THE INFRA-RED ABSORPTION SPECTRA OF SODIUM NITRATE AND CALCITE

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1. Introduction

The infra-red absorption and reflexion spectra of sodium nitrate have been studied in the region of short wavelengths ($\lambda < 20\,\mu$) by Schæfer and his co-workers,[1] while Liebisch and Rubens[2] studied the reflexion spectrum in the long-wave range between $20\,\mu$ to $300\,\mu$. Calcite has been the subject of numerous investigations. Special mention may be made of Schæfer and his collaborators[3] who investigated absorption and reflexion spectra in the range $1\,\mu$ to $20\,\mu$ and Liebisch and Rubens[2] who examined the reflexion spectrum in the range $20\,\mu$ to $300\,\mu$. In view of the greatly improved instruments available at the present time in the field of infra-red spectroscopy, it appeared important to reinvestigate these crystals in order to get a more complete and detailed picture of their infra-red absorption spectra. The author has studied the absorption spectra of calcite and of sodium nitrate in the range $1\,\mu$ to $22\,\mu$ with a Beckman infra-red spectrophotometer provided with potassium bromide optics.

Sodium nitrate and calcite have similar crystal structures and hence should show similar infra-red behaviour. As Bhagavantam and Venkatarayudu[4] have emphasized, the infra-red and Raman spectra of crystals must be interpreted in accordance with the number of normal modes, their selection rules and symmetry properties appropriate to the unit cell of the crystal. In this paper it is proposed to present the experimental results obtained by the author and discuss the infra-red data in the light of the appropriate selection rules and the Raman effect data.

2. Experimental Results

The crystals were studied with the cleavage sections perpendicular to the infra-red radiation; the % transmission was read off directly with the spectrophotometer at $0{\cdot}05\,\mu$ intervals and at still closer intervals near absorption maxima.

Sodium Nitrate.—Figs. 1 and 2 show the % cut-off with wavelength of sodium nitrate specimens (thickness: Sp. I: 2·34 mm., Sp. III: 1 mm.). The following features are noticed in Figs. 1 and 2.

I. Many well-defined and sharp absorption maxima are seen in range 2 μ to 3·5 μ, *viz.*, at 2·3 μ, 2·42 μ, 2·65 μ, 2·85 μ, 3·2 μ. These have come out better with Sp. I than with Sp. III because Sp. I is thicker and hence brings out these weak absorption bands better.

II. Sharp and intense absorption maxima in the range 3·5 μ to 6·5 μ, *viz.*, at 3·6 μ, 4·1 μ, 4·75 μ, 5·6 μ, 5·8 μ, 6·3 μ. These bands have come out better with Sp. III than with Sp. I. The well resolved absorption maxima at 5·6 μ, 5·8 μ and 6·3 μ seen in Fig. 2 merge into an intense and broad absorption band extending from 5·6 μ to 9 μ as can be seen in Fig. 1.

III. Absorption maxima, very intense and broad compared to the bands mentioned in I and II, are seen in the range 6·5 μ to 14 μ. In Fig. 2

