) from Strontian Island, Lake Erie, and anhydrite (CaSO_4) from Roundhouse, Nevada.

Each specimen was powdered in an agate mortar and a KBr disk was made by the usual method (Omori & Kerr, 1964) for infrared study in the wave number region between 4000 and 400 cm^{-1} . The polyethylene plate method was used for the far infrared study, where the plate was covered by nujol mixed with a small amount of sulfate powder (Omori, 1968). Infrared spectra were recorded by using three spectrophotometers. The Perkin-Elmer Type 125 with gratings was used for spectra in the region between 4000 and 400 cm^{-1} and the Hitachi Type EPI-ST with a KBr prism was used for the range between 900 and 400 cm^{-1} . For the far infrared spectrum, the Hitachi Type FIS-1 with gratings was used between 500 and 60 cm^{-1} .

The infrared spectra obtained are shown in Figs. 1 and 2, and the wave numbers of the absorption bands measured are given in Table 1.

Fig. 1. Infrared spectra between 4000 and 400 cm^{-1} for anglesite, barite, celestite and anhydrite.

Four fundamental vibrational modes of the SO_4 molecule

The fundamental vibrational modes of the SO_4 molecule are known as four distinct internal modes, *i. e.* one nondegenerate mode $\nu_1(A_1)$, one doubly degenerate mode $\nu_2(E)$ and two triply degenerate modes $\nu_3(F_2)$ and $\nu_4(F_2)$ as shown in Fig. 3 after Mitra and Geilisse (1964).

The spectra for the minerals of the barite group have two strong bands ν_3 and ν_4 , and one weak band ν_1 , while the spectrum of anhydrite shows two strong bands ν_3 and ν_4 , and one weak band ν_2 .

Fig. 2. Infrared spectra between 900 and 60 cm^{-1} for anglesite, barite, celestite and anhydrite

Differences in the band features between the spectra are caused by the crystal structure.

In the barite group, cations of Pb, Ba or Sr are surrounded by twelve oxygen anions belonging to seven different SO_4 molecules as shown in Fig. 4. While in anhydrite each cation of Ca is surrounded by eight oxygen anions of six different SO_4 molecules.

Each mineral belongs to the orthorhombic holohedral class $2/m\ 2/m\ 2/m$, but the space group of the barite group is $Pnma$, while that of anhydrite is $Bbmm$ with pseudotetragonal constants $b_0=6.96\text{\AA}$ and $c_0=6.97\text{\AA}$. As shown in Table 1, cell constants become smaller as the cation radius decreases from anglesite to anhydrite.

The variation in the atomic weight of the cation causes the change in the wave numbers of the absorption bands, because the vibration of the atom is considered to be that of the nucleus. This will be discussed further in connection with the diffraction angles.

Table 1. Comparative data for anhydrous sulfates of Pb, Ba, Sr and Ca.

Mineral	Anglesite PbSO ₄	Barite BaSO ₄	Celestite SrSO ₄	Anhydrite CaSO ₄
Locality	Los Lamentos Chihuahua Mexico	Tazewell Co., Va.	Strontian Island Lake Erie	Roundhouse Nev.
Absorption band	Meas. Calc.	Meas. Calc.	Meas. Calc.	Meas.
ν_3 (1104 cm ⁻¹)	1165 1164.2	1180 1183.2	1195 1194.0	1190
	1105 1104.0	1120 1121.2	1130 1128.1	1153
	1045 1043.8	1080 1077.6	1095 1093.5	1119
ν_1 (981 cm ⁻¹)	960 958.0	980 979.8	990 989.6	—
ν_4 (613 cm ⁻¹)	620 619.0	633 635.4	639 641.8	675
	592 592.0	608 607.0	610 611.1	612
	—	—	—	595
ν_2 (451 cm ⁻¹)	—	—	—	510
Far infrared bands	185	198	212	283
	150	167	170	238
	120	142	147	191
	—	—	—	173
	104	125	132	140
	73	100	120	120
	—	—	—	105
Space Group	<i>Pnma</i>	<i>Pnma</i>	<i>Pnma</i>	<i>Bbmm</i>
Unit cell constants (Å)	a_0 8.54 b_0 5.38 c_0 6.93	8.85 5.43 7.13	8.36 5.35 6.87	6.22 6.96 6.97
Radius of cation (Å)	1.20	1.35	1.13	0.99
Atomic weight of cation	207.19	137.34	87.62	40.08

