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THE RAMAN SPECTRUM OF CALCITE AND ITS INTERPRETATION

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1. Introduction

The present memoir embodies the results of experimental studies undertaken in the newly built spectroscopic laboratory of the Raman Research Institute. It is also the first report on the results of a programme of research on the Raman spectra of crystals undertaken with a view to obtain a fuller experimental knowledge as well as a deeper theoretical understanding of the phenomena which present themselves in this field. The present memoir concerns itself with the case of calcite. This was, quite naturally, one of the crystals to be investigated by the earliest workers in the field. An extensive literature has therefore accumulated which deals with the Raman spectrum of calcite and its theoretical interpretation. Nevertheless, the present investigation has brought to light several new facts with important theoretical implications.

It appears appropriate in the present memoir to begin with a brief description of the special features of the new laboratory which was designed and built with a view to carrying out investigations in this field of research. It also appears appropriate to give some details of the experimental techniques adopted in the present investigation which have enabled the results described in it to be achieved.

2. The New Spectroscopic Laboratory

The Raman effect being inherently a phenomenon of low intensity, its study usually requires the employment of fast spectrographs and of powerful sources of monochromatic illumination. Even so, it is necessary to give long exposures in order to record the fainter details of the spectra with satisfactory intensity. A serious difficulty in such work is the blurring of the spectral lines noticed with prolonged exposures, arising mainly because of the variations in the temperature of the spectrographs and of the dispersing prisms contained in them. The new laboratory and its equipment were designed with the special aim of eliminating this difficulty as completely as possible.

The new laboratory is a massive structure of granite which faces north and south without any doors or windows on the eastern and western walls. The building contains two large spectrographic rooms, each 30 feet square and 18 feet high, these being separated from each other by a small hall through which they can be entered, by a photometer room and by a dark room for photographic work; entry into the latter can be made through labyrinths connecting them with the spectrographic rooms on either side. Each of the latter is provided with a false roof of thermally insulating material containing apertures which permit of a low-draught ventilation upwards. The windows of the spectrographic rooms face north and south and are set in such a position that no sunlight ever falls on them. Each of the windows is double, the outer one being of glass and the inner of wood. The admission of light and air into the rooms can thus be strictly controlled. With these arrangements, the diurnal variation of temperature within the laboratory was kept at a minimum and the continued operation of mercury lamps within the laboratory did not result in any noticeable fluctuations in temperature.

It was found of advantage to use two spectrographs in the present investigation, both of them being Hilger instruments with quartz prisms and lenses; one of them was the well-known medium size spectrograph of the ordinary or direct type and the other was a large automatic spectrograph of the Littrow type. The smaller instrument was some twenty times as fast as the larger instrument and was therefore to be preferred when the object was to record the fainter details of the spectrum as completely as possible. The larger instrument had a greater resolving power and was therefore more suitable for exhibiting the finer details of the spectrum. However, it suffers from the disadvantage of the so-called " Littrow fog " which sets the limit to the length of exposures which could usefully be given with it. Each spectrograph was placed on a massive teakwood table inside a double-walled box enclosing the instrument completely, the inner walls of the box being of insulating boards and the outer walls of compressed fibre boards impervious to air; the two walls are separated by an air gap. The small aperture through which the slit of the spectrograph was illuminated was closed by a polished plate of quartz. This arrangement successfully prevented any changes in the temperature of the air of the room penetrating through the enclosures into the instrument, so much so that single exposures could be continued as long as desired over several days or even weeks without any blurring of the spectral lines.

3. THE EXPERIMENTAL ARRANGEMENTS

The monochromatic illumination used was the λ 2536·5 resonance radiation of a water-cooled magnet controlled mercury arc in silica, the current being kept well below two amperes. A heavy inductance was introduced in series with the arc to make it stable. It was found much preferable to use, instead of a completely sealed arc, one that was continuously evacuated. It was however necessary to employ an efficient high-speed pump and to run the arc for a sufficient time for the lines due to oxygen and nitrogen of the air to be eliminated before starting an exposure. The water-cooling of the arc was effected internally and only at the mercury pool electrodes, the arrangement being similar to that adopted in the Toronto type of mercury lamps. The most successful type of electrode was one with parallel strands of fine molybdenum wire sealed up by pressure in a narrow tubule of silica and finally closed up by molten lead. The current was led in by copper wires fixed in the lead.

The crystal was illuminated by placing it quite close to the arc, a current of air from a fan being directed against it continuously to prevent it from warming up. The scattered radiations were focussed on the slit of the spectrograph with a quartz lens, suitable apertures being introduced in the path of both incident and scattered radiations to minimise parasitic illumination. Dishes of mercury inside the spectrograph provided enough mercury vapour to filter out the resonance radiation from the scattered light before it reaches the photographic plate. A comparison spectrum of the light of the mercury arc was recorded in each case on the same plate with an exposure sufficient to bring out even the faintest lines.

It should be mentioned that not all crystals of calcite are equally transparent to the λ 2536·5 resonance radiation. The best of the specimens available in the museum of this Institute were used in the present investigation. One of them was a large, flawless and transparent rhomb 3″×2″×2″ purchased some years ago in New York. A smaller specimen presented by Prof. A. Neuhaus of the Mineralogical Institute of Bonn proved to be of excellent quality and was also used in the research. The advantage of using such clear crystals is that the lines of the mercury arc other than the λ 2536·5 appear only feebly and some of them not at all even in strongly exposed spectrograms. Such of the lines as do appear are readily identified by reference to the comparison spectrum of the mercury arc. The possibility of a mercury arc line being mistaken for a Raman shift or *vice versa* is thereby rendered negligible. The distribution of intensity in the Raman lines along their length is usually different from that of the mercury lines and this is a further clue which enables them to be distinguished from each other. The analysis of the spectrograms is further facilitated by the extraordinary intensity of the λ 2536·5 radiation in comparison with that of the other lines of the mercury arc run under the conditions employed in the present investigation. Even with the very long exposures given in order to record the faintest Raman shifts, the other lines of the mercury arc do not give observable Raman shifts except in a very few cases. In particular, it has been noticed that the triplet of mercury lines λ 2652·04, λ 2653·68 and λ 2655·13 as well as the line λ 2576·29 do excite the strongest Raman lines observably. As the positions of these lines are exactly calculable, it is easy to locate and eliminate them.

4. GENERAL DESCRIPTION OF THE RESULTS

Five frequency shifts which expressed in wave-numbers are respectively 155, 282, 712, 1086 and 1436 are the most conspicuous features in the Raman spectrum of calcite and were recognized by the earliest investigators, notably Cabannes, Nisi and Rasetti. The three larger frequency shifts arise from the internal vibrations of the CO_3 groups contained in the crystal, while the two smaller frequency shifts arise from the external vibrations of the CO_3 groups which involve translatory and rotatory oscillations of those groups.

We are concerned in the present paper with the study of the various features which make their appearance in the spectra when the exposures are sufficiently prolonged. These changes are most conveniently exhibited in reproductions by recording the spectra with the maximum exposures practicable and then printing them to different depths. The deeper prints exhibit only the most conspicuous features, while in the lighter prints the fainter details are by comparison strongly emphasized. It is found that the reproductions thus obtained represent approximately the effect of varying the original period of exposure of the spectrogram.

Figure 1 (*a*) in Plate IV is a reproduction of a deep print of a spectrogram recorded with our larger instrument by giving an exposure of 100 hours and using a slit-width of 0·05 mm. Fig. 1 (*b*) in the same Plate is a comparison spectrum of the mercury arc. The five principal Raman lines referred to above and their anti-Stokes components are immediately recognized by comparing the two photographs. Fig. 1 (*c*) in the same Plate is a light print of the same spectrogram. It shows various additional features to which we shall return later. A microphotometer record on the scale 1 : 4 of the same spectrogram is reproduced as Fig. 2 in Plate V.

