

THE DISTRIBUTION OF INTENSITY IN THE RAMAN SPECTRUM OF DIAMOND

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I. INTRODUCTION

THE theory of the normal vibrations of crystal lattices developed by Sir C. V. Raman (1943) leads to the result that the crystal structure of diamond has eight monochromatic frequencies of vibration. Of these, one is triply degenerate, two are four-fold degenerate, three are six-fold degenerate and two are eight-fold degenerate. From the nature of the modes, it follows that only the triply degenerate mode would be Raman active in the first approximation, and hence only one frequency shift should be ordinarily observed in the spectrum of light-scattering by diamond, as is actually found to be the case (Ramaswamy, 1930). In the second approximation, however, all the modes should be active in greater or less measure. Accordingly, it is to be expected that when adequate exposures are given, frequency shifts corresponding to overtones and combinations of the eight fundamental frequencies should be observable. Their intensities would be determined by the second-order changes of optical polarisability arising in each case and hence would necessarily be small.

The theoretical prediction stated above was strikingly confirmed by the investigations of R. S. Krishnan commenced in 1944 and continued in later years. Even in his earliest studies made with a tiny diamond only 40 milligrams in weight, a second-order spectrum exhibiting a structure of the kind indicated by the theory was recorded. Subsequently, a plate of diamond became available which weighed 2.5 milligrams and was fully transparent to the $\lambda 2537$ rays of the mercury arc. The use of this larger specimen made it possible to employ more powerful spectrographs and to photograph the second-order spectrum under high resolution and dispersion. The published reproductions of the original spectra thus obtained and their

microphotometric records exhibit the discrete character predicted by the theory in an unmistakeable fashion (R. S. Krishnan, 1947).

The distribution of intensity in the second-order Raman spectrum of diamond is a matter of considerable interest. Remarkably enough, the octaves of some of the inactive modes surpass in intensity the octave of the principal or active Raman frequency, while on the other hand, there are other octaves and combinations which appear with much smaller intensities. It has been shown by Sir C. V. Raman (1947) that these features follow necessarily as a consequence of the particular modes of vibration prescribed by the theory. The quantitative estimation of the relative intensities of the various features observable in the second-order Raman spectrum of diamond thus acquires a measure of importance. It is proposed here to present some studies on this subject made by the author. The data obtained are specially significant in relation to the claims made by Miss Helen Smith, a pupil of Professor Max Born, in a paper on the Raman spectrum of diamond (1948). Indeed, the present investigation demonstrates that the consequences of the Born-Karman lattice dynamics developed in Miss Smith's paper for the case of diamond are toally incompatible with the observed behaviour of that substance in the Raman effect.

2. SOME CONSEQUENCES OF THE THEORY

It will be useful here to give a brief resumé of the features theoretically to be expected in the second-order spectrum of diamond. A rigorous calculation of the eight fundamental frequencies of vibration of the diamond structure has been made by K. G. Ramanathan (1947), taking into account the forces between each atom and its 28 nearest neighbours. Expressed in wave-numbers, they came out as follows, the number enclosed in brackets being the respective degeneracies: 1332 (3), 1250 (8), 1232 (6), 1149 (4), 1088 (6), 1008 (4), 752 (6) and 620 (8). The triply degenerate mode having the highest frequency is Raman-active by reason of its symmetry characters. The other modes are inactive in the first order by reason of the fact that the vibrations are in opposite phases in adjacent cells of the lattice, and the resulting variations of optical polarisability therefore cancel out. In the two modes of lowest frequency, the bonds between adjacent carbon atoms do not vary in length; only the bond-angles alter. Hence, the variations of optical polarisability arising in these two modes are negligibly small and they cannot therefore appear either as overtones or as combinations with other modes. The octaves and summations of the remaining six modes are listed below in wave-numbers, the octaves being shown in heavy type along the diagonal of the square.

TABLE I
Octaves and Summational Frequencies

2664	2582	2564	2481	2420	2340
	2500	2482	2399	2338	2258
		2464	2381	2320	2240
			2298	2237	2157
				2176	2096
					2016

Thus, a maximum of twenty-one frequency-shifts may be expected in the second-order spectrum, the highest and lowest being 2664 and 2016 respectively.

To obtain a more definite picture of the observable facts, we have to consider also the question of intensities. The factors determining them would be, *firstly*, the amplitude of variation of the C-C bond-lengths, and *secondly*, the number of bond-lengths which vary in each unit of the structure. Since we are concerned with second-order variations of optical polarisability, the first of these two factors assumes special importance. It is not the same in the different modes, and as a consequence of this, the mode appearing most strongly in the second-order spectrum would be the octave of the third fundamental and not of the first or the second, though the latter would also have fair intensities. Further, the same considerations indicate that the octave of the fifth fundamental would appear with less intensity than the octaves of the first four fundamentals; also that the octave of the sixth fundamental would be extremely weak.