Fig. 3. Four distinct internal modes of the SO_4 molecule (after Mitra and Geilisse, 1964).

Infrared diffraction

Every atom of the SO_4 molecule in solution vibrates freely, but in the crystal, the atom vibrates under additional influences from the cations of Pb, Ba, Sr or Ca. The differences between the two cause the variation in the wave number of the absorption band. The triply degenerate vibrational mode ν_3 of the SO_4 molecule in solution shows a unit wave number 1104 cm^{-1} , while in celestite, for instance, it shows three different wave numbers 1195 , 1130 and 1095 cm^{-1} given in Table 1. Similar relations are found in other minerals and for other vibrational modes.

The relationships for the mode ν_3 are shown schematically in Fig. 5, where the largest circle shows the relation between 1104 and 1195 cm^{-1} , the middle circle found on the right side shows that between 1104 and 1130 cm^{-1} , and the smallest circle on the right outer

Fig. 5. Adaptation of Ewald's X-ray sphere to infrared.

we have

$$\sin \theta = AH/R,$$

where R is the diameter of the circle. Let $AH = \delta$ and $r =$ the radius of the circle ($= R/2$), we then have

$$\delta = 2(r/n) \sin \theta,$$

where n is an integer. The equation is similar to the Bragg equation, $1/d = 2(1/n\lambda) \sin \theta$.

Thus the relationship may be considered as infrared diffraction, and the infrared spectrum can be analysed in terms of wave motion.

Similar relationships are also found in the middle circle and in the smallest circle in Fig. 5.

Then, draw the line OH normal to the line AC at point H in Fig. 5. We have three equations,

$$\triangle O_0AH \equiv \triangle OHA,$$

$$\triangle O_0bH \sim \triangle OHB,$$

$$\text{and } \triangle O_0cH \sim \triangle OHC.$$

BH in the middle circle and CH in the smallest circle are equivalent

to bH and cH in the largest circle respectively. Here, AH , bH and cH in the largest circle show the relationships between the three fundamental vibrational modes ν_3 , represented by radii which incline at the center at 70° to each other.

Then, we have

$$\begin{aligned}\angle AO_0H &= \angle AOH = \theta, \\ \angle bO_0H &= \angle BOH = \theta - 35^\circ, \\ \text{and } \angle cO_0H &= \angle COH = 70^\circ - \theta,\end{aligned}$$

where the lines O_0b and OB are bisectrices of $\angle AO_0c$ and $\angle AOC$ respectively.

In the lower illustration of Fig. 5, which shows a part of the upper illustration, we have $OA = 2r = R$ and $\sin \theta = HA/R$, $\angle AOH = \theta$, $\angle AOB = 35^\circ$ and $\angle BOC = 35^\circ$.

Plot A , B , H and C on a line using the wave numbers shown in Table 2, and draw a normal at H to the line AC . Then, plot the three lines OA , OB and OC as shown in Fig. 5, keeping the following angles constant,

$$\angle AOB = \angle BOC = 35^\circ.$$

Analyses for the fundamental vibrational modes of anglesite, barite and celestite are shown in Fig. 6, where the diameter of the circle $R = 2r = OA = 105 \text{ cm}^{-1}$.