Figure 3 (*a*) and Fig. 3 (*c*) are respectively deep and light prints of a spectrogram recorded with the smaller instrument giving an exposure of

60 hours and using a slit-width 0·04 mm. Taking into account the greater speed of the smaller instrument, this exposure is roughly ten times greater than that used in recording Figs. 1 (*a*) and 1 (*c*) in Plate IV. Under the conditions of the experiment, an exposure of five minutes was found to be sufficient to record all the five Raman lines. Thus, the spectrum reproduced in the Plate represents an exposure 720 times greater than that needed to record what is ordinarily regarded as the Raman spectrum of calcite. Comparing Fig. 1 (*a*) in Plate IV with Fig. 3 (*c*) in Plate VI, it seems almost incredible that they represent one and the same phenomenon. The heavy exposure and the light printing adopted for Fig. 3 (*c*) have evidently resulted in enormously emphasizing the fainter features of the spectrum, while in Fig. 1 (*a*) they are not observable at all. The transition from one extreme to the other can be traced in the sequence from Fig. 1 (*a*) to Fig. 1 (*c*) in Plate IV and then from Fig. 3 (*a*) to Fig. 3 (*c*) in Plate VI. A microphotometer record of the heavily exposed spectrum on the scale 1 : 8 is reproduced as Fig. 4 in Plate VII.

Amongst the phenomena with which we are concerned in the present paper is one of great interest which appears to have been passed over by the earlier investigators without notice, *viz.*, the transformation of the principal Raman shifts from more or less sharply defined lines as recorded with the minimum exposures into bands covering an appreciable range of wavelengths in the strongly exposed spectra. This feature is clearly noticeable in the spectrograms and microphotometer records reproduced in Plates IV, V, VI and VII. The phenomenon is *not* of instrumental origin or due to photographic halation. This is clear from the fact that it is not exhibited by the mercury arc lines of comparable intensity simultaneously recorded in the spectra. The latter do indeed show the well-known photographic spread resulting from prolonged exposures. But this is relatively small and the edges of the lines remain quite sharp. The difference in the behaviour of the lines of the mercury arc and of the principal Raman shifts can be seen very readily by comparing them in the series of four spectra reproduced in Plates IV and VI. It is also evident from a comparison of the microphotometer records reproduced as Fig. 2 in Plate V and Fig. 4 in Plate VII. While there is hardly any difference in the aspect of the mercury arc lines in these two records, there is an enormous difference in the behaviour of the Raman shifts. Fig. 4 in Plate VII exhibits several features which are scarcely, if at all, noticeable in Fig. 2 of Plate V. These, of course, are the fainter features which are recorded in the spectrum only when long exposures are given. The principal Raman shifts which appear in both records also present very different aspects in them. In the record of the strongly exposed spectrogram they appear broadened out unsymmetrically. This effect is shown by all the five principal Raman shifts but to very different extents. It is only with difficulty observable in the case of the 712 $cm.^{-1}$ shift which might indeed be mistaken for a mercury arc line in this respect. On the other hand, the 1436 $cm.^{-1}$ shift exhibits it very conspicuously. Its unsymmetrical broadening is noticeable even in Fig. 2 of Plate V as will be apparent on comparing its profile with those of the mercury arc lines and is very conspicuous in Fig. 4 of Plate VII. The principal Raman shift of 1086 $cm.^{-1}$ shows the effect conspicuously. It is also exhibited by the low-frequency shifts 155 $cm.^{-1}$ and 282 $cm.^{-1}$; the unsymmetrical broadening of these two lines is evident even in the weakly exposed spectrum and in its photometer record, while in the strongly exposed spectra, the broadening is so large that these two frequency shifts as well as their anti-Stokes components seem to run into each other and form an apparently continuous band of illumination.

We may interpret these phenomena by describing them as due to satellite radiations which accompany the principal Raman lines and represent shifts of frequency differing from them by relatively small amounts. The unsymmetrical character of the broadening indicates that the frequency shifts of the satellite radiations are for the most part smaller than those of the Raman lines which they accompany. The intensity of the satellite radiations is of course very small and this is indicated by the very long exposures needed to record them.

5. THE PRINCIPAL RAMAN SHIFT WITH ITS SATELLITES AND OVERTONES

Light is thrown on the nature and origin of the phenomenon referred to above by a critical study of the principal Raman frequency shift of 1086 $cm.^{-1}$ arising from the totally symmetric internal vibrations of the CO_3 ion and the accompaniments of that line. Rasetti in his investigation made with an instrument similar to our smaller spectrograph, observed and reported that the principal frequency shift of 1086 $cm.^{-1}$ is accompanied by a frequency shift of 1067 $cm.^{-1}$ to which he assigned an intensity zero as compared with an intensity fifty for the main line. In the present investigation, it has been noted that the spectrogram recorded with the smaller instrument and a fine slit exhibits, besides the frequency shift of 1067 $cm.^{-1}$ recorded by Rasetti, another and much fainter line clearly resolved from it and further removed from the principal frequency shift. This component has been proved by exact measurement to be the 1086 $cm.^{-1}$ shift excited by radiation of wave-length $\lambda\,2534{\cdot}8$ which appears as a companion of the resonance radiation of wave-length $\lambda\,2536{\cdot}5$. The features referred to above are indicated by inflexions in the microphotometer record on the scale 1 : 8 reproduced as Fig. 4 in Plate VII. But they are seen much more clearly in the microphotometer record on the much larger scale of 1 : 50 reproduced as Fig. 6 in Plate IX. The unsymmetrical broadening of the principal Raman shift is very conspicuously exhibited by that record.

The greater dispersion and resolution of the larger spectrograph used in the present investigation has proved itself invaluable in revealing the true characters of the phenomenon now under consideration. In the spectrogram, obtained with that instrument and reproduced as Fig. 1 (*c*) in Plate IV the features mentioned above are both recognizable. They are however shown far more clearly in the greatly enlarged picture of a part of the same spectrogram reproduced as Fig. 5 (*b*) in Plate VIII. The extreme sharpness and discrete character of the 1067 cm.$^{-1}$ shift is clearly shown in that reproduction. The sharpness of the 1086 cm.$^{-1}$ shift given by the radiation λ 2534·8 of the mercury arc also seen in that picture is noteworthy as it serves to emphasize the real monochromatism of the Raman shift given by crystals as recorded with small exposures. The microphotometer record on the scale 1 : 4 of the same spectrogram reproduced as Fig. 2 exhibits these features recognizably. But a microphotometer record on a much larger scale is needed to disclose the finer features of the phenomenon. Such a record on the scale 1 : 50 is reproduced as Fig. 1 in the text.

The principal peak corresponding to the frequency shift of 1086 cm.$^{-1}$ and the clearly separated subsidiary peak with a shift of 1067 cm.$^{-1}$ are both conspicuous features in the record. Intermediately between these peaks, the photometer curve exhibits two inflexions in its course which correspond to frequency shifts of 1072 cm.$^{-1}$ and 1075 cm.$^{-1}$ respectively. The reality of these inflexions has been confirmed by taking microphotometer records at different points along the same spectral line and also with spectrograms recorded with different exposures.

The results of the investigation may thus be stated as follows: The principal Raman frequency shift of 1086 cm.$^{-1}$ is accompanied by *three* satellites having frequency shifts of 1067 cm.$^{-1}$, 1072 cm.$^{-1}$ and 1075 cm.$^{-1}$ respectively. The reason why the two latter are less conspicuous than the first is evidently because that they are closer to the principal shift recorded with much greater intensity and are therefore less clearly resolved from it than the component differing from it in frequency to the greatest extent. Taking the observed facts at their face value, we may explain the appearance of these three satellites as due to independent discrete normal modes of vibration of the structure of the crystal, which, though Raman-inactive in the first approximation, are rendered feebly active by reason of their proximity in frequency to the strongly active mode of frequency 1086 cm.$^{-1}$ and presumably also by reason of their possessing certain features of resemblance to it in their respective modes of vibration.

