

# The infra-red absorption by diamond and its significance—Part IX. The activity of the normal modes

SIR C V RAMAN

Memoir No. 129 of the Raman Research Institute, Bangalore-6

Received December 19, 1961

## 1. Introduction

In the preceding parts of this memoir, the infra-red behaviour of diamond in its relation to other observable properties has been fully set out, and the free vibrations of its structure have also been adequately discussed. We now proceed to consider the explanation of the one in terms of the other. Various questions here arise which need an answer. Why is there any absorption of infra-red radiation in its passage through diamond? What part do the nuclei and the electrons in its structure respectively play in this phenomenon? Why do some diamonds exhibit infra-red absorption both of the first order and of the second order, and why do others exhibit only the second-order absorption? Why do the different normal modes exhibit very different infra-red activities and why do such activities differ respectively in the first-order and second-order absorption? What is the explanation of the relationships actually observed between the infra-red behaviour of diamond and such other properties as ultra-violet transparency and luminescence? It will be our purpose in the present part of the memoir to return answers to these questions.

## 2. The mechanism of infra-red absorption

The absorption of infra-red radiation in its passage through a crystal involves the conversion of the energy of the electromagnetic field into vibrational energy in the solid, in other words, its degradation into heat. The spectrographic records show that the absorption is preferential with respect to certain modes or frequencies of vibration. We naturally, therefore, turn our attention first to the movements of the atomic nuclei in the crystal and consider the action of the electric field of the incident radiation on the positive charges of these massive particles. Here, however, we find in all the normal modes of vibration, that for every nucleus

which is in oscillation, there is another nucleus which is a near neighbour and oscillates with the same amplitude but in an opposite phase. Hence, considering them together, the net transference of energy from the field to the nuclei would be a vanishing quantity. In other words, the atomic nuclei do not play the primary role in infra-red absorption, and we have to recognise the electrons or negative charges in the crystal as the active agents in that process. The field of the radiation disturbs the electrons and their movements result in the nuclei being disturbed from their positions of equilibrium and set into vibration. But it is the electronic movements associated with such vibrations and not the movements of the nuclei themselves which react with the field and result in the absorption of the incident radiation.

From what has been stated, it follows that in seeking for an explanation of infra-red activity, we have to fix our attention on the movements of the electronic charge-clouds in the crystal. It is the symmetry of the distribution of the negative electric charge in its undisturbed state as well as when it is modified by the nuclear movements which determines the appearance or non-appearance of infra-red absorption and its actual magnitude when observed.

### 3. The second-order absorption spectrum

Since all diamonds exhibit the absorption spectrum of the second-order, it is appropriate that we first consider how such absorption arises. We may, for the present, leave out of consideration the mode of highest frequency and discuss the infra-red activity of the other modes of vibration of lower frequencies. It is a specific feature of all these modes that the alternate layers of nuclei located at the points of the same lattice oscillate in opposite phases. Hence the electrons attached to the nuclei in those layers would also oscillate in opposite phases. Hence, it might be thought that the displacements of electric charge when summed up would vanish and hence that these vibrational modes would fail to exhibit any infra-red activity. But this conclusion is subject to an important qualification, viz., the movements considered are of infinitesimally small amplitude. When this is no longer the case, the approach of any two layers towards each other and the recession of the next two layers from each other would not necessarily produce equal displacements of electric charge. Their difference would represent the resultant displacement of charge and this would evidently be periodic with *twice the frequency* of the vibrational mode. It follows that there could, in favourable circumstances, be an absorption of radiation having *double the frequency* of each of the vibrational modes under consideration. This, to put it briefly, is the explanation of the absorption spectrum of the second order exhibited by all diamonds.

Infra-red activity of the second-order demands that the normal mode under

reference should result in the negative charges suffering displacements of substantial magnitude. Whether this is actually the case would depend upon the nature of the vibration. When we compare the different normal modes with each other from this point of view, it becomes evident that their infra-red activity would be very different in the different cases. Indeed, we could without difficulty group the modes in the order of the strength of the infra-red activity which they might be expected to display.

Consider, for example, modes VIII and IX which have the two lowest frequencies, viz.,  $746$  and  $624\text{ cm}^{-1}$  respectively. These movements are tangential respectively to the cubic and the octahedral layers and do not involve any changes in the lengths of the valence bonds between the carbon atoms. In these circumstances, it is not to be expected that they would result in any substantial displacements of electric charge. In mode IX, the layers which move laterally with respect to each other are farthest removed, while the layers which are closer move together. Hence, this mode could exhibit no observable activity. Mode VIII is a slightly different case, since the oscillating layers are not so far apart. Hence it might exhibit a very feeble infra-red activity of the second-order.