When $HA = \nu_{3a}$, $HB = \nu_{3b}$ and $HC = \nu_{3c}$ for anglesite, barite and celestite, we have the following equations from the lower illustration in Fig. 5.

$$\begin{aligned}\nu_{3a} &= 1104 \text{ cm}^{-1} + R \sin \theta, \\ \nu_{3b} &= 1104 \text{ cm}^{-1} + R \cos \theta \cdot \tan (\theta - 35^\circ), \\ \text{and } \nu_{3c} &= 1104 \text{ cm}^{-1} - R \cos \theta \cdot \tan (70^\circ - \theta).\end{aligned}$$

Next, we have the following equations for ν_1 , ν_{4a} and ν_{4b} from Fig. 6.

$$\begin{aligned}\nu_1 &= 981 \text{ cm}^{-1} - R \cos \theta \cdot \tan (50^\circ - \theta), \\ \nu_{4a} &= 613 \text{ cm}^{-1} + R \cos \theta \cdot \tan (\theta - 31^\circ), \\ \text{and } \nu_{4b} &= 1.5 \nu_{4a} - 0.5 R \cdot \sin \theta - 0.5 \times 613 \text{ cm}^{-1}.\end{aligned}$$

Fig. 6. Analyses for the fundamental vibrational modes of anglesite, barite and celestite.

Table 2. Diffraction angles for anglesite, barite, and celestite.

Mineral	Chemical formula	Atomic weight of cation	Diffraction angle for ν_{3a}	
			Measured	Calculated
Anglesite	PbSO ₄	207.19	35°	35.15°
Barite	BaSO ₄	137.34	49	49.12
Celestite	SrSO ₄	87.62	59	59.07

Then, take $R=105\text{ cm}^{-1}$ and take θ as the angle shown in Table 2. The wave numbers of the fundamental mode for each mineral may be calculated as shown in Table 1. The measured wave numbers agree well with the calculated numbers.

Diffraction angles

The diffraction angles θ for ν_{3a} were measured for anglesite, barite and celestite as shown in Fig. 6. The angles were then plotted on the line θ , ν_{3a} versus the atomic weights of Pb, Ba and Sr shown

Fig. 7. Lattice lines derived from angles of the infrared diffraction.

in Fig. 7, which yields the equation,

$$\theta = 76.59^\circ - 0.20 \times (\text{atomic weight of the cation (Pb, Ba or Sr)}) .$$

The diffraction angles calculated from the equation are shown in Table 2.

Straight lines derived from the angles are parallel to the line of ν_{3a} in Fig. 7 except one line, ν_{4b} . The relationships between ν_{3a} , ν_{3b} , ν_{3c} , ν_1 , ν_{4a} and ν_{4b} for the minerals of barite group are shown in Fig. 8. Similar relations also appear in Fig. 6.

In Fig. 8, the line with the points for ν_{4b} , for PbSO_4 , BaSO_4 and SrSO_4 is parallel to that for ν_{4a} , while the other lines converge at one point. This shows that the vibrational relationship of ν_{4b} is not similar to other modes.

Fig. 8. Positions of lattice lines for Sr, Ba and Pb sulfates.

Far infrared spectra of anhydrous sulfates

Far infrared absorption spectra of anglesite, barite, celestite and anhydrite are shown in Fig. 2, while the wave numbers of the absorption bands are shown in Table 1. The wave numbers of anhydrite show no similarity to those of the minerals of the barite group.

For anhydrite, the band at 1190 cm^{-1} in the infrared region is considered to be a double wave number band $2 \times 595\text{ cm}^{-1}$ for ν_4 . The fundamental vibrational mode ν_2 is found at 510 cm^{-1} and three bands of the mode ν_4 are found at 675, 612 and 595 cm^{-1} .

These characteristic features of anhydrite are repeated in the far infrared region. Two bands at 285 and 238 cm^{-1} are considered to be a repetition of ν_8 bands at 1153 and 1119 cm^{-1} respectively, because the differences between them are almost the same, $283 - 238 = 45\text{ cm}^{-1}$ and $1153 - 1119 = 34\text{ cm}^{-1}$.