Some additional features of importance need to be mentioned. The appearance of a mode of vibration as a frequency shift in the second-order spectrum is a consequence of its finite amplitude. Hence, it is necessary to consider the influence of anharmonicity on the frequencies. In particular, since the fundamental frequencies are themselves degenerate, their combination may be expected to result in a removal of the degeneracy, in other words, in a splitting of each combinational frequency into several distinct components. We notice also that in Table I there is a crowding

together of the lines in a particular region of the spectrum. Fourteen of them are concentrated in the region of frequency shifts between 2500 and 2200 wave-numbers, and some of the frequencies are also nearly coincident. In these circumstances, perturbations of frequency are likely to arise by reason of the mutual interactions between the different modes. We have thus reason to anticipate that the shifts of frequency actually observed in the second-order spectrum would not be exactly those listed in the table, and that both displacements and additional components are possible.

3. THE EXPERIMENTAL FACTS

It will be evident from what has been stated above that the second-order Raman spectrum of diamond would be a closely spaced aggregate of lines. The test for ascertaining whether it is actually of that nature is to use a spectrograph of high resolving power; such an instrument would reveal the fine structure of the spectrum clearly even if an instrument of lower power fails to do so. On the other hand, a spectrum which is continuous or consists of diffuse bands would exhibit the same aspect with both the high and low resolving powers.

Three different instruments, viz., the "intermediate", "medium" and "large" quartz spectrographs of Hilger were used by R. S. Krishnan in his investigations, and the spectrograms published by him show notable increases in the clarity of the spectrum and more detail visible in it with the higher resolving power. The spectrum recorded by the "large" quartz spectrograph is reproduced in the issue of *Nature*, dated the 11th of January 1947, and very clearly exhibits twelve sharply defined lines; the power of the instrument as well as the nature of the spectrum itself are both revealed by the fact that the two lines of greatest intensity having wave-number shifts of 2460 and 2470 respectively are seen clearly resolved from each other. Indeed, they are as sharply defined as the lines of the mercury arc or the line with frequency shift 2664 which is the octave of the principal Raman frequency. The detailed paper by R. S. Krishnan published in the *Proceedings of the Academy* for December 1947 contains reproductions of the spectra recorded with the "medium" as well as the "large" instrument. A series of microphotometer traces of these spectra are also reproduced with that paper and they show all the features visually observed in the spectra. For instance, the doublet with frequency shifts 2460 and 2470 is seen to be such both in the spectrum and in the microphotometer record, obtained with the more powerful instrument.

The frequency shifts actually observed are entered in Table II in the same manner as in Table I to facilitate comparison with the latter. The

TABLE II
Observed Frequency Shifts

2665 (4)	<i>2595</i> <i>2565</i>	<i>2547</i> <i>2536</i> (3)	2490 (4) 2470 (3)	<i>2440</i> (4)	2334 (4)
	2520 (4) 2502 (4)	2490 (4) 2470 (3)		2334 (4)	2255 (5)
		2470 (2) 2460 (3)		2334 (4)	2255 (5)
			2297 (4)	2255 (5) 2225 (3)	
				2190 2176 (4)	
					2015

lines which are most conspicuous in the spectrograms are shown in heavy type, the less conspicuous ones in ordinary type and the least conspicuous in italics. The small figures shown in brackets after the wave-number shifts are the respective line-widths estimated from the spectra and their microphotometer traces. It will be noticed that some of the frequency shifts appear more than once, indicating that alternative assignments are possible. It will also be noticed that in some cases, there is a splitting of the frequencies. There are only four blank cages in Table II as compared with Table I. The gaps in the fourth vertical column are due to the presence of mercury lines which make frequency shifts near 2400 unobservable. The gaps in the last vertical column represent combinations which are unobservable by reason of the very low intensity to be expected in those cases.

4. MICROPHOTOMETRIC STUDY OF THE SPECTRUM

The material set out briefly in the two preceding sections makes it evident that the observed behaviour of diamond in the Raman effect is in full accord with that to be expected on the basis of the new crystal dynamics. What the experimental facts prove is that the fundamental vibration frequencies—the overtones and combinations of which appear as frequency

shifts—form a line spectrum and *not* a diffuse or continuous one as contemplated in the older theories. This conclusion is of such fundamental and far-reaching importance that it is not superfluous to put forward further experimental evidence in support of it. Such confirmatory evidence is forthcoming on an examination of the microphotometer traces of the spectrum recorded under appropriate conditions.