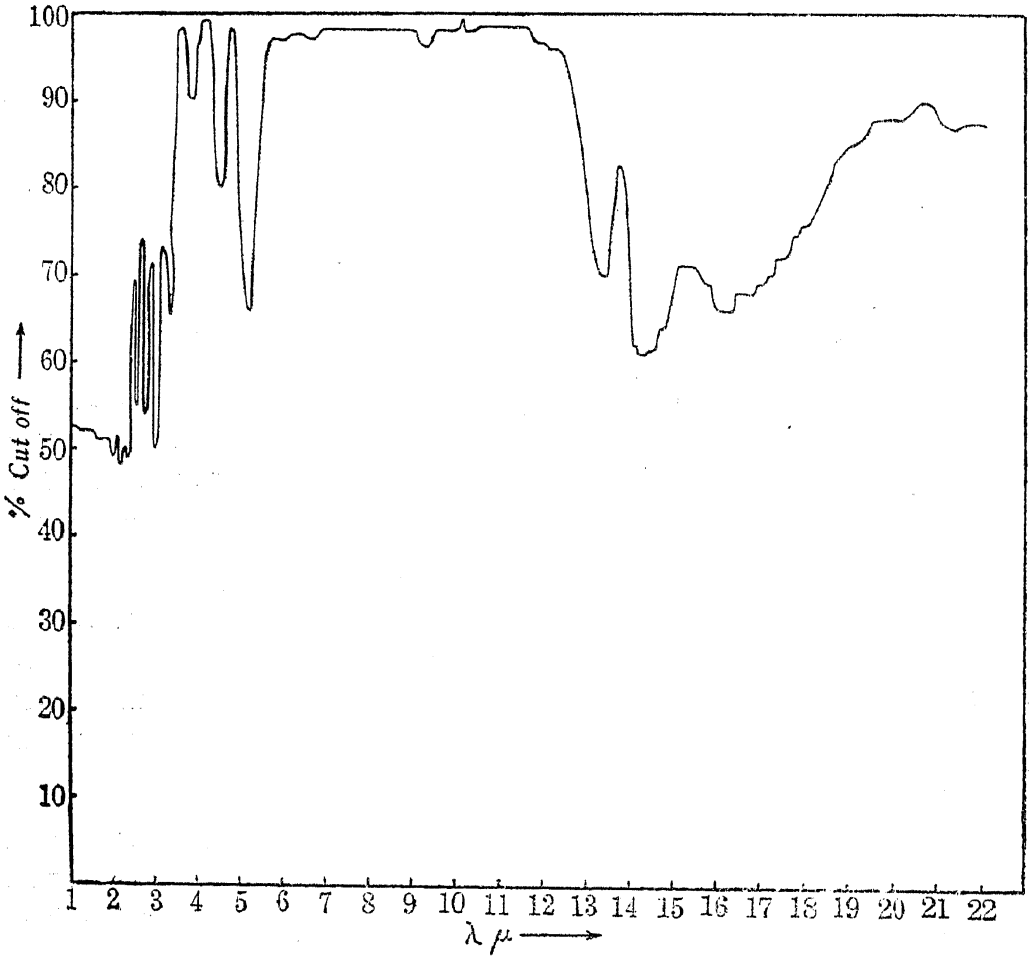

FIG. 1. Infra-red absorption spectrum of sodium nitrate (Specimen I).