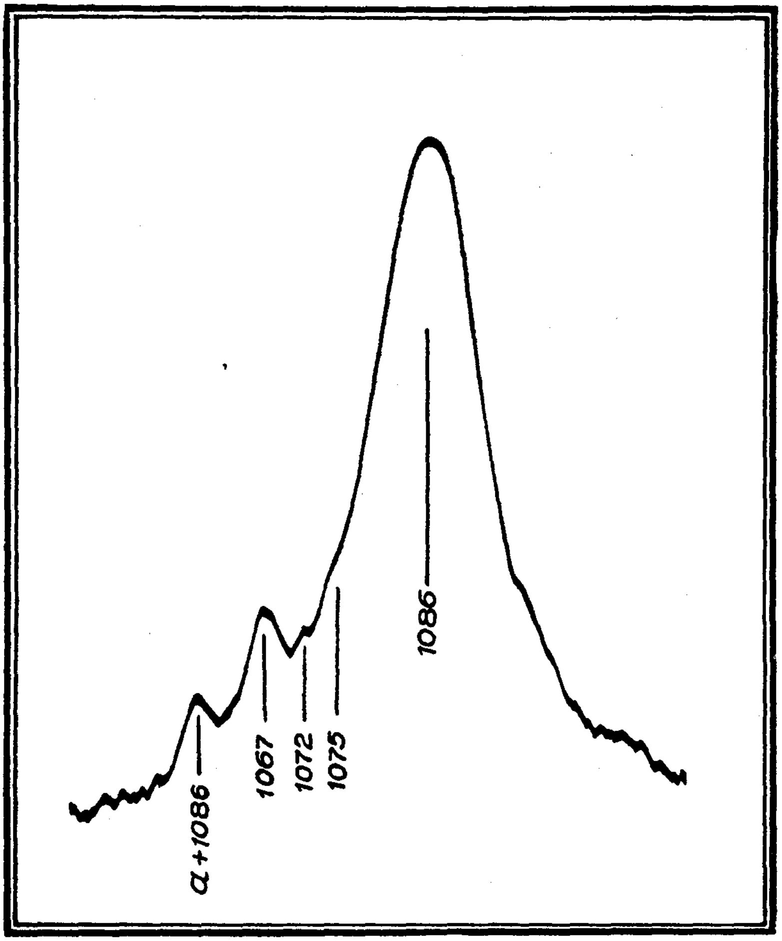

FIG. 1. Enlarged microphotometer record showing the 1086 cm.$^{-1}$ line and its satellites.

The foregoing conclusions receive striking support in the features observable in the strongly exposed Raman spectra in the vicinity of double the frequency shifts under consideration, *viz.*, in the region displaced from the exciting radiation by shifts lying between the range 2172 cm.$^{-1}$ and 2134 cm.$^{-1}$ Shifts of this magnitude would be recorded near the end of the reproduced spectrograms furthest from the exciting radiation. They can be seen very clearly not far from the last mercury line in Fig. 3 (*a*) in Plate VI. We observe a *sharply defined line* with a frequency shift of 2173 cm.^{-1}; and separated from this by a dark region appears a diffuse line of comparable intensity having its peak of intensity at 2148 cm.^{-1} These features are also shown in the spectrum as recorded with the larger instrument and reproduced as Fig. 1 (*c*) in Plate IV. The frequency shift of 2173 cm.^{-1} here appears as a needle-sharp line in striking contrast with the diffuseness of the line clearly separated from it and having its maximum of intensity at a frequency shift of 2148 cm.^{-1} The microphotometer records reproduced as Fig. 2 in Plate V and Fig. 4 in Plate VII exhibit these features quite clearly. The differences in the character of the two microphotometer records arise from the great difference in the photographic exposures and of the resolving powers of the two instruments employed. A microphotometer record on the greatly enlarged scale of 1: 50 showing these features is reproduced in the text as Fig. 2.

The sharp line with a frequency shift of 2173 cm.^{-1} is clearly the octave of the principal Raman frequency shift of 1086 cm.^{-1} The diffuse line with its peak at 2148 cm.^{-1} is explicable as arising from the superposition of the octaves of a number of discrete normal modes whose frequencies are *less* than 1086 cm.^{-1}, the lowest of them being 1067 cm.^{-1} and the two others having higher values. These normal modes, being inactive, manifest themselves only very weakly as fundamentals. But theory indicates they would be Raman-active as octaves to the same extent as the active fundamental of 1086 cm.^{-1} The fact that the band centred at 2148 cm.^{-1} is of comparable intensity with the line at 2173 cm.^{-1} thus receives a natural explanation.

6. THE ORIGIN OF THE SATELLITE RADIATIONS

The frequency shifts observed in the Raman effect arise from the excitation of the normal modes of vibration of the atoms in the structure of the crystal about their positions of equilibrium by the incident radiation. In the determination of these modes and their frequencies, it is usual to consider those modes which can be regarded as characteristic of the groups of atoms included in the unit cells of the crystal structure. If the unit cell contains p atoms, the number of such normal modes of vibration would evidently be $(3p - 3)$, the three excluded degrees of freedom representing the three translations of unit cell. But this way of dealing with the matter is obviously not complete or satisfactory. If we define a normal mode as one in which the atoms in a crystal vibrate with the same frequency and in the same or opposite phases, it can be readily shown to be a consequence of its three-dimensional periodicity of structure, that a crystal has $(24p - 3)$ normal

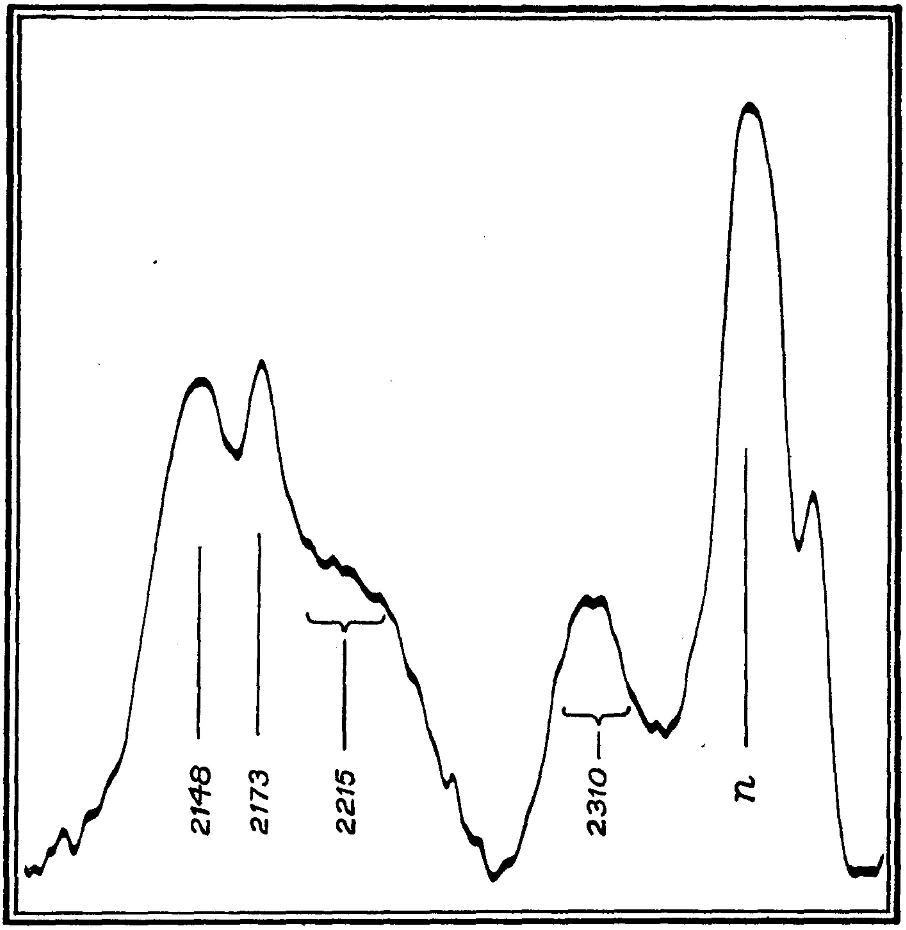

FIG. 2. Enlarged microphotometer record showing the overtone of the principal Raman shift and other features.

modes of vibration, each of which is characterised by a definite monochromatic frequency. In $(3p - 3)$ of these normal modes, equivalent atoms in adjacent cells of the structure have the same amplitude and the same phase of vibration, while in the remaining $21p$ modes they have the same amplitudes of vibration but their phases are opposite along one, two or all the three axes of the crystal structure. The latter may be briefly designated as the superlattice vibrations.