To ascertain the distribution of intensity in the Raman spectrum, it is necessary to avoid or eliminate the background of false illumination recorded simultaneously with it on the photographic plate. This is a matter of great importance in view of the extreme faintness of the second-order spectrum. The radiations diffused or scattered by the diamond and entering the spectrograph have to traverse its optical system before they reach the photographic plate. Since even the most perfect optical surfaces scatter light to some extent, a diffuse continuum appears overlying the real spectrum. The screen of mercury vapour employed in the experiments eliminates the part of this continuum due to the intense λ 2537 radiations of the mercury arc. But the rest of the radiations entering the spectrograph are not thus eliminated and give rise to disturbing effects. The background illumination arising from their presence is found to be relatively more intense with the "large" quartz spectrograph which is of the Littrow type than with the "medium" instrument in which the light traverses the optical train only once. The superior resolution and dispersion provided by the former instrument are useful when it is sought to exhibit the maximum of detail in the spectrum. But the freedom from background of the "medium" spectrograph makes it the appropriate instrument to employ for an investigation of distribution of intensity in the Raman spectrum; it offers also the additional advantage of a vastly greater speed. It has accordingly been used in the present studies which have been made with the same diamond as in R. S. Krishnan's previous work; this is a thick semi-circular plate which is held so that the light from the mercury arc enters the flat face and the scattered light emerges through the edge and enters the spectrograph. The edge which was originally somewhat irregular was smoothed and polished for the purpose of the present investigation. A notable improvement in the recorded spectra has resulted therefrom.

The character of the second-order spectrum and the distribution of intensity in it are elucidated by the following procedure. The spectrum is photographed with a graduated series of exposures, commencing with one of just sufficient duration to record the most intense regions in it, and ending with an exposure sufficiently prolonged for the spectrum itself to be heavily

over-exposed, but without a background coming up having any appreciable intensity. The sequence of spectrograms thus obtained is very instructive; the earlier ones show the more intense features very clearly, while the later ones show the fainter parts best. The microphotometer records of the series of spectrograms show a progressive change in character. The *minor* variations of intensity within the spectrum are less conspicuous in the microphotometer records of the heavily exposed spectrograms; on the other hand, the *major* features remain and are indeed much more strikingly evident than in the microphotometer traces of the weakly exposed spectra.

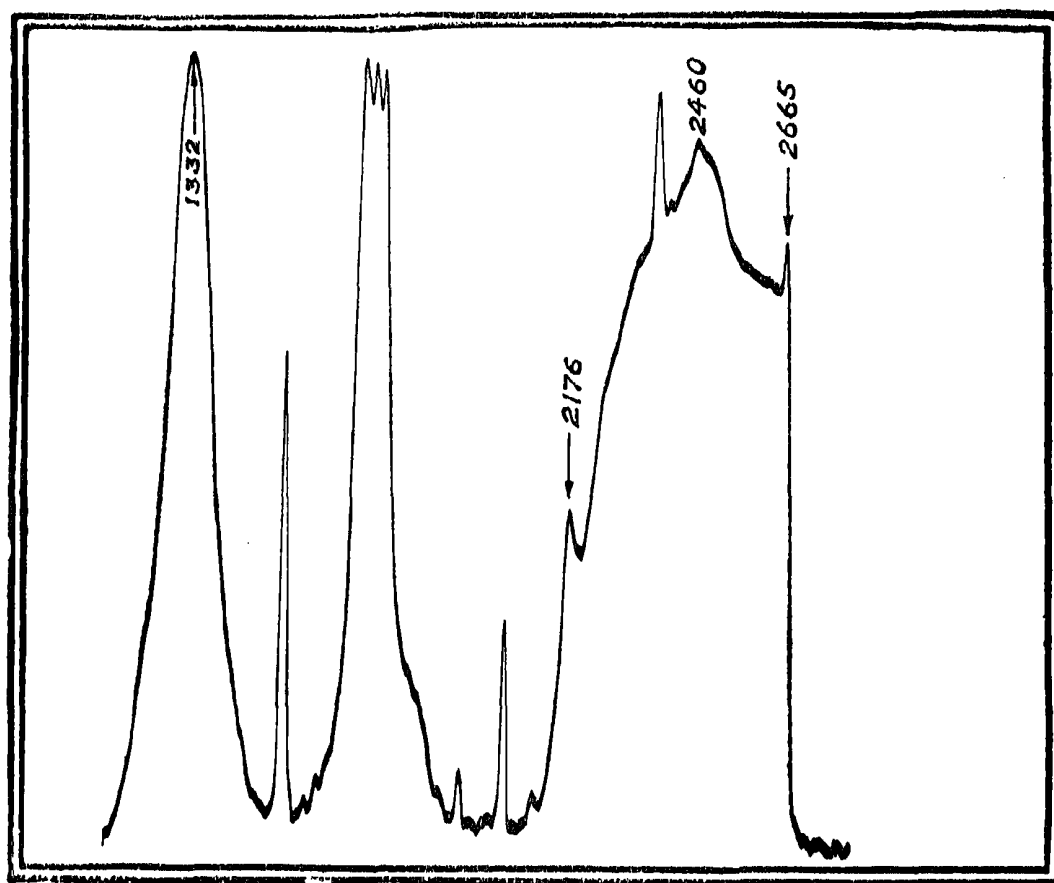


FIG. 1. Microphotometer Record of Heavily Exposed Second-Order Spectrum
(Medium Spectrograph)

Fig. 1 reproduces the microphotometer records of a heavily exposed spectrogram. Reading it from right to left, we notice an *abrupt rise in intensity from zero to a sharply defined peak at a frequency shift of 2665 wave-numbers*, followed again by a steep fall. Reading the record from left to right, we notice another *abrupt rise of intensity from zero to a sharply defined peak at a frequency shift of 2176 wave-numbers*, followed again by a rapid fall. Still another narrow peak of maximum intensity appears nearly midway between these at 2460 wave-numbers. Thus, the microphotometer record indicates the presence in the spectrum of three sharply-defined lines whose widths do not exceed a few wave-numbers in each case and having frequency

shifts 2665, 2460 and 2176 respectively. That this is actually the case is visually evident also from the series of spectrograms recorded with moderate exposures and reproduced as Figs. 1 (a), (b), (c) and (d) of Plate I.