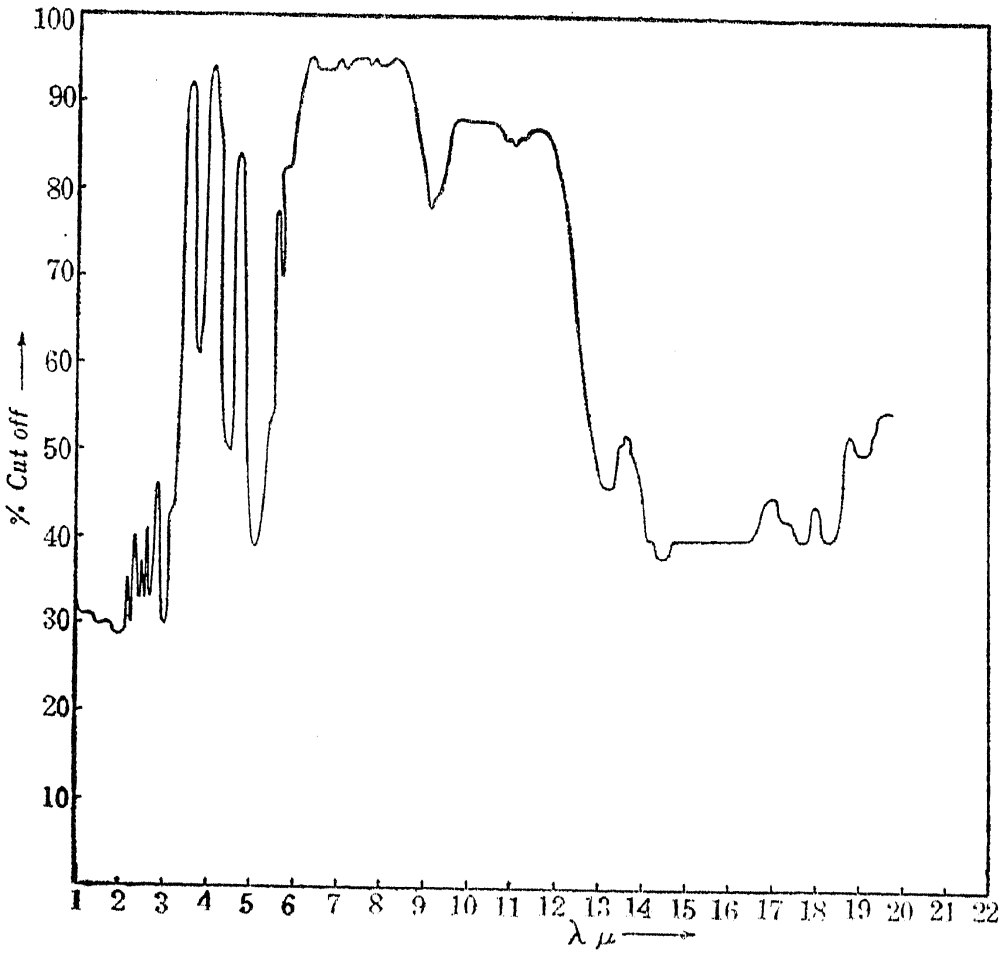

FIG. 2. Infra-red absorption spectrum of sodium nitrate (Specimen III).

we notice the following absorption bands: (1) between 6·7 and 8·0 μ, very strong; (2) at 8·3 μ, a strong companion to the 6·7 μ–8 μ band ; (3) from 9·8 μ to 10·6 μ, medium; (4) a medium strong and fairly sharp absorption maximum at 11·8 μ; (5) a very weak but very sharp and well-defined absorption maximum at 13·8 μ.

In Fig. 1, we notice an extremely broad absorption band running from 6 μ to 9 μ and from 9·5 μ to 11·6 μ and an inflexion at about 11·8 μ. These have been resolved into bands described above, by using the thinner specimen III. The 13·8 μ band, however, has come out sharper and stands out better in Fig. 1.

IV. In the range 14 μ to 22 μ, we notice in Fig. 1, a rather broad band medium in intensity, from 15·0 μ to 15·3 μ and considerable absorption between 19 μ to 22 μ. In Fig. 2, there are indications of these being resolved into constituent bands.

Calcite.—Fig. 3, giving the % cut-off with wave-length of a cleavage section of calcite (Specimen II: 0·33 mm.) shows a great similarity with Figs. 1 and 2. We see (1) weak but well-defined bands at 2·3 μ, 2·5 μ, 2·8 μ; (2) an inflexion at 3·1 μ; (3) exceedingly sharp and intense band at 3·47 μ; (4) a comparatively weaker absorption maximum at 4·8 μ; (5) indication of a band at 5·75 μ; (6) an intense absorption maximum at 6·3 μ clearly separated from an equally intense broad absorption band extending from 6·7 μ to 7·8 μ and in the slope of this band, an inflexion at 8·45 μ; (7) a series of bands at 9·3 μ (very weak), 9·9 μ (medium), 10·6 μ (weak), 11·3 μ (weak), 11·7 μ (inflexion), 12·8 μ (weak), and 14·1 μ (very intense and sharp); (8) beyond 17 μ, there is a very broad absorption band, extending upto the limit of observation; there are some indications of absorption maxima in this region.