Three bands at 238, 191 and 173 cm^{-1} are also the repeated bands of ν_4 at 675, 612 and 595 cm^{-1} and one band 173 cm^{-1} is that of ν_2 at 510 cm^{-1} .

Three other bands of anhydrite at 140, 120 and 105 cm^{-1} are considered to be the half wave number bands for 283, 238 and 191 cm^{-1} respectively.

For the minerals of the barite group, similar repetition occurs,

but more simply between the bands of the infrared and the far infrared region. For anglesite, for instance, three bands at 185, 120 and 73 cm^{-1} represent ν_3 at 1165, 1105 and 1045 cm^{-1} , respectively, one band at 104 cm^{-1} is that of ν_1 at 960 cm^{-1} , and two bands at 120 and 104 cm^{-1} are those of ν_4 at 620 and 592 cm^{-1} respectively.

Barite and celestite show similar features.

Damped vibrational equation for two bands between the infrared region and the far infrared region

The vibrational relationship of a damped curve is considered to exist between the vibration of two bands in the infrared and in the far infrared region.

The general equation of the damped vibrational curve may be shown as $y = \cos ax/e^{bx}$, where y is the frequency. If one assumes constants $a=1$ and $b=1$, the equation is written as $y = \cos x/e^x$. When y is the amplitude of the wave motion, the intensity is shown as $y^2 = (\cos x/e^x)^2$. The calculated values of y^2 are shown for each degree of x in Table 3, where y^2 is very small between $x=242^\circ$ and 300° . The damped curve for y and the intensity curve y^2 are shown in Fig. 9.

When A is the amplitude for the infrared wave motion, we have

$$A = \frac{\cos\left(\frac{\nu_0 \sim \nu_x}{\nu_0 - \nu_{3/4 \cdot \pi}} \times 135^\circ\right)}{e^{\left(\frac{\nu_0 \sim \nu_x}{\nu_0 - \nu_{3/4 \cdot \pi}} \times \frac{3}{4} \pi\right)}},$$

where ν_0 is the wave number of the absorption bands ν_3 , ν_4 , ν_1 and ν_2 , $\nu_{3/4 \cdot \pi}$ is that of each infrared band, and ν_x is that to be calculated.

Intensity I , or the transmittance, of the spectrum is calculated as the sum of each A^2 , namely

$$I = \sum A_i^2.$$

Table 3. Calculated values of y^2 for each degree of x .

y^2	0°	1°	2°	3°	4°	5°	6°	7°	8°	9°	10°
0	1.0000	.9654	.9314	.8981	.8654	.8335	.8021	.7716	.7417	.7125	.6841
1	.6841	.6564	.6293	.6031	.5775	.5527	.5286	.5052	.4825	.4606	.4393
2	.4393	.4187	.3989	.3796	.3611	.3432	.3260	.3093	.2934	.2780	.2632
3	.2632	.2490	.2354	.2223	.2098	.1978	.1863	.1753	.1648	.1548	.1453
4	.1453	.1361	.1274	.1192	.1114	.1039	.0969	.0902	.0838	.0778	.0721
5	.0721	.0668	.0617	.0569	.0525	.0482	.0443	.0406	.0371	.0338	.0308
6	.0308	.0280	.0253	.0229	.0206	.0185	.0165	.0147	.0131	.0116	.0102
7	.0102	.0089	.0077	.0067	.0057	.0049	.0041	.0034	.0028	.0023	.0018
8	.0018	.0014	.0011	.0008	.0006	.0004	.0002	.0001	.0001	.0000	.0000
9	.0000	.0000	.0000	.0001	.0002	.0003	.0004	.0005	.0006	.0008	.0009
10	.0009	.0011	.0012	.0014	.0016	.0017	.0019	.0020	.0022	.0024	.0025
11	.0025	.0027	.0028	.0030	.0031	.0032	.0034	.0035	.0036	.0037	.0038
12	.0038	.0039	.0040	.0041	.0041	.0042	.0042	.0043	.0043	.0044	.0044
13	.0044	.0044	.0045	.0045	.0045	.0045	.0045	.0045	.0045	.0044	.0044
14	.0044	.0044	.0044	.0043	.0043	.0043	.0042	.0042	.0041	.0040	.0040
15	.0040	.0039	.0039	.0038	.0037	.0037	.0036	.0035	.0035	.0034	.0033
16	.0033	.0032	.0032	.0031	.0030	.0029	.0029	.0028	.0027	.0026	.0026
17	.0026	.0025	.0024	.0023	.0023	.0022	.0021	.0021	.0020	.0019	.0019
18	.0019	.0018	.0017	.0017	.0016	.0016	.0015	.0014	.0014	.0013	.0013
19	.0013	.0012	.0012	.0011	.0011	.0010	.0010	.0009	.0009	.0009	.0008
20	.0008	.0008	.0007	.0007	.0007	.0006	.0006	.0006	.0005	.0005	.0005
21	.0005	.0005	.0004	.0004	.0004	.0004	.0003	.0003	.0003	.0003	.0003
22	.0003	.0003	.0002	.0002	.0002	.0002	.0002	.0002	.0002	.0001	.0001
23	.0001	.0001	.0001	.0001	.0001	.0001	.0001	.0001	.0001	.0001	.0001
24	.0001	.0001	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
25	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
26	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
27	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
28	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
29	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000