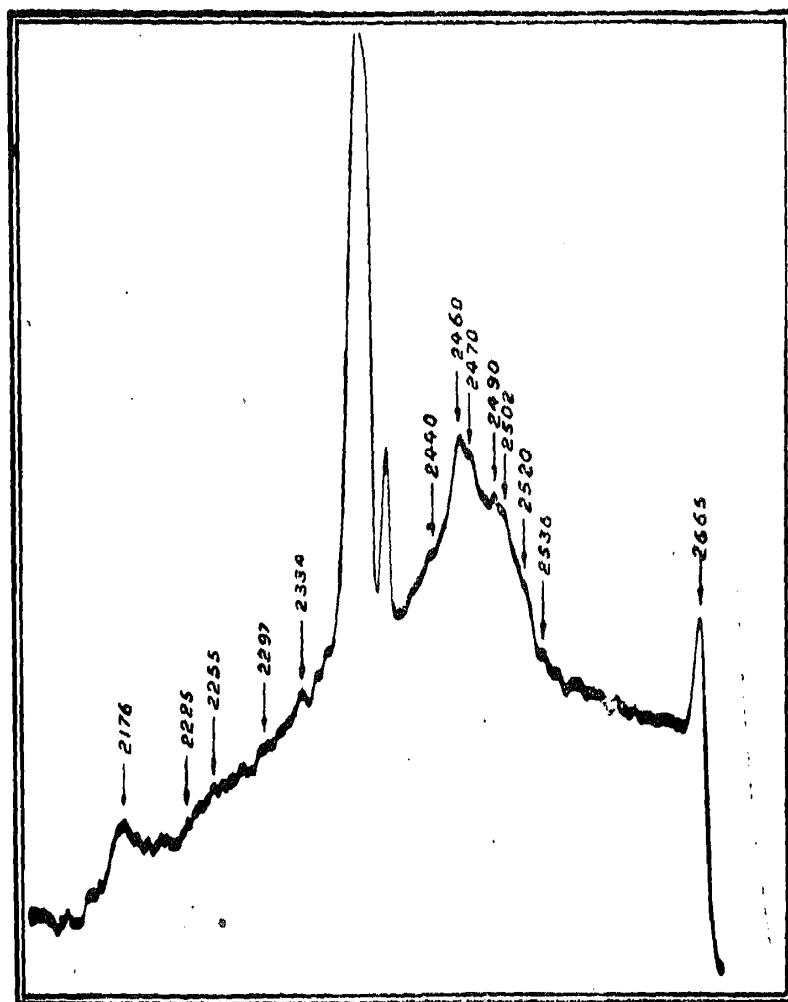


FIG. 2. Microphotometer Record of Moderately Exposed Second-order Spectrum (Large Spectrograph)

The remarks made earlier concerning the relative merits of the "medium" and the "large" spectrographs may be illustrated by a comparison between Figs. 1 and 2 above. Far more detail is visible in the latter than in the former, while only a hint of a fine structure is visible in the former. This is partly because of the heavy exposure employed in the latter case which tends to obliterate the finer details and partly also because of the inadequate power of the smaller instrument. On the other hand, it would scarcely have been possible with the larger instrument to obtain a spectrogram so heavily exposed and so free from background as to exhibit the discontinuous drop of intensity at 2176 wave-numbers seen in Fig. 1. The advantage of the larger instrument thus lies in its capacity to resolve and exhibit the finer details of structure of the spectrum. This will be evident also on a com-

parison of Fig. 1 (b) in Plate I with Fig. 2 in Plate II, taken respectively with the smaller and larger instruments. The exposures in the two cases were such as to yield negatives of comparable densities.

5. DISTRIBUTION OF INTENSITY IN THE SPECTRUM

A microphotometer record does not, of course, represent the actual distribution of intensity, but bears a certain relationship to it determined by the contrast-quality of the photographic plate as well as by the exposure and the development. A microphotometer record can, however, be translated into an intensity curve by appropriate methods, and this has been done in the present case. For this purpose, the photographic plates used were calibrated with the help of the continuous radiation from a hydrogen discharge tube, a set of graded intensity marks being recorded on them alongside of the spectrum. The density versus intensity curve for the wave-length λ 2700 was drawn for the plates by running them through the microphotometer. The data thus obtained enabled the intensity distribution in the Raman spectrum of the second order to be evaluated. No attempt has been made to correct for the finite slit-widths (0.025–0.04 mm.) actually employed in photographing the spectra.