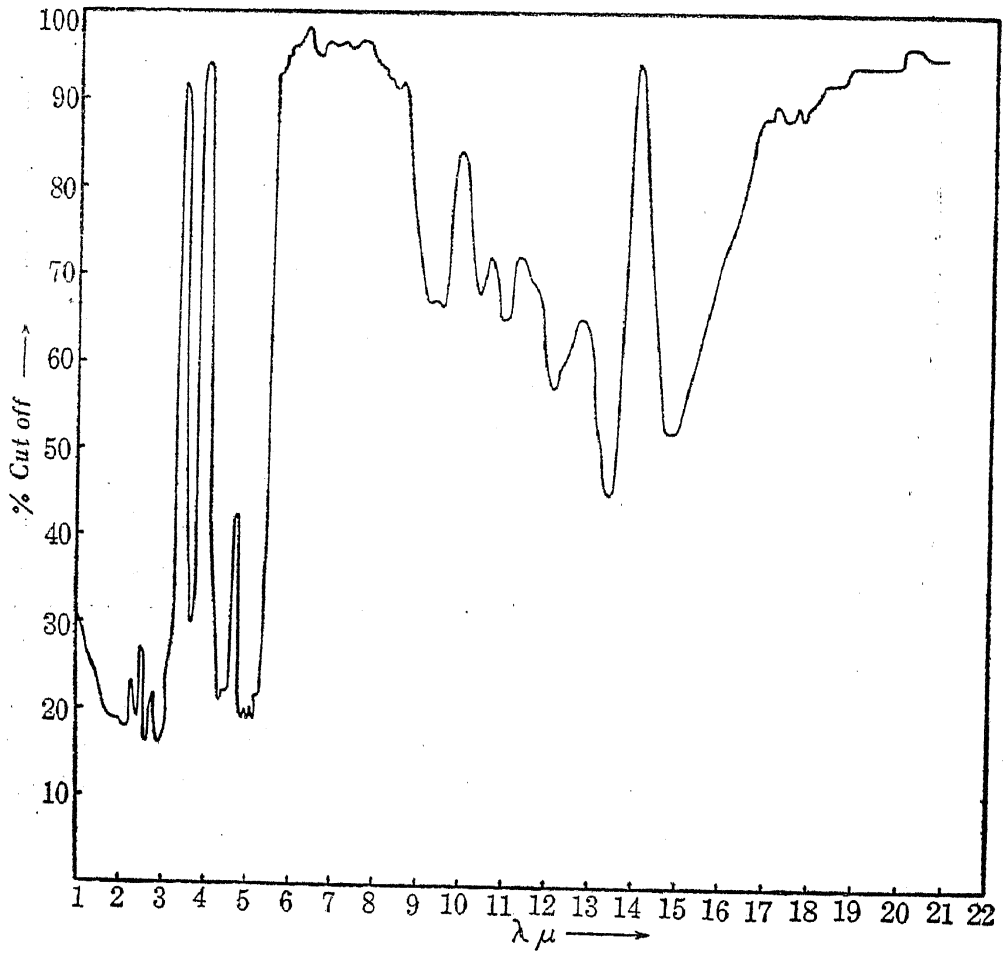

FIG. 3. Infra-red absorption spectrum of calcite (Specimen II).

Special attention may be drawn here to the remarkable sharpness of the harmonics both in calcite and sodium nitrate.

The depolarisation studies of Raman lines with directional excitation with polarised and unpolarised light, and the polarisation of the infra-red absorption bands, enable one to find out and classify the different fundamental oscillations. In Table II we give the Raman active and infra-red active frequencies of sodium nitrate.