Fig. 9. Damped curves for y and intensity curve for y^2 .

Table 4. Calculated intensities of infrared diffraction for anglesite.

	(1)	(2)	(3)	(4)	(5)	(6)	Calculated intensities $\Sigma (y^\circ)$
	1165 cm^{-1} 185	1105 cm^{-1} 120	1045 cm^{-1} 73	960 cm^{-1} 104	620 cm^{-1} 120	592 cm^{-1} 104	
$x=0$	115°	122°	133°	164°	373°	388°	0.0147
$x=3/4 \cdot \pi$	101	109	118	149	346	361	0.0111
2000 cm^{-1}	88	95	105	133	318	333	0.0066
1900	74	82	91	117	292	306	0.0103
1800	60	68	77	101	265	278	0.0478
1700	46	54	63	85	238	251	0.1728
1600	32	40	49	70	211	223	0.4694
1500	19	27	35	54	184	196	1.0228
1400	5	13	22	38	157	168	2.0065
1300	-2	6	15	30	143	154	2.5575
1200	-9	-1	8	22	130	140	2.8273
1150	-16	-7	1	14	116	127	2.8508
1100	-23	-14	-6	6	103	113	2.6660
1050	-30	-21	-13	-2	90	99	2.2172
1000	-37	-28	-20	-10	76	85	1.5966
950	-50	-42	-34	-25	49	57	0.8710
900	-57	-49	-41	-35	35	44	0.7615
850	-64	-56	-48	-41	22	30	0.9469
800	-71	-63	-55	-49	9	16	1.3989
750	-78	-69	-62	-57	-5	2	1.8452
700	-85	-76	-69	-65	-18	-12	1.1464
650	-92	-83	-76	-73	-32	-25	0.5902
600	-106	-97	-90	-88	-59	-53	0.0932
550	-113	-104	-97	-96	-73	-67	0.0269
500	-119	-110	-104	-104	-86	-81	0.0110
450	-126	-117	-111	-112	-100	-95	0.0160
400	-133	-124	-118	-120	-113	-108	0.0212
350	-140	-131	-125	-128	-127	-122	0.0256
300	-147	-138	-132	-136	-141	-136	0.0266

Table 5. Calculated intensities of infrared diffraction for barite.