We may proceed to consider the consequences of the foregoing proposition in the case of calcite. We shall confine our attention at first to the modes involving the totally symmetric internal vibrations of the CO_3 group. Each unit cell of the crystal structure contains two such groups which are non-equivalent, the phases of vibration of which in any normal mode may be either the same or opposite. There are eight different situations regarding the relative phases of vibration in the unit cells of the crystal adjoining each other along the three axes of the structure. Thus, in all, there are 8×2 or sixteen possible kinds of normal modes involving the totally symmetric vibration of the CO_3 groups. The rhombohedral symmetry of the crystal however makes the two axes perpendicular to the trigonal axis equivalent to each other, thereby reducing the number of distinct normal modes from sixteen to eight only. A further simplification becomes possible when we note that the equivalent CO_3 groups located along the trigonal axes are remote from each other in comparison with their relative distances along the two other axes of the crystal. Hence, we may ignore the additional possibilities arising from the reversal of phase of their vibrations along the trigonal axis. The number of *effectively* different normal modes is reduced thereby from eight to four. The mode that is Raman-active would obviously be the one in which any one CO_3 group has the same phase of vibration as all the other groups in its neighbourhood. In each of the three other normal modes, half the number of CO_3 groups vibrate in one phase and the other half in the opposite phase and hence they would be Raman-inactive in the first approximation.

It is evident also that the frequencies of the four normal modes indicated by the foregoing considerations would not be identical. For, these frequencies which are principally determined by the internal forces arising within each group would also be influenced by the interactions between similar groups vibrating with the same frequency in the neighbourhood and such interactions would be altered by a reversal of their relative phases. The order of magnitude of the differences in frequency arising in this manner is indicated by the well-known fact that while the frequency shift as observed in the crystal is 1086 $cm.^{-1}$, a similar vibration in solutions containing CO_3 ions gives a frequency shift of only 1065 $cm.^{-1}$

As already indicated, the strongly Raman-active vibration in calcite gives a frequency shift of 1086 $cm.^{-1}$ which corresponds to the case in which all the CO_3 groups vibrate in identical phases. Hence, the three other modes in which half of them vibrate in opposite phases may be expected to be of lower frequencies. Though, as already stated they would be Raman-inactive in the first approximation, various considerations indicate that they would be rendered feebly active by reason of the general similarity in the character of their vibrations and their close approximation in frequency to the strongly active mode.

We have seen in the preceding section that in the strongly exposed Raman spectra, the frequency shift of 1086 cm.$^{-1}$ is accompanied by weak satellites with lower frequency shifts which are respectively, 1075, 1072 and 1067 cm.$^{-1}$ Further, these satellites manifest themselves as octaves quite as strongly as the octave of the 1086 cm.$^{-1}$ frequency. These facts are in such excellent agreement with the theoretical considerations set forth above as to leave no doubt regarding the correctness of the explanation. It is also easy to understand why the 1086 cm.$^{-1}$ frequency exhibits the phenomenon of the satellites in such a clear and conspicuous manner. Being itself an extremely intense line, the satellites which derive from it have observable intensities and being themselves also sharp are seen resolved from it when a spectrograph of adequate power is brought to bear on them.

7. SATELLITES AND OVERTONES OF OTHER FREQUENCY SHIFTS

Besides the three modes of internal vibration of the CO_3 groups appearing as frequency shifts in the Raman spectrum, there is still another in which the carbon and oxygen atoms in these groups oscillate in opposite phases along the trigonal axis of symmetry. Theory indicates that such an oscillation would be infra-red active but would not give a Raman shift of the same frequency, though it might give one with double that frequency. These indications of theory are in agreement with observation. A sharply defined maximum located at 877 cm.$^{-1}$ is observed in the infra-red absorption by thin layers of very finely powdered calcite. *Per contra,* no frequency shift in that vicinity is observable even in the most strongly exposed Raman spectra. Cabannes, Nisi and others noticed and recorded a sharp line with a frequency shift of 1749 cm.$^{-1}$ in the Raman spectrum of calcite. This is clearly identifiable as the octave of the mode of vibration referred to above. Fig. 5 (*c*) in Plate VIII recorded with the λ 4358 excitation exhibits this frequency shift with a notable intensity. In the excitation by λ 2536·5, the same frequency shift appears as a line falling between the second and third components of the triplet in the spectrum of the mercury arc; though it can be observed in that position, a detailed investigation is difficult. So far as is ascertainable, the frequency shift is a single line not accompanied by any satellites or companions.

As already reported in an earlier section, the frequency shift of 1436 cm.$^{-1}$ conspicuously exhibits an unsymmetrical broadening in strongly exposed spectra. In the microphotometer record reproduced in Fig. 2 of Plate V, three satellites can be recognized whose frequency shifts are respectively 1399, 1412 and 1418 cm.$^{-1}$ In the microphotometer record of the more heavily exposed spectrum reproduced in Fig. 4 of Plate VII, the unsymmetrical broadening is clearly visible but the satellites are not resolved from the parent line. Their presence however is clearly indicated in the record obtained on a larger scale 1 : 50 and reproduced below as Fig. 3 in the text.

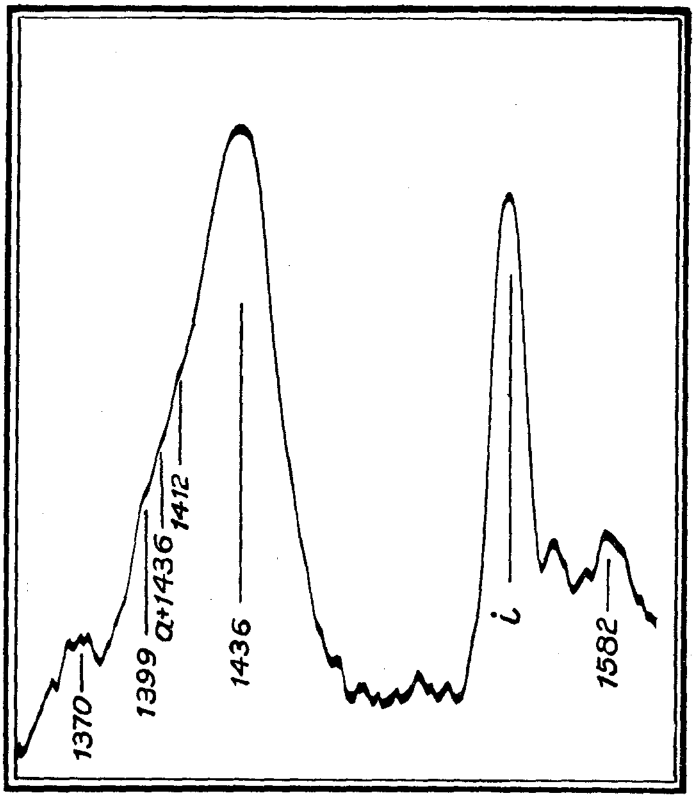

FIG. 3. Enlarged microphotometer record showing 1436 cm.$^{-1}$ line and other features.

In Fig. 4 (Plate VII), the positions where the octaves of the 1436 cm.$^{-1}$ shift and of its satellites appear are indicated in the microphotometer record. They fall on and near the triplet of Raman lines having a common frequency shift of 1086 cm.$^{-1}$ excited by the triplet of the mercury arc and this makes it difficult to describe them completely. It is evident, however, that the intensity of the overtones of 1436 cm.$^{-1}$ and its satellites is very small compared with the intensity of the octaves of the 1086 cm.$^{-1}$ and of its satellites. The enlarged microphotometer record reproduced in the text as Fig. 4 however makes it clear that the satellites of the 1436 cm.$^{-1}$ shift manifest themselves as octaves no less conspicuously than their parent line.

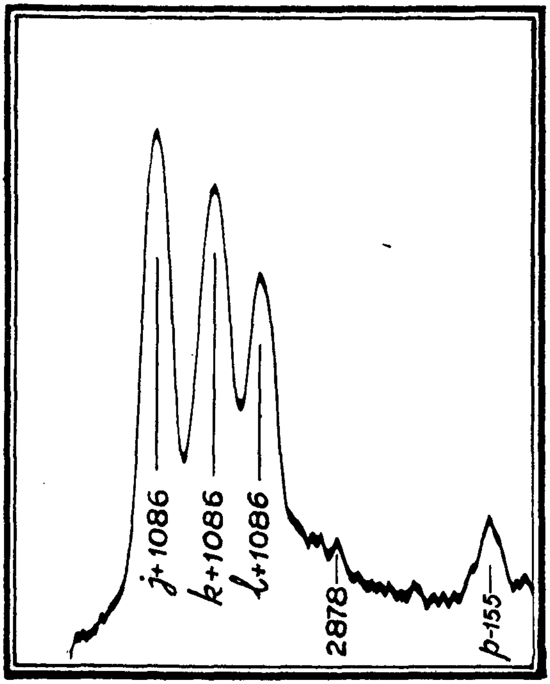

FIG. 4. Enlarged microphotometer record showing the overtones of 1436 cm.$^{-1}$ line and of its satellites.