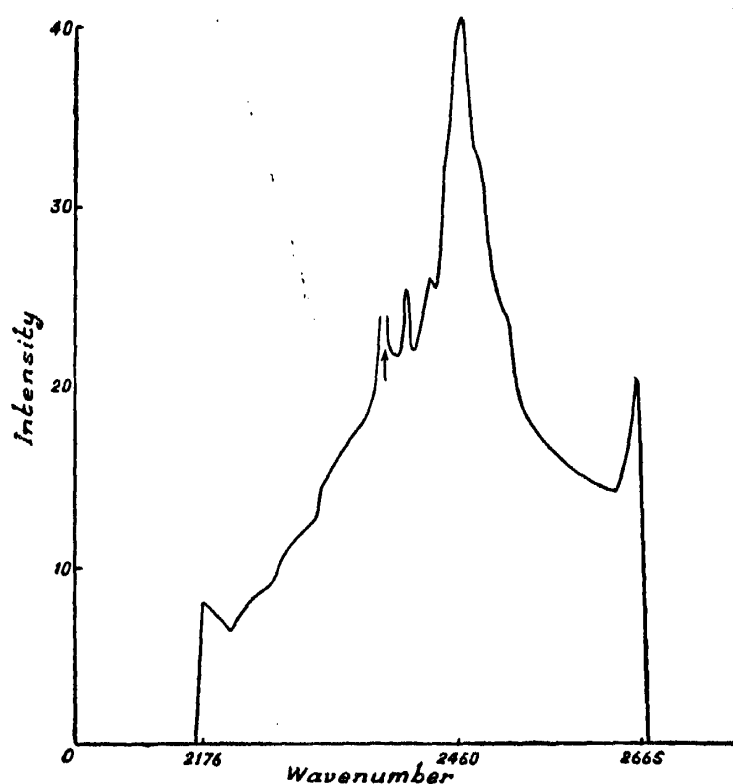


FIG. 3. Intensity Curve of Second-Order Raman Spectrum of Diamond

Fig. 3 above is a sketch of the intensity-curve deduced in the manner explained from the microphotometer records. Since the spectrograms from which it was derived were obtained with an instrument of moderate resolving power, it cannot claim to represent the finer details of the variations of intensity in the spectrum, as for instance those shown in Fig. 2 above, with any degree of fidelity. There can be no doubt, however, as to the correctness of the main features appearing in it. Reading from right to left, we find in the diagram, (1) a steep straight rise of intensity from zero to an extremely sharp peak at 2665 wave-numbers, (2) a trough of low intensity following it and extending up to 2500 wave-numbers, (3) a rapid rise following this and culminating in the great peak of intensity at 2460 wave-numbers, (4) the subsequent rapid fall leading to a trough of low intensity at 2200 wave-numbers, (5) the rise following this to a well-defined peak at 2176 wave-numbers and (6) the subsequent sudden drop to zero. All these features appear also in Fig. 1 above, except that the actual variations of intensity are much more pronounced than the ups and downs of the microphotometer record for the denser regions of the spectrographic negative.