	(1)	(2)	(3)	(4)	(5)	(6)	Calculated intensities $\Sigma (j^2)$
	1180 cm ⁻¹ 198	1120 cm ⁻¹ 142	1080 cm ⁻¹ 100	980 cm ⁻¹ 125	633 cm ⁻¹ 142	608 cm ⁻¹ 125	
$x=0$	112°	121°	127°	161°	376°	388°	0.0142
$x=3/4 \cdot \pi$	99	108	113	145	348	361	0.0103
2000 cm ⁻¹	85	94	100	130	321	333	0.0059
1900	71	80	86	114	293	305	0.0140
1800	58	66	72	98	266	277	0.0619
1700	44	52	58	82	238	249	0.2114
1600	30	37	44	66	211	221	0.5672
1500	16	25	30	51	184	193	1.2045
1400	-3	11	17	35	156	165	2.2640
1300	-7	4	10	27	142	151	2.6388
1200	-11	-3	3	19	128	137	2.9220
1150	-18	-10	-4	11	115	123	2.6958
1100	-25	-17	11	3	101	109	2.4064
1050	-32	-24	18	-5	87	95	1.9129
1000	-38	-30	25	-13	73	81	1.3842
950	-45	-37	31	-21	60	68	0.9908
900	-52	-44	37	-28	46	54	0.7912
850	-59	-51	45	-36	32	40	0.7715
800	-66	-58	52	-44	18	25	1.0524
750	-73	-65	59	-52	5	12	1.5835
700	-79	-72	66	-60	-9	-2	1.7012
650	-86	-79	73	-68	-23	-16	0.9306
600	-93	-86	80	-76	-37	-30	0.4447
550	-107	-100	94	-92	-64	-58	0.0608
500	-114	-107	101	-100	-78	-72	0.0176
450	-121	-113	108	-108	-92	-86	0.0115
400	-128	-120	115	-116	-106	-100	0.0175
350	-134	-127	121	-123	-119	-114	0.0236
300	-141	-134	128	-131	-133	-128	0.0264
250	-148	-141	135	-139	-147	-142	0.0260

Table 6. Calculated intensities of infrared diffraction for celestite.

$x=0$ $x=3/4 \cdot \pi$	(1)	(2)	(3)	(4)	(5)	(6)	Calculated intensities $\Sigma(y^2)$
	1195 cm ⁻¹ 212	1130 cm ⁻¹ 147	1095 cm ⁻¹ 120	990 cm ⁻¹ 132	639 cm ⁻¹ 147	610 cm ⁻¹ 132	
2000 cm ⁻¹	110°	119°	126°	159°	373°	392°	0.0138
1900	97	106	112	143	346	364	0.0140
1800	83	92	98	127	318	336	0.0057
1700	69	78	84	111	291	307	0.0177
1600	56	64	70	96	264	279	0.0755
1500	42	51	56	80	236	251	0.2405
1400	28	37	42	64	209	223	0.6175
1300	14	23	29	49	183	195	1.3157
1200	1	10	15	33	154	166	2.4311
1150	-7	3	7	25	140	152	2.7928
1100	-13	-4	1	17	126	138	2.9479
1050	-20	-11	-6	10	113	124	2.5891
1000	-27	-18	-13	2	99	110	2.3296
950	-34	-25	-20	-6	86	96	1.7951
900	-40	-32	-27	-14	72	82	1.2763
850	-47	-39	-34	-22	58	68	0.9039
800	-54	-45	-41	-30	44	54	0.7196
750	-61	-52	-48	-38	31	40	0.7326
700	-68	-59	-55	-46	17	25	1.0404
650	-75	-66	-62	-54	3	11	1.6537
600	-82	-73	-69	-61	-11	-3	1.6019
550	-89	-80	-76	-69	-25	-17	0.8659
500	-95	-86	-83	-77	-38	-31	0.4183
400	-109	-100	-97	-93	-65	-59	0.0562
350	-116	-107	-104	-101	-79	-73	0.0171
300	-123	-114	-110	-108	-93	-87	0.0121
250	-130	-121	-117	-116	-107	-100	0.0181
200	-136	-127	-124	-124	-120	-116	0.0242
150	-143	-134	-131	-132	-134	-130	0.0266
100	-150	-141	-138	-140	-148	-144	0.0257