The 712 cm.$^{-1}$ frequency shift is much less intense than the 1436 cm.$^{-1}$ and its unsymmetrical broadening is barely perceptible. The microphotometer record reproduced as Fig. 6 in Plate IX however shows a weak companion which may be interpreted as a satellite line with a frequency shift of 685 cm.$^{-1}$ It is however difficult to exclude the possibility that this may be only the 712 cm.$^{-1}$ shift excited by the weak λ 2534·8 line of the mercury arc.

The octave of the 712 cm.$^{-1}$ frequency may be expected to be extremely weak. Even otherwise, it could scarcely be expected to be observable, since it would overlap the 1436 cm.$^{-1}$ shift in the spectra recorded with the necessary exposures.

8. THE LOW-FREQUENCY SPECTRUM

We now proceed to consider the characters of the Raman spectrum in the region of the smaller frequency shifts ($<$ 600 cm.$^{-1}$). The most conspicuous features in this region are of course the frequency shifts of 155 cm.$^{-1}$ and 282 cm.$^{-1}$, the latter being much the stronger of the two. They have been identified as arising from the translatory oscillations of the CO_3 groups in their own plane combined with rotational oscillations about an axis also lying in that plane. The two other types of oscillation of the CO_3 groups which are possible are translations along the trigonal axis and rotations also about the same axis. Theory indicates that such oscillations would be Raman-inactive. The question however arises whether movements of the latter two types might not in the second approximation exhibit themselves weakly as frequency shifts. The answer to this question appears to be in the affirmative. Cabannes in his earliest studies noticed and recorded a line in the spectrum with a frequency shift of 221 $cm.^{-1}$ The reality of this has been definitely established by the present investigation. It is visible as a sharp line between the two strong Raman lines in the spectrograms reproduced as Fig. 1 (*c*) in Plate IV and Fig. 5 (*a*) in Plate VIII. It also manifests itself conspicuously as peaks on both sides of the exciting radiation in the microphotometer record of the same spectrogram as Fig. 2 of Plate V.

Various considerations indicate that the frequency shift of 221 $cm.^{-1}$ the reality of which is thus definitely established represents the normal mode in which the CO_3 groups in the crystal oscillate in a direction normal to their planes, neighbouring layers of the CO_3 groups periodically approaching and receding from each other, the layers of Ca ions intermediate between them remaining at rest. The frequency of such an oscillation may be expected to be that actually observed. Confirmatory evidence of the correctness of this explanation of the 221 $cm.^{-1}$ shift of frequency comes to hand from a comparison of the low-frequency Raman spectra of calcite and aragonite. There are striking resemblances and also noteworthy differences between the two spectra, these being evidently consequences of the close similarities as well as the specific differences in the structures of the two crystals. Modes of oscillation of the CO_3 groups similar to those now under consideration are Raman-active in aragonite by reason of its lower symmetry of structure. Indeed, a close group of lines with an average frequency shift of 215 $cm.^{-1}$ and having a notable intensity is a very striking feature in the spectrum of aragonite.

Hibben in his book reports having observed frequency shifts of $\pm$ 86 $cm.^{-1}$ in the Raman spectrum of calcite. Some support for this claim is forthcoming in the present investigation, though the matter has not been placed completely beyond doubt. The rotational oscillation of the CO_3 groups about the trigonal axis of symmetry might be expected to have a frequency of that order of magnitude.

We may now briefly comment upon the explanation of the behaviour of the two principal Raman shifts in this region in strongly exposed spectra already described earlier in the present paper. Dynamical theory indicates that the unit cell in the calcite structure consisting of two CO_3 groups and two

Ca ions intervening between them has ten different normal modes of vibration. If the alternations in the phase of the vibration in adjacent unit cells along the three axes of the structure are also taken into account, this number would be increased to forty in all. The additional thirty modes would have frequencies different from those of the corresponding modes in the group of ten first referred to. Only two out of these forty modes would, strictly speaking, be Raman-active. But it appears inevitable that when one or the other of these two modes is excited, other modes approximating to them in frequency would also be excited, though only very feebly. The spectrum consisting of such a crowd of satellite radiations with different frequencies would naturally appear more or less continuous and this is what is actually observed.

The nature of the vibrations now under consideration is such that we could scarcely expect them to exhibit overtones with any notable intensities, and indeed no evidence is forthcoming of such overtones as *discrete* frequency shifts in the region under consideration. But we do observe a weak band of illumination in the spectrum covering the whole range of frequency shifts upto 600 cm.$^{-1}$ This may be regarded as a superposition of the effects arising from all the forty possible normal modes of vibration.

9. COMBINATIONAL FREQUENCY SHIFTS

We proceed to consider and report on the various features observed in the strongly exposed Raman spectra of calcite other than those already discussed above. It appears desirable to make some comments of a general nature regarding the principles on which the interpretations suggested are based. It is essential in the first place to make the most accurate measurements of the frequency shifts proposed to be interpreted as well as of the frequency shifts to which they might be related as overtones or combinations. It is not possible, however, to base interpretations solely on arithmetical agreements, as the latter might be purely fortuitous. Nor is it permissible to base the interpretations entirely on the selection rules which have been proposed on theoretical grounds. Frequency shifts might be permitted by those rules and yet be unobservable by reason of vanishingly small intensity or other circumstances. Further, the selection rules themselves rest on certain assumptions and are therefore not necessarily valid in all cases. In view of these remarks, it is important that other factors are also taken into consideration. The intensity and spectral character of the frequency shifts are factors of particular importance in this respect. These remarks are made, since the reservations which they imply have been overlooked in several instances in the earlier literature and assignments have been proposed which are wholly unacceptable.

An examination of the strongly exposed spectra and of their microphotometer records reveals numerous features calling for explanation. After a careful review of the various possibilities, we find the most reasonable interpretation to be that they arise from combinations of the various normal modes of vibrations of the unit cells in the crystal structure with the two normal modes having frequencies respectively of 1086 and 875 cm.$^{-1}$ The former is the totally symmetric oscillation of the CO_3 groups which gives by far the most intense line in the Raman spectrum, while the other is an infra-red active mode which gives a Raman shift of double its frequency with notable intensity. We find it possible in the manner indicated to explain practically every one of the observed features in the spectrum. Table I gives a list of the combinations of the first kind and Table II a list of the combinations of the second kind. It is significant that while the octaves of the two frequencies 1086 and 875 cm.$^{-1}$ are conspicuous features in the Raman spectrum, no frequency shift in the vicinity of 1961 cm.$^{-1}$ which would represent a summation of them is observable even in the most strongly exposed spectra. This is readily understood, since the atomic vibrations in these two modes occur in mutually perpendicular directions and that while one of them is totally absent in the infra-red absorption spectrum, the other is conspicuously present.

TABLE I

Observed frequency shifts: Their characters and suggested origins

1186 cm.$^{-1}$	Diffuse and weak	1086+ 100 cm.$^{-1}$
1241 ,,	Sharp and weak	1086+ 155 ,,
1275 ,,	Diffuse and very weak	1086+ 189 ,,
1305 ,,	Sharp and very weak	1086+ 221 ,,
1370 ,,	Sharp and strong	1086+ 282 ,,
1795 ,,	Sharp but weak	1086+ 712 ,,
2522 ,,	Indication only	1086+1436 ,,

The following comments may be offered on the entries in Table I. That the strongly Raman-active frequency 1086 cm.$^{-1}$ would combine with other strongly Raman-active frequencies, *viz.*, 155, 282, 712 and 1436 cm.$^{-1}$ to give sharply defined summational shifts is only to be expected. That the strongest of them is also the combination with the strongly active 282 cm.$^{-1}$ is also intelligible. That no summations appear in Table I corresponding to the strongly infra-red active normal modes with frequencies 330 and 357 cm.$^{-1}$ might have been anticipated on theoretical grounds. The corresponding summations, *viz.*, 1416 and 1443 cm.$^{-1}$ would in any event, however, have been unobservable owing to their overlap with the strong 1436 cm.$^{-1}$ Raman shift. Table I also records summations with three other low frequencies, *viz.*, 100, 189 and 221 cm.$^{-1}$, the former two as weak and diffuse lines and the latter as a weak but sharp line. The first two frequencies are presumably to be identified with two normal modes which are infra-red active, while the 221 cm.$^{-1}$ represents a normal mode which itself appears weakly as a Raman shift and the nature of which has been discussed earlier in this paper.

