

RAMAN SPECTRA OF THE SECOND ORDER IN CRYSTALS

Part I: Calcite

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1. INTRODUCTION

The Importance of the Second Order Raman Effect.—It is well known that in the Raman spectra of certain substances, for example BF_3 , CCl_4 , etc., a few fainter lines are recorded, the frequency shifts of which cannot be identified with fundamental vibration frequencies of the molecule. These shifts have therefore been sought to be explained as octaves or combinations of the fundamental vibration frequencies. From theoretical considerations, Placzek (1934) showed that the appearance of the first overtone of every normal oscillation of a molecule is allowed in the Raman effect irrespective of whether it is permitted or forbidden as a fundamental. On the assumption that the molecule is a linear harmonic oscillator, Placzek attributed the appearance of overtone lines to the fact that the variations of optical polarisability are not directly proportional to the displacements, and hence the second order derivative of the polarisability with respect to the normal coordinate cannot be neglected. Later, Bhagavantam (1939) showed that even if the second order term was neglected, overtone lines would still appear with a finite intensity on account of the fact that all molecules should really be treated as harmonic oscillators. He calculated the relative intensities of the fundamental and overtone Raman lines for a few diatomic molecules. Even after taking into consideration the anharmonicity and the finite value of the second order derivative of polarisability, the theory shows that the overtone and combinational lines are ordinarily very weak compared with the fundamentals. Hence to record them the use of intense sources and of long exposures is necessary. The extra effort is, however, worth while since the knowledge of the frequency shifts and of the intensities with which these lines are recorded, gives us valuable additional information regarding the dynamical and optical properties of the molecules.

Precisely the same considerations that are detailed above apply also in the case of crystals. There is, however, a further interest attaching to the

study of the second order spectra of crystals. According to the Raman dynamics of crystal lattices, (Raman, 1943) every crystal has in addition to the $(3p - 3)$ modes of internal oscillations of the group of p non-equivalent atoms contained in the unit cell, $21p$ more modes of oscillation of the lattice in which the equivalent atoms in adjacent cells vibrate in opposite phases. By their very nature, these $21p$ modes are inactive as fundamentals in light-scattering, and hence they can only manifest themselves as octaves or combinations in the second order Raman effect.

Technique of Study.—As already remarked, it is essential to employ a monochromatic light source which is very intense for recording the second order Raman frequency shifts. It is also of great importance that there should be no continuous spectrum accompanying the same. This is secured by using the 2536.5 A.U. mercury resonance radiation from a water-cooled magnet-controlled quartz arc. The enormously increased scattering power of the resonance radiation arising from its exceptional intensity as compared with the other mercury radiations and from the λ^{-4} law has made it an ideal source for Raman effect studies in the case of crystals that are transparent to the ultra-violet and do not get coloured by prolonged exposure to this radiation. The 2536.5 A.U. radiation from the light scattered by the medium is effectively suppressed before its entry into the spectrograph by absorption in a column of mercury vapour, as otherwise the photographic plate would be fogged. This makes it possible to record faint Raman lines with small frequency shifts on a clear background. Rasetti (1929) was the first to use this technique for the study of the Raman effect in gases and crystals. He did not, however, push the technique to the limit of its usefulness. The power of the Rasetti technique can be judged from the fact that by employing the same the author (Krishnan, 1944) succeeded in recording the Raman spectrum of the second order in diamond and obtained results affording a direct experimental verification of the predictions of the Raman theory of crystal dynamics.

Using the technique described in the previous paragraph, a systematic investigation of the Raman spectra of the second order in various crystals has been undertaken. This paper which is first of a series deals with the results obtained with calcite together with a brief review of the previous work on the Raman effect in calcite.

2. PREVIOUS WORK ON CALCITE

Next to quartz, calcite has been the crystal most frequently examined in Raman effect studies. Most of the earlier work on the subject was confined to the cataloguing the frequency shifts of the lines and estimating their

relative intensities, viz., Landsberg and Mandelstam (1928), Wood (1928), Kimura and Uchida (1928), Krishnan (1929), Nisi (1929, 1932), Schaefer, Matossi and Aderhold (1929, 1930), Venkatesachar and Sibaiya (1930), Rasetti (1931) and Tomaschek (1931). On the whole, seven Raman lines with frequency shifts 155, 221, 282, 709, 1084, 1434 and 1749 cm^{-1} and two anti-Stokes lines corresponding to 155 and 282 cm^{-1} have been reported. The line with frequency shift of 221 cm^{-1} is reported only by a few investigators. The line at 1749 cm^{-1} has been assigned as the overtone of the infra-red active, Raman inactive fundamental frequency at 879 cm^{-1} . So far, this is the only second order Raman line that has been definitely observed in calcite.