TABLE II. *Sodium nitrate*

Raman active*	Infra-red active
ν_1 (A_1) : 1068 cm.$^{-1}$	ν_4 (B_1) : 845 cm.$^{-1}$
ν_2 (E_2) : 720 ,,	ν_5 (E_1) : 725 ,,
ν_3 (E_2) : 1385 ,,	ν_6 (E_1) : 1385 ,,
L_6 (E_2) : 98 ,,	L_1 (B_1) : 71 ,,
L_7 (E_2) : 185 ,,	L_2 (B_1) : 217 ,,
	L_3 (E_1) : 71 ,,
	L_4 (E_1) : 133 ,,
	L_5 (E_1) : 217 ,,

Note.—The Raman active frequencies are those actually observed, while infra-red frequencies are derived from the reststrahlen data for the remote frequencies and from the present studies for the nearer ones.

Similarly we give the frequencies for calcite in Table III.

TABLE III. *Calcite*

Raman active†	Infra-red active
ν_1 (A_1) : 1086 cm.$^{-1}$	ν_4 (B_1) : 885 cm.$^{-1}$
ν_2 (E_2) : 712 ,,	ν_5 (E_1) : 706 ,,
ν_3 (E_2) : 1434 ,,	ν_6 (E_1) : 1484 ,,
L_6 (E_2) : 156 ,,	L_1 (B_1) : 106 ,,
L_7 (E_2) : 284 ,,	L_2 (B_1) : 357 ,,
	L_3 (E_1) : 106 ,,
	L_4 (E_1) : 182 ,,
	L_5 (E_1) : 330 ,,

* T. M. K. Nedungadi[5]; † Bhagavantam[6]

Note.—See remarks made under Table II.

Schæfer and his co-workers[3] gave a detailed analysis of their infra-red absorption and reflexion data for calcite. Their assignments were based on the assumption of a free carbonate ion. However, as we have seen above, the normal modes of the free ion (carbonate and nitrate) split and increase in number, in the crystalline state; this as well as the selection rules governing them are found to be verified experimentally. Hence, in this paper, the assignments are made according to selection rules appropriate to the crystal.

Besides these internal frequencies, there are low frequency lattice frequencies characteristic of the crystal structure. Though these frequencies lie beyond the range studied to be observed as fundamentals, we may expect harmonics of the lattice frequencies, and combinations and differences between internal frequencies and lattice frequencies, when permitted by the selection rules.

In giving the assignments to the observed absorption bands, the following principles are to be borne in mind. A difference band is observed only if the corresponding summation also occurs. Though the combination between high frequency internal vibrations are likely to occur, the possibility of difference bands between them can be ruled out. The polarisation character of the vibration must be considered while giving the assignments to the different absorption bands.

In the light of these facts, the interpretation of the absorption data has been given in Tables IV and V. In the short wavelengths ($\lambda < 6\,\mu$), Schæfer and his collaborators have further resolved some of the absorption bands using rock-salt and quartz optics. Using a very thick specimen (2 cm. thick $\perp$ to optic axis), and quartz optics, Plyler[7] was able to record some absorption bands for calcite in the range $1\,\mu$ to $3\,\mu$. The data of these workers as well as those obtained in this work, are used in the following tables. Following the above considerations, it has been possible to give proper assignments to almost all the observed absorption bands and from Tables IV and V, we see that the assignments are unique in most cases. It is interesting to note that many of the absorption bands can be only explained as combinations (or differences) between internal and external vibrations and some as harmonics of external vibrations alone.

In conclusion, the author wishes to express his thanks to Prof. Sir C. V. Raman, F.R.S., N.L., for his keen interest and guidance and to the Investigator-in-charge, C.S.I.R. Radiation Scheme, Poona, for his permission to use the infra-red spectrophotometer.

3. Discussion of the Results

Sodium nitrate and calcite have the same crystal structure, their space group being D_{3d}^6 with two molecules per unit cell. Bhagavantam and Venkatarayudu[4] have shown that for these cases the number of modes of vibrations and the selection rules with respect to their infra-red and Raman activity are as given in Table I.