In strong contrast with the entries in Table I, the frequency shifts listed in Table II appear in most cases as diffuse bands but with notable intensities. The two bands of lowest frequency are respectively a summational and a differential, the former being the more intense of the two, the frequency involved being in either case 84 cm.$^{-1}$ As remarked earlier in the paper, this frequency probably represents the rotational oscillations of the CO_3 groups in their own plane. The appearance in Table II of summations with the Raman-active frequencies of 155 and 282 cm.$^{-1}$ is very surprising, but there is no question as to their reality, since they are recorded with notable intensities and no alternative explanation of these features is forthcoming. Here, as in three other cases listed in Table I, there is a clear-cut violation of the selection rules of which the explanation must be left an open question. The other frequencies of which the summations are listed in Table II are those manifesting themselves strongly in infra-red absorption. Investigators in the latter field are agreed that the maximum which appears in nearly the same position as the Raman frequency shift of 712 cm.$^{-1}$ is a sharply defined one. It is therefore not surprising that the corresponding summation listed in Table II also appears as a strong sharp line. The position is however different with regard to the last two summations appearing in the table. Hunt and collaborators who have investigated the infra-red absorption by a very thin layer of powdered calcite record a peak at 1439 cm.$^{-1}$, but this is only the crest of a very broad maximum and it is therefore not surprising that the corresponding summation appears in Table II as a diffuse band. Perhaps the most remarkable entry in the table is that of the extremely diffuse band which corresponds to a summation with an infra-red absorption band having a maximum at 1340 cm.$^{-1}$ There is no place for such a frequency in the scheme of normal

TABLE II

Observed frequency shifts : Their characters and suggested origins

794 cm.$^{-1}$	Diffuse and weak	875− 84 cm.$^{-1}$
957 ,,	Diffuse and strong	875+ 84 ,,
1025 ,,	Diffuse and strong	875+ 155 ,,
1159 ,,	Diffuse and strong	875+ 282 ,,
1207 ,,	Diffuse and weak	875+ 330 ,,
1232 ,,	Sharp and weak	875+ 357 ,,
1582 ,,	Strong and sharp	875+ 706 ,,
2215 ,,	Diffuse and strong	875+1340 ,,
2310 ,,	Diffuse and strong	875+1439 ,,

modes of vibration of the unit cell of the calcite structure. The suggestion may therefore be hazarded that this band is a satellite or an aggregate of satellites accompanying the infra-red absorption at 1439 cm.$^{-1}$ but distinctly separated from it and analogous to the satellites accompanying the 1436 cm.$^{-1}$ Raman frequency shift already discussed. This suggestion, it may be remarked, is strongly supported by the shape of the absorption curve reproduced in the paper by Hunt and collaborators. Their diagram shows that the absorption of which the crest appears at 1439 cm.$^{-1}$ is of a highly unsymmetrical shape; it rises steeply from nearly perfect transmission at 1650 cm.$^{-1}$ to almost complete opacity at 1439 cm.$^{-1}$ and then drops down quite gradually to nearly perfect transmission again only at 890 cm.$^{-1}$

In conclusion the author wishes to express his sincere thanks to Prof. Sir C. V. Raman, F.R.S., N.L., for the keen interest he took in this investigation and for the valuable suggestions that he gave for the preparation of this paper.

10. SUMMARY

The paper reports the results of a study of the Raman spectrum of calcite recorded with prolonged exposures.

(*a*) The principal Raman shift of 1086 cm.$^{-1}$ is accompanied by much weaker satellites whose frequency shifts are 1067, 1072 and 1075 cm.$^{-1}$ The octave of the principal mode is recorded as a sharp line with a frequency shift

of 2173 cm.$^{-1}$ with a diffuse companion of comparable intensity which is a superposition of the octaves of the three satellites. The 1436 cm.$^{-1}$ Raman shift likewise has satellites at 1399, 1412 and 1418 cm.$^{-1}$ and its octave is feebly recorded as a sharp line, while the octaves of the satellites are also observed in its vicinity. The origin of the satellite radiations is discussed and it is shown that they represent the superlattice vibration frequencies of the calcite structure which are feebly excited.

(*b*) The appearance of a sharp Raman line with a frequency shift of ± 221 cm.$^{-1}$ is confirmed and it is shown to arise from a normal mode usually considered as inactive.

(*c*) The two intense Raman shifts of 155 and 282 cm.$^{-1}$ exhibit a highly unsymmetrical broadening, as also wings of low intensity spread out over the whole range of frequency shifts between − 300 cm.$^{-1}$ to + 600 cm.$^{-1}$ This spectrum is explicable as arising from a very feeble excitation of the whole group of forty lattice and superlattice frequencies of the calcite structure and their overtones and combinations.

(*d*) Sixteen combinational frequency shifts have been recorded. Seven of them are explained as combinations with the 1086 cm.$^{-1}$ Raman line and the the nine others as combinations with 875 cm.$^{-1}$ Some of the observed combinations violate the selection rules.

REFERENCES

The literature on the Raman spectrum of calcite and its theoretical interpretation is very extensive. Only the papers which have been referred to in the text and which have a bearing on the results of the present investigation are quoted below.

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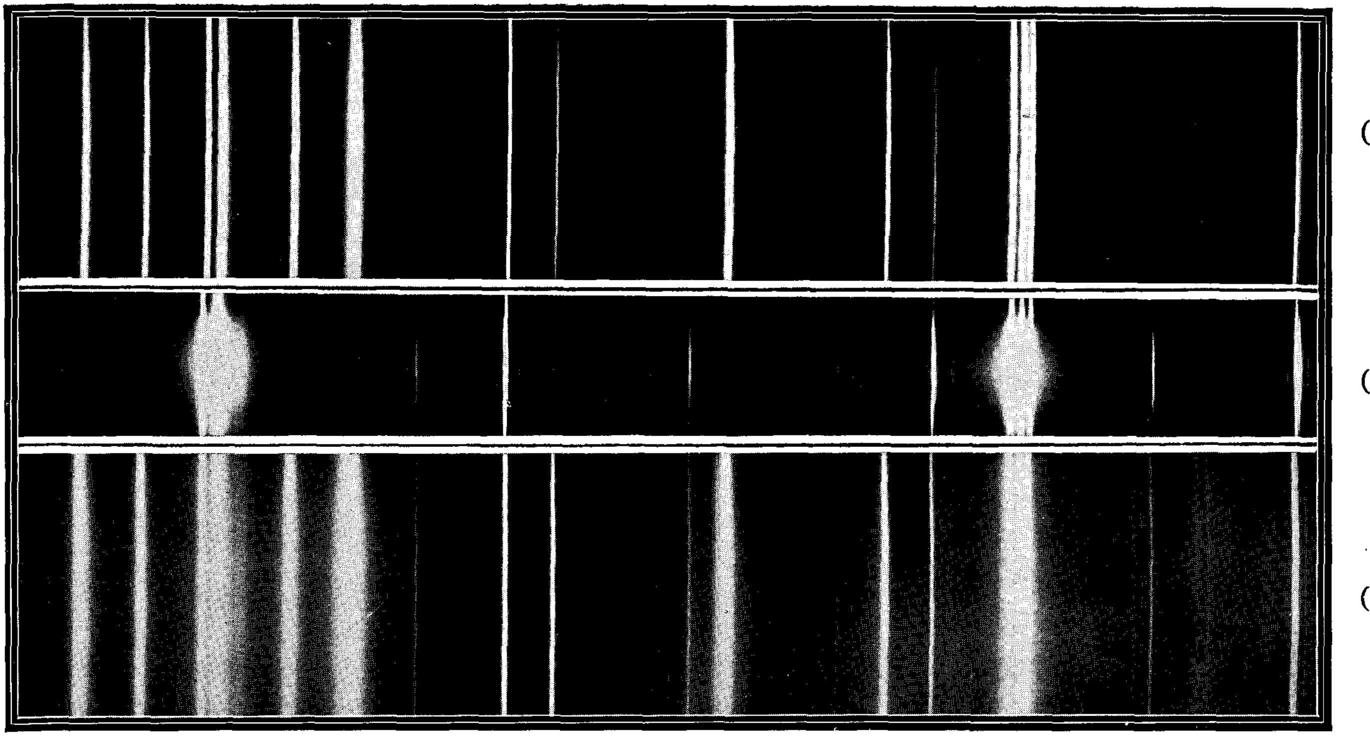

FIG. 1. The Raman spectrum of calcite recorded with Littrow spectrograph. (*a*) Deeply printed, (*b*) Spectrum of the mercury arc, (*c*) Lightly printed.