Besides measuring the frequency shifts and relative intensities, Kimura and Uchida (1929) studied the variations in intensity of the Raman lines in calcite for various orientations of the crystal. Cabannes (1929, 1933), Daure (1929), Matossi (1930), Cabannes and Osborne (1931) and Michalke (1938) investigated the state of polarisation of the Raman lines using incident unpolarised light for various orientations of the crystal. Miss Osborne (1932), Bhagavantam (1939, 1940) and Bhagavantam and Rao (1940) on the other hand, made a detailed study of the relative intensities and depolarisation of the Raman lines of calcite for various orientations of the optic axis and the important result emerging out of these investigations is the reciprocal behaviour of the lattice oscillations on the one hand and the total symmetric oscillation on the other. Bhagavantam has given a satisfactory explanation of the results by studying in detail the character table, Bhagavantam and Venkatarayudu (1939), and the selection rules, Bhagavantam (1941), for calcite.

The influence of temperature on the intensity, frequency shift and width of the Raman lines in calcite, has been studied by Ornstein and Went (1935) over the range of temperature from 90°K to 423° K, by Kopcewicz (1937) over the range from 293°K, to 683° K, and by Venkateswarlu (1942) from 305° K to 493° K. The main results obtained by them can be summarised in the following words. The ratio of the intensities of the Stokes to the anti-Stokes line is found to obey the modified Boltzmann formula throughout the range of temperature investigated. There is a decrease of intensity with increase of temperature which is more rapid in the case of the low frequency or lattice lines than for internal lines corresponding to the oscillations of the CO_3 group. The lattice lines with frequency shifts 155 and 282 cm^{-1} exhibit marked shifts towards the exciting line and an appreciable broadening with increase of temperature the width being proportional to

the square root of the absolute temperature, whereas the lines due to the internal oscillations and especially the symmetric oscillation with frequency shift 1084 cm.^{-1} are practically unaffected by variations of temperature over the range investigated.

Some miscellaneous investigations have also been reported in the literature concerning the Raman effect in calcite. Embirikos (1930) reported that the frequencies of the CO_3 group are higher in the calcite crystal than in solution of carbonates. A comparative study of the Raman spectra of calcite and aragonite was made by Bhagavantam (1931) who concluded that the CO_3 group retained the same structure in both. A similar comparative study of the Raman spectra of calcite and sodium nitrate without reference to directional excitation was made by Cabannes and Canals (1931) and more recently by Sundara Rama Rao (1939). Ornstein and Went (1935) investigated the dependence of the intensity of Raman lines in calcite on the wavelength of the exciting line. They reported that the increase in intensity of the lines was more rapid than to be expected on the basis of the fourth power law as the wavelength of the exciting line was decreased.

By adopting a set of seven force constants, four of which pertain to the forces of the free ion and the remaining three to the inter-ionic forces in the crystal and giving appropriate numerical values for the same, Bhagavantam and Sundara Rama Rao (1944) have evaluated the frequencies of oscillation of calcite and compared the same with those observed in Raman effect and infra-red absorption.

3. DETAILS OF THE EXPERIMENT

In all the earlier investigations on the Raman effect in calcite except the one by Rasetti (1931), the 4046 A.U. and 4358 A.U. radiations of the mercury arc were used for exciting the Raman spectrum. The technique of using these radiations as exciter has already been exploited to the limit of its utility and it is rather unlikely that any further useful information regarding the second order Raman spectrum of calcite would be got by adopting the same. In the present investigation, the well-known Rasetti technique which consisted in the use of the 2536.5 A.U. resonance radiation, has been employed.