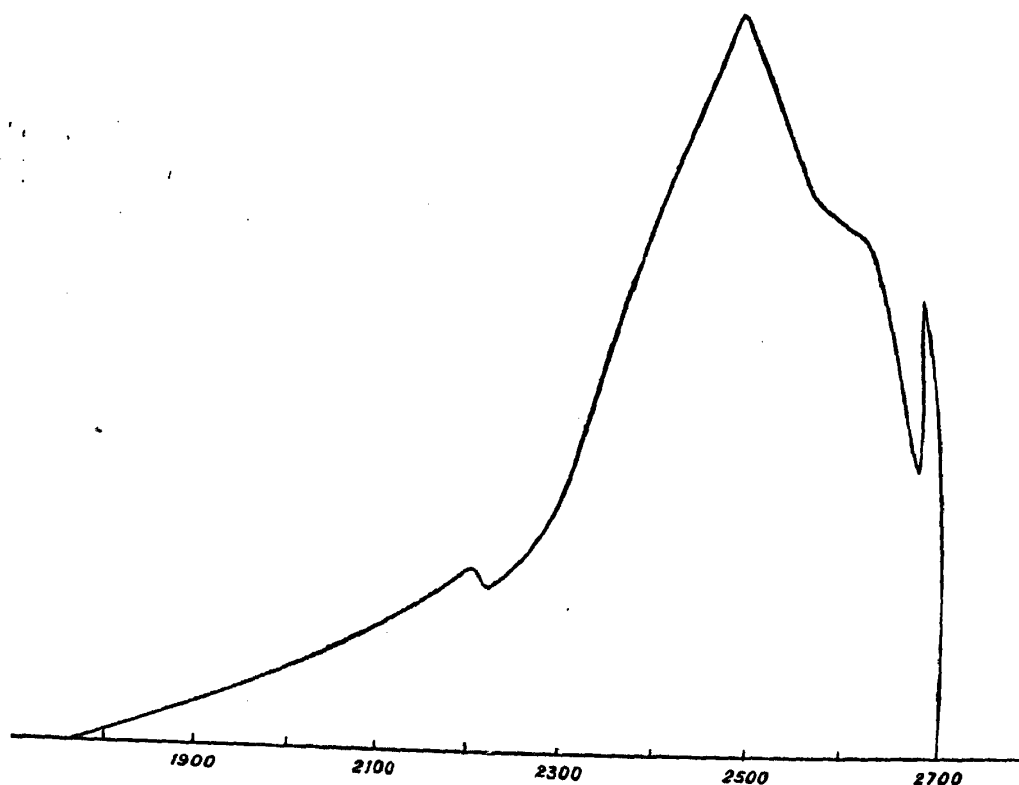


FIG. 4. Intensity Distribution according to the Born-Karman Theory

In the paper by Miss Helen Smith cited above, there appears a curve claiming to represent the distribution of intensity in the Raman spectrum expected theoretically on the basis of the Born-Karman lattice dynamics.

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This curve is reproduced above (Fig. 4) on the same scale of wave-numbers as Fig. 3 for comparison with the distribution of intensity derived from observation and shown in the latter. It will be noticed that none of the characteristic features of Fig. 3 listed above appear in Fig. 4, while on the other hand, the latter exhibits several curious features for which there is no counterpart in the experimentally determined intensity distribution.

6. THE BORN-KARMAN THEORY AND ITS CONSEQUENCES

The reasons for the striking lack of resemblance between the actual distribution of intensity in the Raman spectrum of diamond and that put forward in Miss Helen Smith's paper will become clear when we consider the process by which the curve reproduced above in Fig. 4 was constructed by her.

As is well known, the Born-Karman lattice dynamics bases itself on the idea that the possible vibrations of the atoms in a crystal can be described as waves in the solid, their lengths and directions being those defined by the cyclic postulate. An immense number of waves is possible according to the postulate, and the vibration spectrum of the crystal deduced therefrom, becomes a continuum stretching from zero frequency upwards to a high limit. A great part of Miss Helen Smith's paper is taken up with a calculation of the frequency distribution in the vibration spectrum of diamond, and for this purpose of these calculations, the distribution is represented as the sum of six separate distributions or branches. Three of these branches lie in the higher part of the frequency range, one of them extends throughout the whole range and the remaining two others lie in its lower part. From these six frequency distributions again, are derived thirteen others representing the octaves, sums and differences of their respective frequencies. Branches 1, 2, 3 and 6 lie in the upper part of the frequency range, 4, 5, 7, 8 and 9 appear in the middle of the range, while 10, 11, 12 and 13 lie in its lower parts. To derive the intensity distribution in the second-order spectrum, it is *assumed* that the light-scattering power associated with the branches 4, 5, 7, 8, 9, 11, 12 and 13 is zero, while to the branches 1, 2, 3 and 6 are assigned respectively the relative scattering powers 1:40:12:1. The ordinates of these four curves are added up and the curve shown above in Fig. 4 is thus derived.

We may remark in the first place, that no reason or physical justification is given in Miss Smith's paper for the assumption made that most of branches are ineffective, as also for selecting only four of them as operative and assigning to them the specific ratios quoted above. These arbitrary assumptions were evidently made for securing a pre-determined result, viz., a graph which—without any regard being paid to its actual shape or specific features—would exhibit humps at 2665, 2460 and 2176 wave-numbers.

A paper of 1946 by R. S. Krishnan is quoted by Miss Smith in this connection. But one can find as little resemblance between the microphotometer curve appearing in that paper and the "theoretical" diagram of Miss Smith as there is between Fig. 3 and Fig. 4 in the present paper. Indeed, the microphotometer record reproduced in Krishnan's paper of 1946 is of a spectrum taken with moderate exposures and the "medium" spectrograph, and it shows much recognizable detail besides three sharp peaks at the positions mentioned above. It is quite gratuitously suggested in Miss Smith's paper that all such details were spurious features. That such a suggestion should have been put forward is the more surprising in view of the publication by R. S. Krishnan of a note in *Nature* of the 11th January 1947, in which a spectrogram is reproduced showing very clearly the presence of 12 sharply defined lines in the very same regions of the spectrum. It is very strange also that no reference appears in Miss Smith's paper either to this note or to the two later ones in *Nature* of the 31st May and 16th August 1947, respectively, on the subject of the Raman spectrum of diamond, though all three notes had appeared many months before her paper was sent in for publication.

Then again, we may remark that all the 13 "branches" referred to above cover wide ranges of frequency. In particular, the ranges for the branches 1, 2, 3 and 6 are respectively 140, 430, 1050 and 320 wave-numbers. The positions of the maxima obtained by superposing four smooth curves extending over such wide ranges would depend upon the amplitudes arbitrarily assigned to them. Hence no significance can be attached to any agreement thus artificially secured with the positions of the observed maxima of intensity. It is clearly also not possible by superposing four such curves to reproduce the numerous sharply defined peaks of intensity appearing in the microphotometer record of the spectrogram taken under high resolution (see Fig. 2 above), the positions of which can be determined and specified to within the nearest wave-number. Further, it is clearly impossible by superposing a finite number of such curves to reproduce the steep drops of intensity actually observed in the vicinity of the frequency shifts 2665 and 2176 and shown in Figs. 1 and 3 above.