TABLE I

Class	Total No.	Internal	External R.	External T.	Translations	R.	I.R.
A_1	1	1	0	0	0	a*	ia*
A_2	3	1	1	1	0	ia	ia
B_1	4	1	1	1	1	ia	a
B_2	2	1	0	1	0	ia	ia
E_1	6	2	1	2	1	ia	a
E_2	4	2	1	1	0	a	ia

* *a* = Active; *ia* = Inactive

Thus we see that there are three internal frequencies active in infra-red and three active in Raman effect, the two sets being mutually exclusive as a result of the presence of a centre of symmetry. In addition there are two internal and three external frequencies which are inactive in both infra-red and Raman effect. The free carbonate and nitrate ion belong to the point group D_{3h} which has one frequency active in Raman effect only, one active in infra-red only and two active in both. The transformation from free ion to the crystal can be pictured as follows:

Free ion	Crystal	
(A_1) ω_1 (Raman active)	$\rightarrow$ (A_1) ν_1 (Raman active),	(A_2) ν_1' (inactive in both)
(B_1) ω_2 (Infra-red active)	$\rightarrow$ (B_2) ν_4' (inactive in both),	(B_1) ν_4 (I. red active)
(E) ω_3 (active in both)	$\rightarrow$ (E_1) ν_2 (Raman active),	(E_2) ν_5 (,,)
(E) ω_4 (,,)	$\rightarrow$ (E_1) ν_3 (,,),	(E_2) ν_6 (,,)

The extent of this splitting will naturally depend on the strength of the coupling between the two carbonate (or nitrate) ions. As regards the lattice oscillations, we notice that there are two Raman active external vibrations and five infra-red active.

TABLE IV

Sodium Nitrate

Observed		Assignment		Calculated
λμ	cm.$^{-1}$	Combination	Type	cm.$^{-1}$
2·3	4348	$\nu_3+\nu_4+\nu_5+\nu_6$	$B_1+B_2+3E_1$	4340
2·42	4132	$3\nu_6$, $2\nu_3+\nu_6$	$B_1+B_2+E_1$, $B_1+B_2+2E_1$	4155
2·45	4082	——		——
2·61	3831	$\nu_1+\nu_3+\nu_6$	$B_1+B_2+E_1$	3838
2·65	3774	——		——
2·85	3509	$2\nu_3+\nu_5$	$B_1+B_2+2E_1$	3495
2·885	3466	——		——
3·2	3125	——		——
3·325	3008	——		——
3·56	2809			
3·65	2740	$\nu_3+\nu_6$	$B_1+B_2+E_1$	2770
4·10	2439	$\nu_1+\nu_6$	E_1	2453
4·75	2105	$\nu_2+\nu_6$	$B_1+B_2+E_1$	2105
		$\nu_3+\nu_5$	,,	2110
4·79	2088	——		——
5·28	1894	——		——
5·6	1786	$\nu_1+\nu_5$	E_1	1793
5·8	1724	——		——
6·35	1575	$\nu_2+\nu_4$	E_1	1565
		ν_6+L_7	$B_1+B_2+E_1$	1570
6·7	1493	ν_6+L_6	$B_1+B_2+E_1$	1483
↓	↓	ν_3+L_3	,,	1456
		$\underline{\underline{\nu_6}}$	E_1	1385
8·0	1250	ν_3-L_3	$B_1+B_2+E_1$	1314
8·3	1205	ν_6-L_6	$B_1+B_2+E_1$	1287
		ν_1+L_4	E_1	1201
9·8	1020	ν_6-L_7	$B_1+B_2+E_1$	1200
↓	↓	ν_4+L_7	E_1	1030
10·6	943			
11·83	845	ν_1-L_4	E_1	935
		$\underline{\underline{\nu_4}}$	B_1	845
13·8	725	$\underline{\underline{\nu_5}}$	E_1	725
15·0	667	ν_4-L_7	E_1	660
↓	↓			
15·3	654			
18	556	Harmonics of lattice frequencies		
↓	↓			
?	?			