The details of the construction and the running of the quartz mercury arc specially designed for the emission of the resonance radiation with an exceptional intensity have already been described by the author in an earlier paper (Krishnan, 1944). A transparent crystal of calcite $2'' \times 2'' \times 1\frac{1}{4}''$ and a smaller specimen of size $\frac{3}{4}'' \times \frac{3}{4}'' \times \frac{3}{4}''$ were chosen for the present

investigation from Sir C. V. Raman's personal collection. The specimen was usually mounted with one of its flat faces in front of the most intense portion of the arc. The transversely scattered light was taken through one of its edges and was condensed on the slit of a quartz spectrograph. A column of mercury vapour was introduced in the path of the scattered light to suppress the 2536.5 A.U. line. The crystal was cooled by means of a fan.

Two different instruments were used for photographing the Raman spectrum of calcite; (1) A Hilger E1 quartz spectrograph which has a dispersion of about 50 wavenumbers/mm. in the 2536 region; and (2) a Hilger E3 quartz spectrograph which is relatively fast and has a dispersion of about $140 \text{ cm.}^{-1}/\text{mm.}$ in the same region. The higher dispersion instrument was used in order to measure the frequency shifts and widths of the principal Raman lines very accurately. Using a very fine slit (0.01 mm.) and the smaller crystal, exposures of the order of 24 hours were given to photograph the Raman spectrum of the first order with reasonable intensity.

The smaller instrument was used to get an intense photograph of the Raman spectrum of calcite showing the second order lines. With this instrument and using the bigger crystal, the first order Raman lines could be photographed in a couple of minutes using a slit width of 0.03 mm. Exposures varying from 12 to 48 hours were given to get an intense spectrogram.

The negatives were measured under a Hilger cross-slide micrometer.

4. RESULTS

First Order Raman Spectrum.—The frequency shifts together with the widths of the first order or fundamental Raman lines as measured from the spectrogram taken with the high dispersion instrument are given in Table I. The values reported earlier by Cabannes and Osborne and by Rasetti are also included in the same table.

TABLE I. *Raman Spectrum of the First Order in Calcite*

	Lattice Oscillation		Internal Oscillation		
	E ₂	E ₂	E ₂	A ₁	E ₂
Author ..	Cm. ⁻¹ 155.5 (7.5) [8]	Cm. ⁻¹ 283.9 (10.5) [15]	Cm. ⁻¹ 711.8 (3.0) [2]	Cm. ⁻¹ 1085.6 (5.5) [20]	Cm. ⁻¹ 1433.8 (3.5) [5]
Cabannes and Osborne ..	157.5	283.8	712.1	1087.3	1436.6
Rasetti ..	155.7	283	713.8	1087.6	1436.7

The figures enclosed in () represent the widths of the lines in wave numbers, while those given in square brackets represent the relative peak intensities of the lines on an arbitrary scale. As the slit width used was very narrow and the spectrogram was very lightly exposed, the widths of the lines given in Table I are considered genuine and not due to photographic broadening. The temperature of the crystal which was slightly above the room temperature, would have wandered by five degrees either way. The finite width of the lines may be responsible for the discrepancies in the values of the frequency shifts given by the author and those reported by the earlier investigators. The anti-Stokes Raman lines corresponding to 155.5, 283.8, 711.8 and 1085.6 cm^{-1} have been clearly recorded in the spectrum of the scattered light.

Second Order Spectrum.—A heavily exposed spectrogram taken with the E3 spectrograph is reproduced in Fig. 1 together with a photograph of the direct arc. The microphotometric record of the same is reproduced in Fig. 2. The second-order Raman lines are clearly seen on the microphotometric record. They can also be identified on the reproduced photograph. Their positions as well as the frequency shifts have been marked in both the figures. In addition to the five intense principal lines belonging to the first order spectrum, there are not less than eleven Raman lines of comparatively feeble intensity belonging to the second order spectrum. Of these, nine lines have been recorded for the first time. The frequency shifts of these lines have been measured and are listed in Table II. The line with the frequency shift of 1750 cm^{-1} should naturally be the most intense one, as is evident from the fact that most of the earlier investigators who worked in the visible region have invariably recorded a line with the same frequency shift. With the 2536.5 A.U. excitation, this modified line falls in the region of the Hg triplet at 2652.0, 2653.7 and 2655.1 A.U. A comparative study of the two depressions in the microphotometric record of the mercury triplet with the corresponding ones of the direct arc shows that the Raman line actually falls in the region between the Hg lines at 2653.7 and 2655.1 A.U. The frequency shifts of this line has therefore been taken as 1750 cm^{-1} , this being the mean of the separations in wave-number of the two mercury lines from the exciting line, namely 2536.5 A.U.