In striking contrast with the two modes of the lowest frequency are modes V and VI which have a common frequency of  $1087\text{ cm}^{-1}$ , and mode VII which has a frequency of  $1010\text{ cm}^{-1}$ . Modes V and VI are oscillations of the cubic layers, while mode VII is an oscillation of the octahedral layers, in both cases in directions normal to themselves. These modes involve changes in the lengths of the valence bonds as well as changes in the bond angles and adjacent atomic layers alternately approach and recede from each other along their common normal. Hence we should expect these modes to exhibit infra-red activity of the second-order in a high degree.

Mode IV which has a frequency of  $1176\text{ cm}^{-1}$  stands in a category by itself. It resembles mode VII in being an oscillation of the octahedral layers normal to themselves, but differs from it by reason of the fact that the layers which are close to each other move together and only the layers which are farthest apart alternately approach and recede from each other. In consequence, only one bond length out of the four changes its length periodically and all the bond angles remain unaltered. In these circumstances, we may indeed expect displacements of charge which would give rise to absorption of the second-order, but they would necessarily be very much smaller than in the case of the modes V, VI or VII.

Finally, we may consider modes II and III whose frequencies are respectively  $1273\text{ cm}^{-1}$  and  $1219\text{ cm}^{-1}$ . These are tangential oscillations of the octahedral and cubic layers respectively, but they involve changes of bond lengths as well as of bond angles. It follows that these modes would give rise to substantial displacements of electric charge. But their infra-red activity would necessarily be weaker than those of the modes VI and VII where the movements are normal to the layers concerned.

The foregoing remarks may be regarded as an interpretation or elucidation of

the actually observed features of the second-order spectrum of diamond described and illustrated in the seventh part of this memoir.

#### 4. Infra-red activity of the first order

We shall now proceed to consider the activity of the principal mode of vibration having the highest frequency which is manifested by the perfect diamonds. Expressed in wave-numbers, this frequency is shown by studies on the scattering of light to be  $1332\text{ cm}^{-1}$ . This is also the value exhibited in the first-order absorption spectrum. The feature which distinguishes this mode from the several others of lower frequencies is that the vibrations appear in the same phase in the successive cells of the structure along its axes and not alternately in opposite phases as in these other modes. As a consequence, the effects arising from the individual cells of the structure are coherent and cumulative and the observable result attains large values. We may illustrate this remark by reference to the case of magnesium oxide which has been thoroughly investigated and reported on by the author in a recent publication. MgO has a cubic structure resulting from the interpenetration of two rhombohedral lattices occupied by Mg and O respectively. The highest fundamental frequency of vibration of the MgO structure is  $490\text{ cm}^{-1}$ . The absorbing power at the corresponding wavelength of  $20.4\ \mu$  is so extremely large that radiations of that wavelength incident on the crystal are totally reflected. To exhibit the absorption spectrum of MgO in the wavelength region between  $15\ \mu$  and  $24\ \mu$ , it is found necessary to use specially prepared films in which the absorption path does not exceed  $3\ \mu$ . On the other hand, the second-order absorption spectrum of MgO appearing in the wavelength region between  $10\ \mu$  and  $15\ \mu$  is readily recorded with plates whose thickness may be as great as one millimetre. It is evident from this that the first-order absorption of MgO is enormously more powerful than the absorption of the second-order.

Diamond, on the other hand, does not exhibit any enhanced reflecting power in the region of wavelengths between  $7.5\ \mu$  and  $10\ \mu$ , and the fact that we can use plate thicknesses of a millimetre or more in studying its absorption spectrum in this range of wavelengths is a clear indication that the first-order absorption is extremely weak. That it is, however, not a spurious effect due to defects of structure or extraneous impurities is made abundantly clear by the facts set forth earlier in this memoir. In particular, it should be mentioned that though the first-order is weak, it is not weaker than the second-order absorption. The constancy of the relative strength of the first and second-order absorption spectra in numerous specimens of perfect diamond, and the fact that the same vibrational modes which are manifested in the first-order appear with doubled frequencies in the second-order is a clear indication that the first-order absorption exhibited by the perfect diamonds is a fundamental property of such diamonds.