TABLE IV

Sodium Nitrate

Observed		Assignment		Calculated
$\lambda\mu$	cm.$^{-1}$	Combination	Type	cm.$^{-1}$
2·3	4348	$\nu_3+\nu_4+\nu_5+\nu_6$	$B_1+B_2+3E_1$	4340
2·42	4132	$3\nu_6$, $2\nu_3+\nu_6$	$B_1+B_2+E_1$, $B_1+B_2+2E_1$	4155
2·45	4082	——		
2·61	3831	$\nu_1+\nu_3+\nu_6$	$B_1+B_2+E_1$	3838
2·65	3774	——		
2·85	3509	$2\nu_3+\nu_5$	$B_1+B_2+2E_1$	3495
2·885	3466	——		
3·2	3125	——		
3·325	3008	——		
3·56	2809	$\nu_3+\nu_6$	$B_1+B_2+E_1$	2770
3·65	2740			
4·10	2439	$\nu_1+\nu_6$	E_1	2463
4·75	2105	$\nu_2+\nu_6$	$B_1+B_2+E_1$	2105
		$\nu_3+\nu_5$	,,	2110
4·79	2088	——		
5·28	1894	——		
5·6	1786	$\nu_1+\nu_5$	E_1	1793
5·8	1724	——		
6·35	1575	$\nu_2+\nu_4$	E_1	1565
		ν_6+L_7	$B_1+B_2+E_1$	1570
6·7	1493	ν_6+L_6	$B_1+B_2+E_1$	1483
↓	↓	ν_3+L_3	,,	1456
		$\underline{\nu_6}$	E_1	1385
8·0	1250	ν_3-L_3	$B_1+B_2+E_1$	1314
8·3	1205	ν_6-L_6	$B_1+B_2+E_1$	1287
		ν_1+L_4	E_1	1201
9·8	1020	ν_6-L_7	$B_1+B_2+E_1$	1200
↓	↓	ν_4+L_7	E_1	1030
10·6	943			
11·83	845	ν_1-L_4	E_1	935
		$\underline{\nu_4}$	B_1	845
13·8	725			
		$\underline{\nu_5}$	E_1	725
15·0	667	ν_4-L_7	E_1	660
↓	↓			
15·3	654			
18	556	Harmonics of lattice frequencies		
↓	↓			
?	?			

TABLE V

Calcite

Observed λ	[illegible]	Polarization	Assignment: Combination	Assignment: Type	Calculated cm^{-1}
[illegible]	[illegible]	[illegible]	[illegible]	$B_1 + B_2 + 2E_1$	5287
[illegible]	[illegible]	[illegible]	[illegible]	$B_1 + B_2 + 3E_1$	5008
[illegible]	[illegible]	[illegible]	[illegible]	$B_1 + B_2 + 3E_1$	4509
[illegible]	[illegible]	[illegible]	[illegible]	$B_1 + B_2 + 2E_1$	4352
[illegible]	[illegible]	[illegible]	[illegible]	$B_1 + B_2 + E_1$	4317
[illegible]	[illegible]	[illegible]	[illegible]	$B_1 + B_2 + E_1$	4004
[illegible]	[illegible]	[illegible]	[illegible]	E_1	3656
[illegible]	[illegible]	[illegible]	[illegible]	$B_1 + B_2 + 2E_1$	3574
[illegible]	[illegible]	[illegible]	[illegible]	$B_1 + B_2 + E_1$	3282
[illegible]	[illegible]	[illegible]	[illegible]	$B_1 + B_2 + E_1$	3226
[illegible]	[illegible]	[illegible]	[illegible]	E_1	3057
[illegible]	[illegible]	[illegible]	[illegible]	$B_1 + B_2 + E_1$	2918
[illegible]	[illegible]	[illegible]	[illegible]	B_2	2655
[illegible]	[illegible]	[illegible]	[illegible]	E_1	2570
[illegible]	[illegible]	[illegible]	[illegible]	$B_1 + B_2 + E_1$	2196
[illegible]	[illegible]	[illegible]	[illegible]	$B_1 + B_2 + E_1$	2140
[illegible]	[illegible]	[illegible]	[illegible]	B_2	1871
[illegible]	[illegible]	[illegible]	[illegible]	E_1	1797
[illegible]	[illegible]	[illegible]	[illegible]	E_1	1791
[illegible]	[illegible]	[illegible]	[illegible]	$B_1 + B_2 + E_1$	1768
[illegible]	[illegible]	[illegible]	[illegible]	E_1	1592
[illegible]	[illegible]	[illegible]	[illegible]	E_1	1464
[illegible]	[illegible]	[illegible]	[illegible]	$B_1 + B_2 + E_1$	1418
[illegible]	[illegible]	[illegible]	[illegible]	E_1	1192
[illegible]	[illegible]	[illegible]	[illegible]	E_1	1165
[illegible]	[illegible]	[illegible]	[illegible]	E_1	1077
[illegible]	[illegible]	[illegible]	[illegible]	$B_1 + B_2 + E_1$	990
[illegible]	[illegible]	[illegible]	[illegible]	E_1	960
[illegible]	945	[illegible]	[illegible]	$B_1 + B_2 + E_1$	906
[illegible]	[illegible]	[illegible]	[illegible]	$E_1 + E_1$	923
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	885
[illegible]	[illegible]	[illegible]	[illegible]	$B_1 + B_2 + 2E_1$	766
[illegible]	[illegible]	[illegible]	[illegible]	$B_1 + B_2 + 3E_1$	720
[illegible]	[illegible]	[illegible]	[illegible]	E_1	706