The principal Raman line at 1085.6 cm^{-1} corresponding to the total symmetric oscillation has a companion to the left with a frequency shift of 1065 cm^{-1} . It is too intense and too near the main line to be assigned as arising from the total symmetric oscillation excited by the mercury line λ 2534.8 A.U.

The lines with frequency shifts 2147 and 2172.5 cm^{-1} form a close doublet and come next in order of intensity. They stand out prominently in the spectrum. The former is comparatively broad and shows a subsidiary maximum at about 2130 cm^{-1} , while the latter is sharp.

The existence of a feeble line with a frequency shift of 221 cm^{-1} was reported by some of the earlier investigators. This has been confirmed by the author. The Raman bands with mean frequency shifts 2220 cm^{-1} and 2310 cm^{-1} are rather broad and diffuse. The former one has a width of about 40 cm^{-1} with the peak intensity displaced towards the left, while the latter has a width of 30 wavenumbers and is more or less of uniform intensity throughout.

The Raman line at 864 cm^{-1} unfortunately falls close to a faint mercury line. A critical examination of the two photographs reproduced in Fig. 1, shows that in the spectrum of the scattered light, the line in this region appears to be broad, while in the mercury arc spectrum it is definitely sharper. The microphotometric record shows the line at 864 cm^{-1} clearly resolved from the faint mercury line on the longer wavelength side.

The remaining three second order Raman lines are weak in intensity. They are easily discernible in the microphotometric record.

The heavily exposed spectrum of the scattered light in calcite shows the presence of a feeble continuum on either side of the exciting line and extending up to about 300 cm^{-1} from it. The intensity of the continuum at any point is definitely less than one hundredth part of the intensity of the weakest of the first order Raman lines.

It will be noticed from the microphotometric records reproduced in Fig. 2 that the intensity of the 2536.5 A.U. line relative to that of its companion at 2534.8 A. U. is greater in the spectrum of the scattered light than in that of the direct arc, although the same column of mercury vapour was used in both cases. This can be explained as due to the fact that in the so-called unmodified scattered radiation there are also Brillouin components which arise from the reflection of the incident radiation by the standing elastic waves inside the crystal. These components have a finite though small wave number separation from the unmodified line and are hence not absorbed by the column of mercury vapour. By using instruments with high resolving power, it should be possible to record the Brillouin components clearly separated from the unmodified line.

Close to and on the left side of the mercury line at 2675.0 A. U. there is a Raman line. As the separation of this line from the strongest of the

TABLE II. *Second order Raman spectrum of calcite*

Serial No.	Measured frequency shifts in cm^{-1}	Assignment	Calculated frequency shifts in cm^{-1}	Observed frequency shifts in infra-red absorption
1	221	$2 E_1 (l)$	106 + 106	..
2	864	$E_2 (i) + E_2 (l)$	712 + 156	..
3	1065	$B_1 (l) + E_1 (i)$	357 + 706	..
4	1360	$A_1 + E_2 (l)$	1086 + 284	1358
5	1583	$B_1 (i) + E_1 (l)$	879 + 706	1586
6	1750	$2 B_1 (i)$	879 + 879	1735
	(2130)*	$E_1 (i) + E_1 (i)$	706 + 1430	
7	2147	$E_2 (i) + E_2 (i)$	712 + 1434	2155
8	2172.5	$2 A_1$	1086 + 1086	..
9	2220	$B_1 (i) + E_1 (i)$	879 + 1350	2220
10	2310	$B_1 (i) + E_1 (i)$	879 + 1430	..
11	2500	$A_1 + E_2 (i)$	1086 + 1434	2545

(i) signifies internal oscillation and (l) lattice oscillation. * The figure given in brackets represents the frequency shift of the subsidiary maximum of the broad line at 2147 cm^{-1}

mercury triplet in the 2650 A. U. region corresponds to the frequency shift of the stronger of the two lattice lines, it is assigned, as a first order Raman shift 284 cm^{-1} excited by mercury line $\lambda 2652.0$ A. U.