Thus, in the final analysis, we can state without fear of contradiction that the consequences of the Born-Karman lattice dynamics are wholly incompatible with the experimentally observed behaviour of diamond in the Raman effect. A further serious criticism of a more general nature can also be put forward regarding the approach to the subject made by Max Born and his co-workers. It is evident that for overtones or combinations to appear as frequency shifts in light scattering, the amplitudes of vibration of the atomic systems under consideration should *not* be infinitesimal. For,

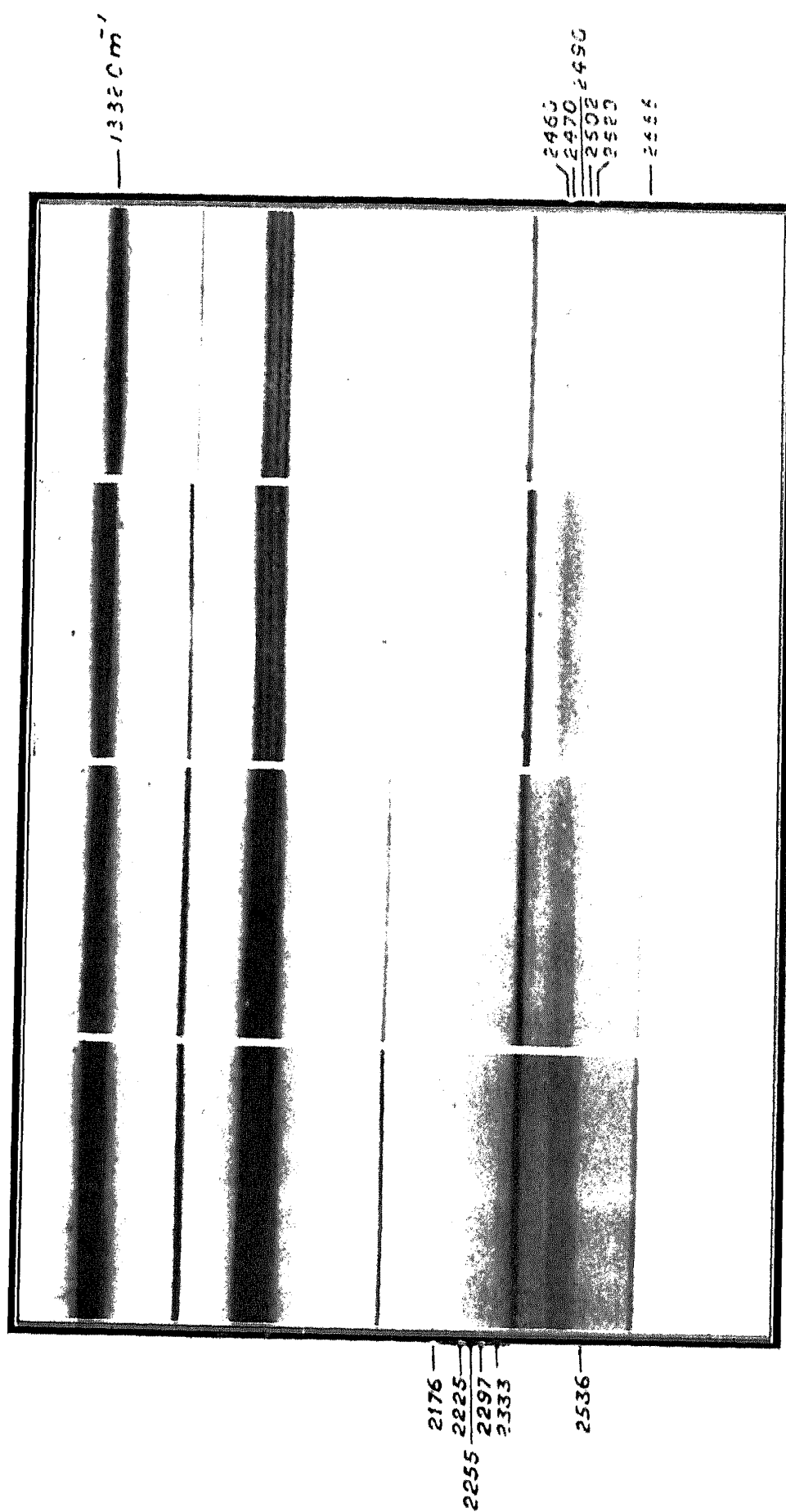


FIG. 1. Raman Spectrum of Diamond (Medium Spectrograph)