The case of MgO mentioned above serves as a useful pointer in other respects

as well. The powerful infra-red activity of the first-order which MgO exhibits is a consequence of the two interpenetrating lattices in its structure carrying atoms which are different. In the case of diamond, on the other hand, the nuclei located at the points of the two interpenetrating lattices are identical. But, as has already been remarked, what we are here concerned with are the symmetry properties of the distribution of negative electric charge in the crystal. As the two lattices are constituted of nuclei carrying the same positive charge, any suggestion that one of the lattices carries a larger share of the electronic charge-cloud than the other can be ruled out immediately. Not only is such a situation inherently improbable, but it would also have consequences which are disproved by the facts of the case. Any lack of symmetry in the density of the charge distribution as between the two lattices would result in an enormously more powerful first-order absorption than that actually observed. All that we can legitimately infer from the observed infra-red behaviour is that in the structure of the diamonds which exhibit the first-order absorption, the electronic configuration, meaning thereby the variables which specify the state of the electrons in the crystal, including especially the orientations of their spins, do not conform to the requirements of octahedral symmetry, whereas in the diamonds in which the first-order absorption is absent, these requirements are satisfied.

The foregoing may be summed up by the statement that the electronic states in perfect diamonds possess only the lower or tetrahedral symmetry of the cubic class, while in the non-luminescent class of diamond they have the higher or octahedral symmetry. The situation here recognised enables us to understand the very significant relationship which is observed between the spectroscopic behaviour of diamond in regions of the spectrum which are so far apart as the infra-red between  $7\ \mu$  and  $12\ \mu$  and the ultra-violet between  $0.2\ \mu$  and  $0.3\ \mu$ . If the differences in infra-red behaviour are ascribable to differences in the electronic configuration, corresponding differences are necessarily expected in the ultra-violet absorption spectra. It also becomes intelligible why the diamonds of group A and group B exhibit contrasting behaviours in respect of luminescence. Absorption of the incident radiation is a *sine qua non* for its re-emission in a modified form which is termed luminescence. Whereas diamonds of group A do absorb radiation in the near ultra-violet, group B diamonds are transparent to such radiations. It is, therefore, not surprising that group A diamonds exhibit luminescence whereas group B diamonds do not.

It may also be remarked that the inference from the infra-red data that group A diamonds possess only tetrahedral symmetry of the electronic configuration whereas group B diamonds exhibit the full octahedral symmetry receives massive support from the well-established facts regarding the crystal morphology of diamond, as well as from the phenomena of X-ray diffraction in diamond. But it would take us too far from our present theme to enter into these matters in detail. We therefore now return to a discussion of the details of the first-order absorption spectrum.

## 5. Characters of the first-order spectrum

As has been amply illustrated by the spectrographic records reproduced in the earlier parts of this memoir, one of the remarkable features of the first-order absorption is the sudden change from a high degree of transparency to complete or nearly complete opacity occurring at the characteristic frequency of  $1332\text{ cm}^{-1}$  or wavelength  $7.5\ \mu$ . At lower frequencies or longer wavelengths, the absorption shows a progressive diminution and ceases to be significant beyond  $12\ \mu$ . The curve of the percentage transmission between these wavelengths represents the effect of the movements of the electronic charge-clouds in the crystal excited by the incident radiation. The changes in its course at various points indicate the influence of the nuclear vibrations of lower frequencies. The activity of these modes in the first-order absorption rapidly decreases as the difference between their frequencies and the frequency of the active fundamental of highest frequency increases. This indicates that the electronic linkages in the crystal result in a coupling between the various possible modes of vibration of the nuclei. A striking illustration of such a coupling is furnished by the astonishing intensity and sharpness of the absorption peak at  $7.3\ \mu$  or  $1370\text{ cm}^{-1}$ , which appears separated in the records from the steep increase in absorption at  $7.5\ \mu$  or  $1332\text{ cm}^{-1}$ . The absorption at  $1370\text{ cm}^{-1}$  is clearly the result of the summation of the two lowest frequencies ( $746\text{ cm}^{-1} + 624\text{ cm}^{-1}$ ) of the diamond structure. That it shows up in such a remarkable fashion is a consequence of its close approximation in frequency to the major absorption at  $1332\text{ cm}^{-1}$ . It is also an impressive demonstration that the vibrational modes which manifest themselves in the infra-red absorption of diamond have sharply defined monochromatic frequencies.

## 6. Summary

The features appearing in the second-order absorption of diamond are discussed and explained in terms of the periodic variations with doubled frequency of the electronic charge-density resulting from the nuclear vibrations. The origin of the first-order absorption spectrum exhibited by the perfect diamonds is also discussed. The observed facts indicate that the electronic states in these diamonds possess only tetrahedral symmetry, while in the diamonds which do not show the first-order absorption exhibit the full octahedral symmetry.