Rasetti (1931) had reported the existence of a group of lines with frequency shifts from 7270.3 to 7455.5 cm^{-1} for calcite. In the spectrum of the mercury arc which was kept continuously evacuated by an ordinary Cenco pump, there were a host of nitrogen lines falling approximately in the same region and hence it was not possible to prove or disprove the existence of the lines with these high frequency shifts. The point will be examined in detail later.

5. DISCUSSION OF RESULTS

A complete group-theoretical analysis of the normal modes of oscillation of the calcite lattice has been carried out by Bhagavantam and Venkatarayudu (1939), taking the unit cell containing two molecules of CaCO_3 as the repeating unit in the dynamic crystal. The main results obtained by them are summarised in Table III. The four distinct normal modes of the CO_3 ion in solution splits up into eight internal modes in the crystal. The doubling arises from the fact that the basis contains more than one free ion. The distribution of the eight modes among the various classes is shown in Table III.

TABLE III

Class	n_l	n_i	Raman	Infra-red	Observed frequencies	
					Lattice cm^{-1}	Internal cm^{-1}
A_1	..	0	1	P	f	1086
A_2	..	2	1	f	f	
B_1	..	2	1	f	P	106, 357
B_2	..	1	1	f	f	879
E_1	..	3	2	f	P	106, 182, 330
E_2	..	2	2	P	f	706, 1350-1430 712, 1434

n_l = No. of distinct modes belonging to lattice oscillations. n_i No. of distinct modes of belonging to internal oscillations. P = Permitted to appear. f = forbidden.

The notations have the usual significance as understood in group theoretical analysis. There are on the whole ten lattice frequencies, five single and five doubly degenerate. They are also listed in the table. The analysis shows that those oscillations belonging to the internal group or to the lattice group that are active in the Raman effect, should be inactive in infra-red absorption and *vice versa*. Consequently there will not be any exact coincidence between the Raman and infra-red absorption frequencies. The infra-red absorption and reflection of calcite has been studied by numerous investigators (refer to the Bibliography at the end of the paper) and some of the results are summarised by Schæfer and Matossi (1930). The observed frequencies are 106, 182, 330, and 357 cm^{-1} belonging to lattice group and 706, 879 and 1350-1430 cm^{-1} belonging to the internal group. The observed Raman and infra-red frequencies are classified in Table III.

Applying the usual selection rules, it is easily seen that in the second order Raman spectrum the overtones of all the fundamental frequencies and also the following combinations, namely $A_1 + E_2$, $E_1 + B_1$, any two E_1 s and any 2 E_2 s can appear. Those combinations, one component of which belongs to either class A_2 or B_2 which is inactive in both, are neglected. It should be pointed out that all overtones and combinations that are allowed will not necessarily be recorded in the spectrum as some of them may be too faint to be observed.

On the basis of the above selection rules, satisfactory assignments have been given to most of the lines appearing in the second order Raman spectrum, see Table II. The calculated frequency shifts agree reasonably well with the observed lines. The corresponding combinational frequencies observed in infra-red absorption are also included in Table II for purposes of comparison. The two broad bands with mean frequency shifts of 2220 and 2310 cm^{-1} have been assigned as the combinations of the infra-red

active, Raman inactive fundamental frequency at 879 cm.^{-1} coming under class B_1 , with doublet frequencies reported in infra-red absorption in the region of 7μ coming under class E_1 . The values given for the two frequencies are very varied. I have taken them as 1350 cm.^{-1} and 1430 cm.^{-1} .

It is important to point out that the octaves of the intense lattice lines which appear as fundamentals with frequency shifts 156 and 284 cm.^{-1} do not appear in the Raman spectrum. Only the octaves of the far infra-red reststrahlen frequency of calcite which is at 106 cm.^{-1} and which comes under class B_1 , is recorded as a Raman line at 221 cm.^{-1} in the second order spectrum. The octave of another infra-red frequency at 357 cm.^{-1} which is also coming under class B_1 (lattice) even if present, would fall on the principal Raman line at 712 cm.^{-1} . The extreme feebleness of other second order lattice lines and consequent difficulty in recording the same are to be attributed to the fact that calcite is an ionic crystal, and the changes of polarisability involved in lattice oscillations should necessarily be very small. This explains why none of the $(21p)$ super lattice oscillations that are contemplated on the basis of the Raman dynamics of crystal lattices, in which the atoms in the neighbouring cells vibrate in opposite phases, is recorded either as an octave or as a combination in the second order Raman spectrum.