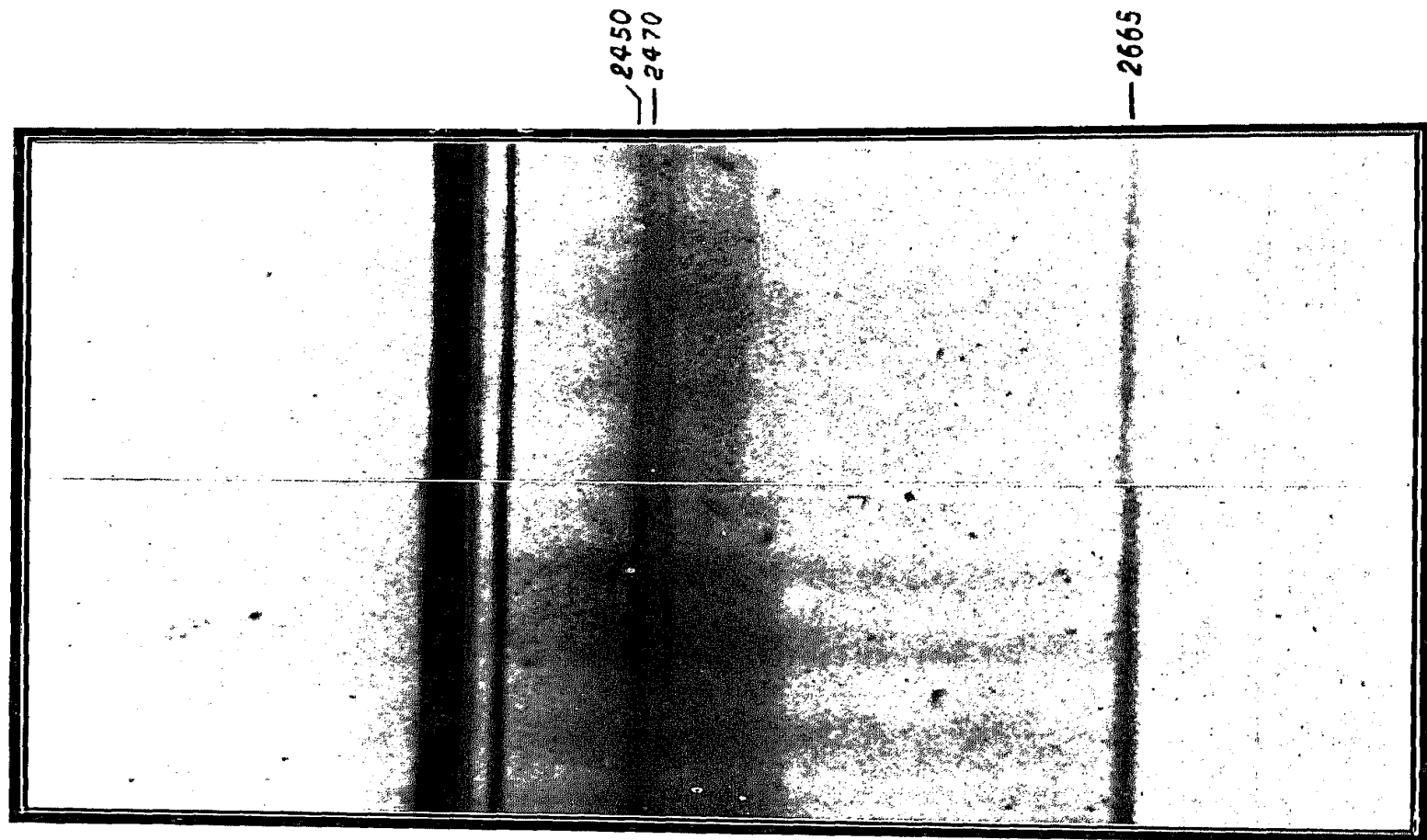


FIG. 2. Second-Order Raman Spectrum of Diamond
(Large Spectrograph)

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if they were, the second-order changes in polarisability and the resulting optical effects would vanish. In the Born-Karman lattice dynamics, each individual frequency is regarded as associated with a wave extending through the volume of the crystal. The amplitude of vibration in such a wave would necessarily be infinitesimal. Frequency shifts of the first order might arise as in the case of the coherent reflection of light waves by sound waves (Brillouin effect), but no effect of the second-order would be possible.

We can summarise the situation by stating that, if the basic ideas of the Born-Karman lattice dynamics were valid, no crystal could give frequency shifts in light scattering corresponding to the octaves and combinations of its fundamental frequencies of vibration. Many crystals, however, have been observed to exhibit second-order Raman spectra. It is reasonable to conclude from this that the fundamental ideas of the Born-Karman theory are incompatible with the observed facts of light scattering in crystals.

The author wishes to express his sincere thanks to Prof. R. S. Krishnan for his constant help and encouragement.

SUMMARY

From microphotometric studies of the Raman spectrum of diamond, the distribution of intensity in it has been derived. The spectra themselves exhibit much observable fine structure, including several sharply-defined and intense lines. The intensity curve also exhibits steep drops to zero near the frequency shifts 2176 and 2665 cm^{-1} . These facts are discussed and it is shown that the features mentioned, as also the appearance of second-order Raman spectra generally with crystals, are irreconcilable with the Born-Karman theory of lattice vibrations.

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