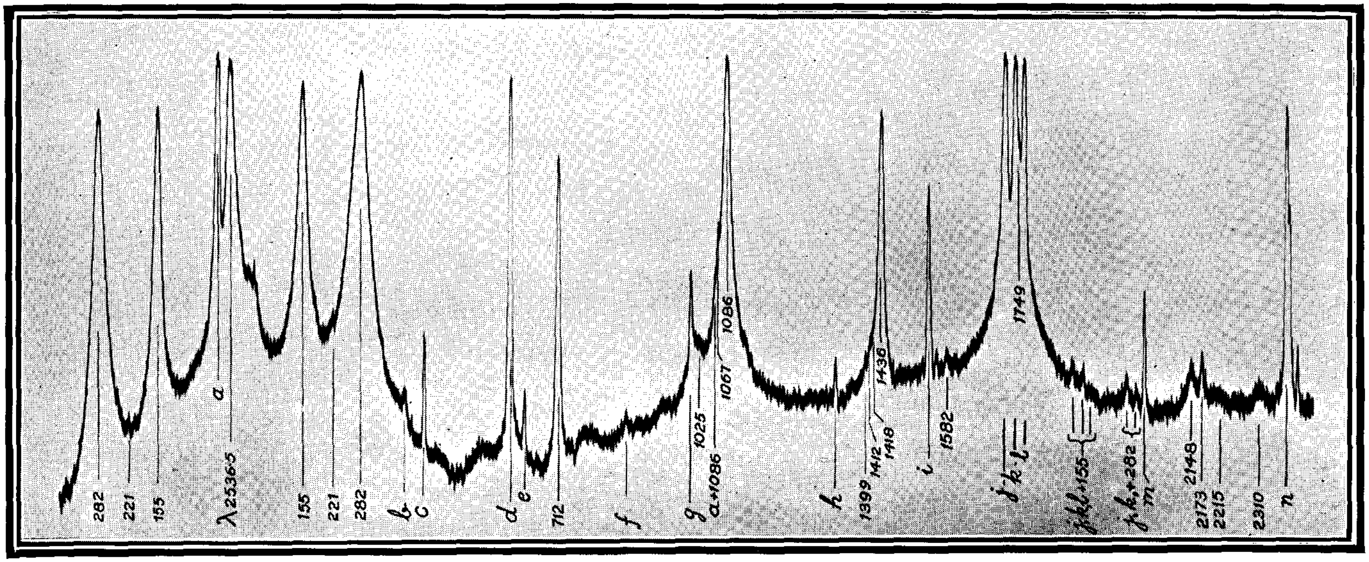

FIG. 2. Microphotometer record of the Raman spectrum of calcite recorded with the Littrow spectrograph.

Note.—The numbers denote the Raman shifts in cm.$^{-1}$ while *a, b, c,* etc., refer to the mercury arc lines.

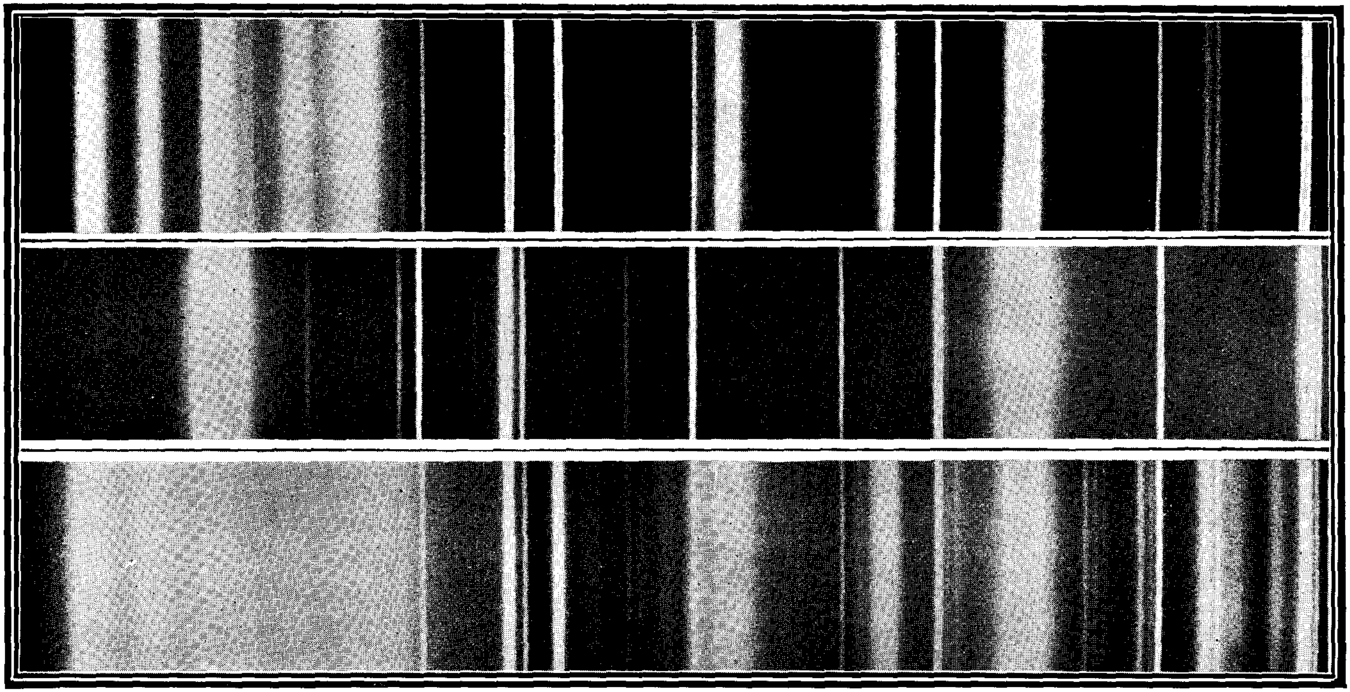

FIG. 3. The Raman spectrum of calcite recorded with the medium quartz spectrograph.
(*a*) Deeply printed, (*b*) Spectrum of the mercury arc, (*c*) Lightly printed.