Table 7. Calculated intensities of infrared diffraction for anhydrite.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	Calculated intensities $\Sigma(j^2)$
	1190 cm^{-1} 173	1153 cm^{-1} 283	1119 cm^{-1} 238	675 cm^{-1} 238	612 cm^{-1} 191	595 cm^{-1} 173	510 cm^{-1} 173	
$x=0$								
$x=3/4 \cdot \pi$								
2000 cm^{-1}	108°	131°	135°	409°	445°	450°	596°	0.0111
1900	94	116	120	378	413	418	556	0.0074
1800	81	100	104	348	381	386	516	0.0039
1700	68	85	89	317	349	354	476	0.0135
1600	55	69	74	286	318	321	436	0.0655
1500	41	54	58	255	285	290	396	0.2257
1400	28	38	43	224	253	258	356	0.5776
1300	15	23	28	193	221	226	316	1.2273
1200	1	7	12	162	189	194	276	2.3719
1150	-6	0	7	147	173	178	256	2.5822
1100	-12	-8	-3	131	157	162	236	2.2808
1050	-18	-16	-11	116	141	146	216	1.6798
1000	-25	-24	-18	100	125	130	196	1.1973
950	-32	-32	-26	85	109	114	176	0.8048
900	-39	-39	-34	70	92	98	156	0.5331
850	-46	-47	-42	55	76	82	136	0.3767
800	-52	-55	-49	39	60	66	116	0.3832
750	-58	-63	-57	24	44	50	96	0.6856
700	-65	-70	-64	8	28	34	76	1.2983
650	-72	-78	-72	-8	12	16	56	1.9621
600	-78	-86	-79	-23	-4	2	36	2.3680
550	-85	-94	-87	-39	-20	-14	16	1.7009
500	-92	-101	-95	-54	-36	-30	-4	1.3748
450	-99	-109	-103	-70	-52	-46	-24	0.5345
400	-105	-117	-110	-85	-68	-62	-44	0.1579
350	-114	-125	-118	-101	-84	-78	-64	0.0340
300	-118	-133	-125	-116	-100	-94	-84	0.0174
250	-125	-141	-133	-132	-116	-110	-104	0.0251
200	-132	-148	-140	-147	-132	-126	-124	0.0304
150	-138	-156	-148	-163	-148	-142	-144	0.0281
100	-145	-163	-156	-178	-164	-158	-164	0.0225

Calculated spectra and observed spectra

The intensities of the whole region of spectra can be calculated from the equation $\sum A_i^2$. The calculated results for the wave number region 2000 cm^{-1} to 100 cm^{-1} are shown for anglesite (Table 4), barite (Table 5), celestite (Table 6) and anhydrite (Table 7).

Spectra illustrating the curves derived are shown in Fig. 10. These spectra correspond similarly in general to the observed spectra shown in Figs. 1 and 2.

Fig. 10. Calculated spectra for anglesite, barite, celestite and anhydrite.

The method is useful for the interpretation of infrared spectra by using the damped equation of the wave motion. It shows that an intimate relationship exists between the bands of the infrared region and the far infrared region, *i. e.* between the inner molecular vibrations and the outer lattice vibrations.

Conclusions

Infrared absorption bands of anglesite, barite, celestite and anhydrite are shown in the infrared and the far infrared regions. The relationship described as infrared diffraction has been developed, which is similar in many respects to X-ray diffraction.

A relationship is shown by the equation $\delta = 2(r/n) \sin \theta$, where the diffraction angle θ is inversely proportional to the atomic weights of cations Pb, Ba, Sr or Ca.

It is shown that a wave motion relationship exists between bands in the infrared and the far infrared regions. The relationship can be shown by the equation of the damped vibration. The spectra of anglesite, barite, celestite and anhydrite have been calculated from this equation, and show features similar to those recorded by the infrared spectrophotometers.

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