[illegible]

[illegible] — [illegible], [illegible] — [illegible], [illegible] — cleavage

TABLE IV

Sodium Nitrate

Observed		Assignment
λμ	cm.$^{-1}$	Combination
2·3	4348	$\nu_3+\nu_4+\nu_5+\nu_6$
2·42	4132	$3\nu_6,\ 2\nu_3+\nu_6$
2·45	4082	
2·61	3831	$\nu_1+\nu_3+\nu_6$
2·65	3774	
2·85	3509	$2\nu_3+\nu_5$
2·885	3466	
3·2	3125	
3·325	3008	
3·56	2809	
3·65	2740	$\nu_3+\nu_6$
4·10	2439	$\nu_1+\nu_6$
4·75	2105	$\nu_2+\nu_6$ / $\nu_3+\nu_5$
4·79	2088	
5·28	1894	
5·6	1786	
5·8	1724	$\nu_1+\nu_5$
6·35	1575	
6·7	1493	$\nu_2+\nu_4$ / ν_6+L_7 / ν_6+L_6 / ν_3+L_3 / ν_6
↓	↓	
8·0	1250	ν_3-L_3 / ν_6-L_6
8·3	1205	ν_1+L_4 / ν_6-L_7
9·8	1020	ν_4+L_7
↓	↓	
10·6	943	
11·83	845	ν_1-L_4 / ν_4
13·8	725	ν_5
15·0	667	
↓	↓	
15·3	654	ν_4-L_7
18	556	
↓	↓	
?	?	Harmonics of lattice frequencies

SUMMARY

The infra-red absorption spectra of sodium nitrate and calcite crystals have been studied in the range 1 μ to 22 μ with a Beckman infra-red spectrophotometer, using three different thicknesses of a cleavage section in each case. The thinner plates exhibit the structure of the more intense absorption bands while the thicker ones show their harmonics as well as the weaker bands very clearly. The remarkable sharpness of the harmonics is a noteworthy feature. Much new detail has been observed with sodium nitrate in the region of wavelength greater than 8 μ. A strong absorption in the region beyond 17 μ has been found in both crystals. This is ascribable to harmonics of lattice oscillations. The entire body of data is satisfactorily explained in terms of the normal modes of vibration jointly of the two units ($NaNO_3$ or $CaCO_3$) contained in the unit cell of the crystal lattice.

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