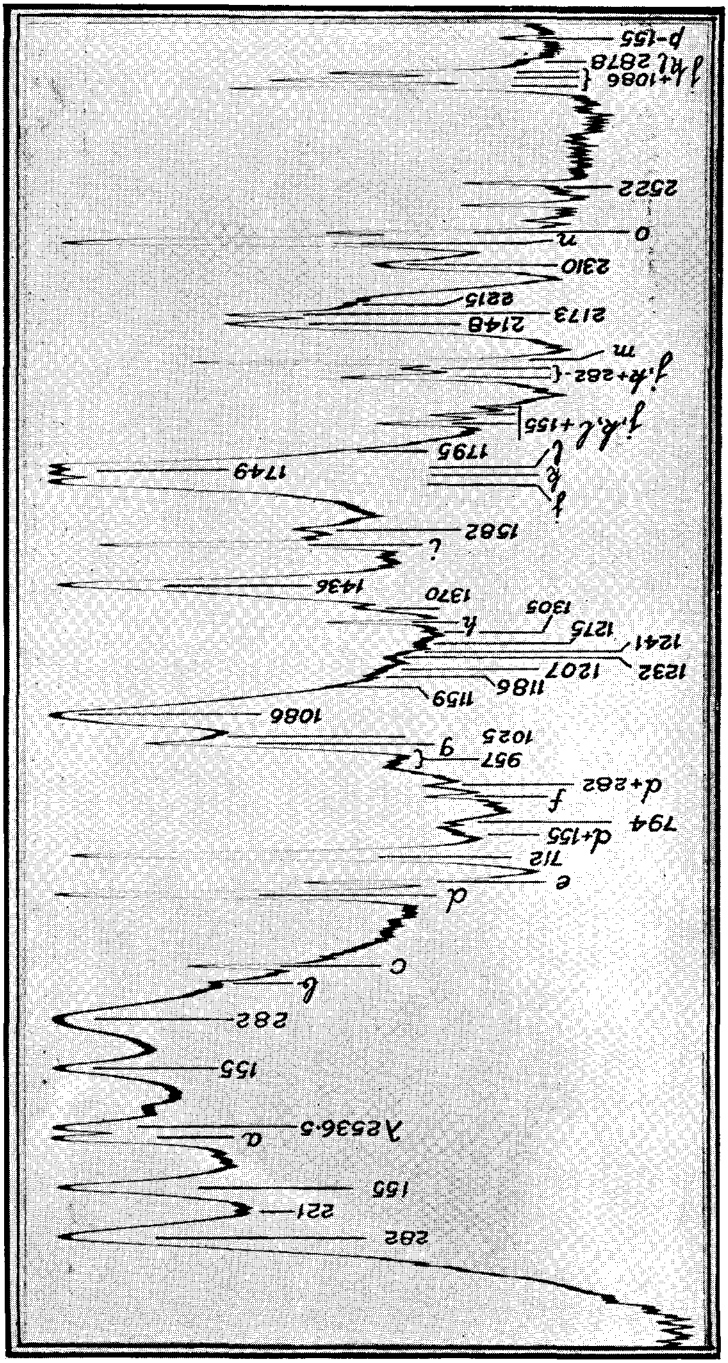

FIG. 4. Microphotometer record of the Raman spectrum of calcite recorded with the medium quartz spectrograph.

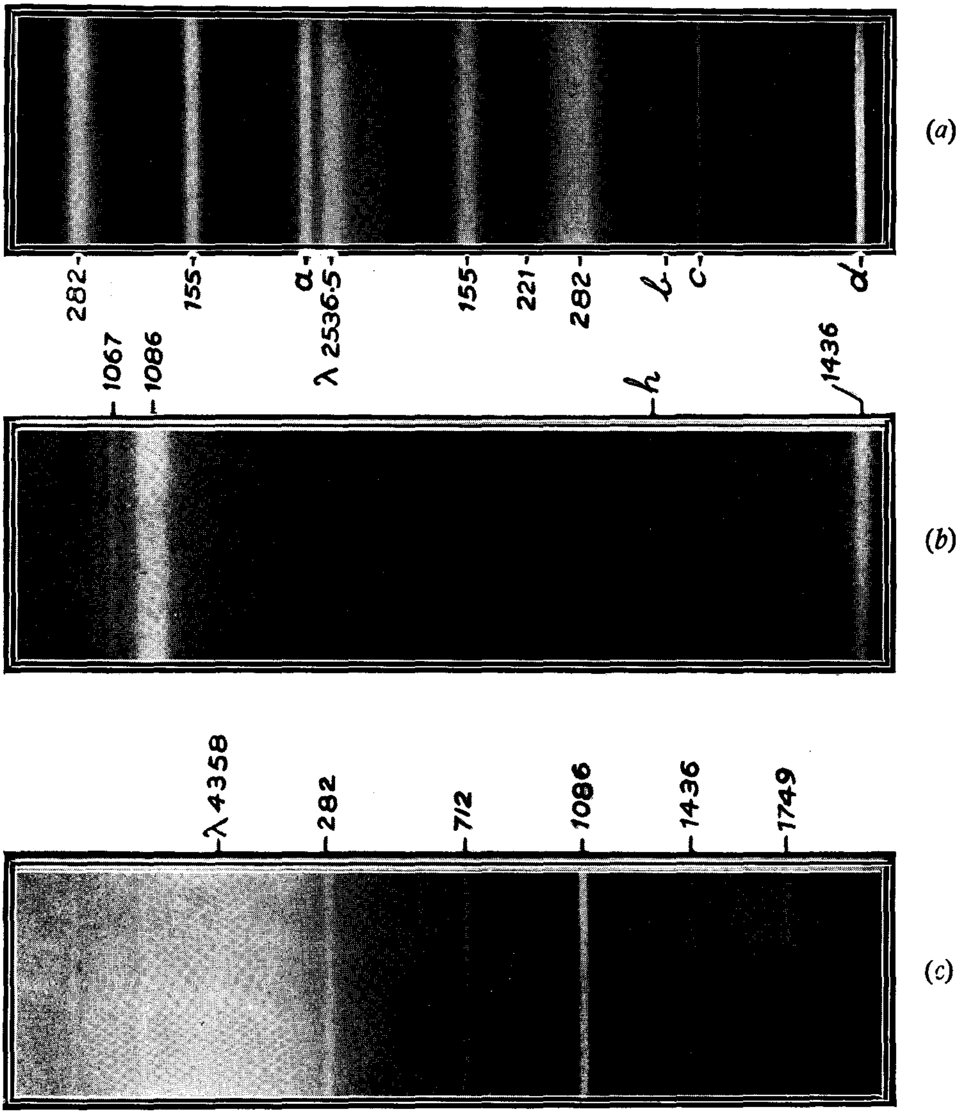

FIG. 5. The Raman spectrum of calcite; (*a*) and (*b*) Enlargements of some portions of Fig. 1 (*c*); (*c*) Spectrum recorded with λ 4358 excitation.

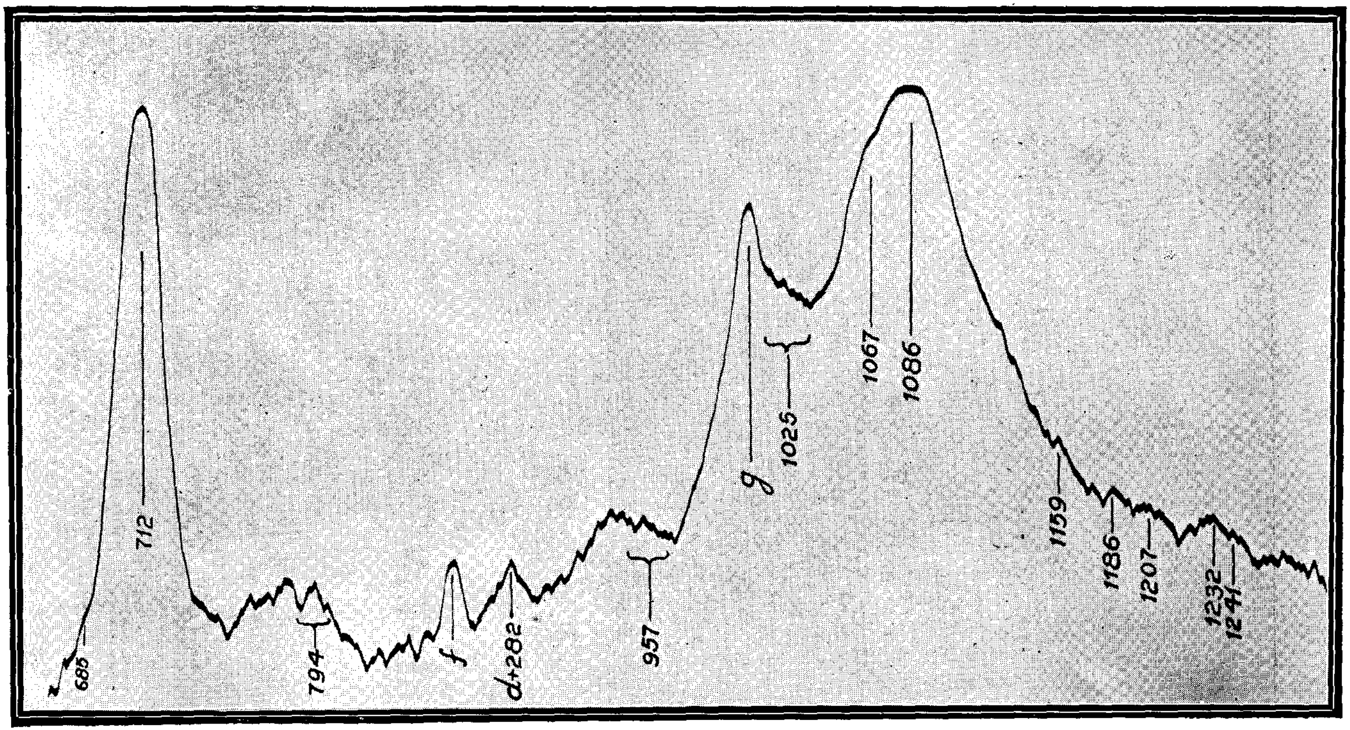

FIG. 6. Enlarged microphotometer record of an intense spectrum obtained with the medium quartz spectrograph.