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6. SUMMARY

The importance of the study of the second order Raman spectra in crystals for getting a deeper insight into dynamical and optical properties of crystals has been pointed out.

The previous work on the Raman effect in calcite has been briefly reviewed.

Using the 2536.5 A.U. mercury resonance radiation, the first and second order Raman spectra of calcite have been photographed. As has already been reported the first order spectrum consists of five lines. The frequency shifts and widths of these have been accurately measured.

The second order spectrum exhibits a series of eleven lines of varying intensity and width. The frequency shifts of these lines are $221, 864, 1065, 1360, 1583, 1750, 2147, 2172.5, 2220, 2310$ and 2500 cm.^{-1} . Some of these appear also in the infra-red absorption spectrum of calcite with very nearly the same frequencies. On the basis of the group theoretical analysis given

by Bhagavantam, the observed second order Raman lines have been assigned as some of the octaves and allowed combinations of the fundamental frequencies of vibration of the calcite lattice.

The existence of Brillouin components along with the unmodified radiation in the light scattered by the crystal of calcite has been demonstrated in a very simple way.

A complete bibliography on the Raman effect and infra-red studies in calcite is also included.

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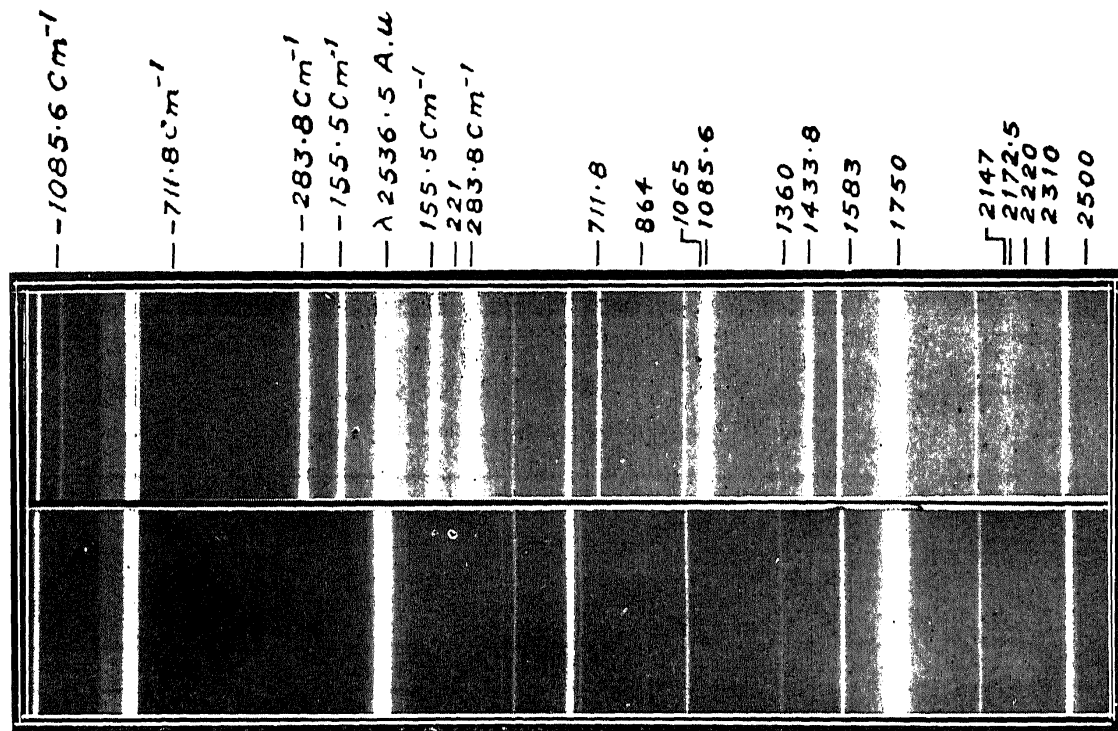
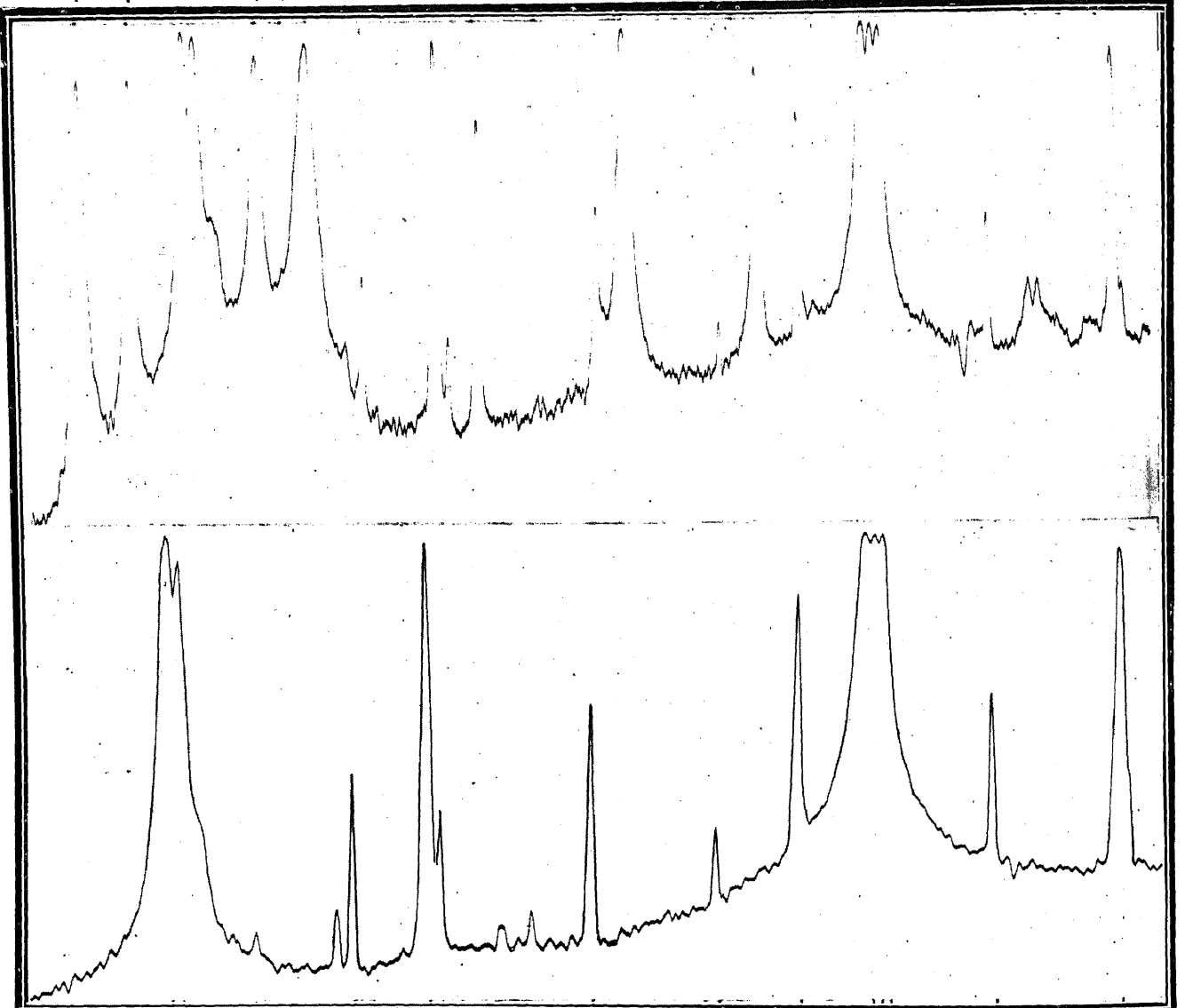


FIG. 1. (a) Raman spectrum of calcite

(b) Mercury spectrum

Raman Lines
 ν in cm^{-1}

-283.8
 -155.5
 -155.5
 -221
 -283.8
 -711.8
 -864
 -1065
 -1085.6
 -1360
 -1433.8
 -1583
 -1750
 -2147
 -2172.5
 -2220
 -2310
 -2500



Hg. Lines
 λ in A.u

2534.8
 2536.5
 2563.9
 2576.3
 2578.4
 2603.2
 2625.2
 2639.9
 2652.0
 2653.7
 2655.1
 2675.0
 2698.9

FIG. 2. Microphotometric records (a) Raman spectrum of calcite
 (b) Mercury spectrum

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