

The infra-red absorption by diamond and its significance—Part VII. The characteristic frequencies

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1. Introduction

The four largest plates of diamond in the author's collection are roughly circular or oval in shape and have a superficial area of about 3 square centimetres each. Their thickness ranges between 1.1 and 1.5 millimetres. By recording their transmission curves in the range between 2μ and 12μ at the very slow speed of 10 minutes per μ of wavelength, very satisfactory records have been obtained which are reproduced in the text respectively as figures 1, 2, 3 and 4, these being arranged in the order of the increasing thickness of the plate. It should be mentioned that these plates are not perfect diamonds in the sense in which these words were used in the third part of the memoir. For, they exhibit a birefringence pattern. Tests for ultra-violet transparency however indicate that they resemble the perfect diamonds somewhat in their behaviour and this is also evident from their infra-red transmission records. We shall accordingly proceed to find from these records the eight characteristic frequencies of vibration of the structure of diamond, reserving for a later part of this memoir a discussion of the activities of these modes in respect of infra-red absorption of various orders.

As has already been explained in the previous parts of the memoir, the first-order absorption spectrum of diamond makes its appearance at 7.5μ and extends towards greater wavelengths. Likewise, the second-order absorption commences at 3.75μ and continues towards the region where the first-order appears. The quantitative relationships between the two orders enable us to recognise and identify the normal modes which give rise to the observed features and to determine their frequencies with considerable precision.

2. The first-order absorption

The infra-red records leave us in no doubt whatever regarding the vibrational mode of the highest frequency. In figure 3, this manifests itself as a sudden fall of

the transmission percentage from 50% at $7.4\ \mu$ to complete opacity at $7.48\ \mu$ followed by a small rise in transmission to 5% at $7.5\ \mu$, after which it diminishes again. The other figures also indicate that this absorption may be located at $7.5\ \mu$. Expressed in wave-numbers, this is $1332\ \text{cm}^{-1}$ which is also the frequency derived from studies on the scattering of light by diamond.

The position of the wavelength of the second maximum of absorption is not determinable with the same measure of precision. With thick diamond plates, the curve spreads out as it approaches the line of zero transmission. Hence, the position of this absorption peak is best determined from the records obtained with thinner plates. The mean derived from the records of several diamonds is $7.85\ \mu$ or in wave-numbers $1273\ \text{cm}^{-1}$.

Between $8\ \mu$ and $9\ \mu$, the records clearly show two other turning points, or maxima of absorption if we so choose to regard them. These may be placed at $8.2\ \mu$ and $8.5\ \mu$ respectively. In wave-numbers, these are $1219\ \text{cm}^{-1}$ and $1176\ \text{cm}^{-1}$ respectively. At greater wavelengths or lower frequencies, the transmission increases rapidly. There is an arrest in such increase between $9\ \mu$ and $9.2\ \mu$. At the latter wavelength, it becomes once again very rapid. If we take the dip at $9.1\ \mu$ to represent the characteristic wavelength, the characteristic frequency would be $1098\ \text{cm}^{-1}$. If, on the other hand, we take $9.2\ \mu$ where the curve has its greatest slope as the characteristic wavelength, the characteristic frequency would be $1087\ \text{cm}^{-1}$. At still greater wavelengths, the peak of absorption at $9.9\ \mu$ is sharply defined and the characteristic frequency can therefore be precisely stated as $1010\ \text{cm}^{-1}$.

3. The second-order absorption

There is a steep fall in transmission which is very conspicuous in the records and is particularly well shown by figure 3 and which commences at $3.75\ \mu$, or in wave-numbers $2666\ \text{cm}^{-1}$. This is just double the highest absorption frequency observed in the first order. We can therefore recognise this sudden increase in absorption of the second-order as the counterpart of the sudden increase observed in the first-order at $1332\ \text{cm}^{-1}$. This quantitative relationship demonstrates that the structure of diamond is itself responsible for the absorption spectra of both the first and the second-orders.

We have seen that in the first-order absorption the two highest characteristic frequencies of $1332\ \text{cm}^{-1}$ and $1273\ \text{cm}^{-1}$ are not fully resolved from each other, the steep rise which indicates the former joining up with the second practically over the whole of its course. Why this is so is a matter which will be considered later in this memoir. It is mentioned here for the reason if the absorptions due to these normal modes are not separated from each other in the first-order, we could scarcely expect that they would be seen clearly separated in the second-order. Following the steep increase in absorption which commences at $3.75\ \mu$ or

2666 cm^{-1} , there is an arrest at $4\ \mu$, and then a diffuse maximum at which we may locate at $4.1\ \mu$ or in wave-numbers $2439\ \text{cm}^{-1}$. This is exactly double the characteristic frequency of $1219\ \text{cm}^{-1}$ which we have recognised as the third of the series in the first-order absorption, thereby confirming its determination. The diffuseness of the absorption band having its deepest point at $4.1\ \mu$ would be explained by its overlap with the second-order absorption due to the modes of vibration whose frequencies as fundamentals have been located at $1332\ \text{cm}^{-1}$ and $1273\ \text{cm}^{-1}$ respectively.

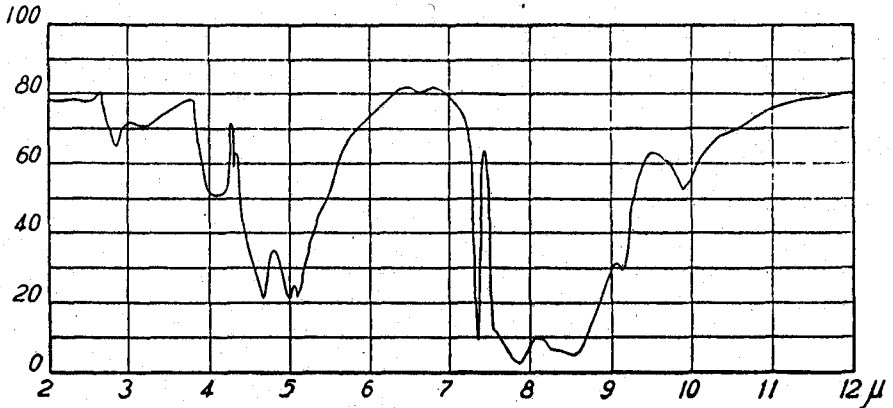


Figure 1. Percentage transmission by diamond; plate thickness 1.19 mm.

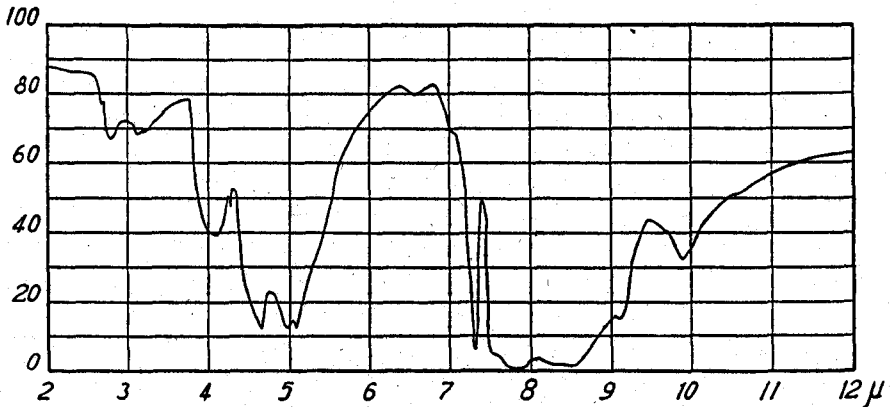


Figure 2. Percentage transmission by diamond; plate thickness 1.40 mm.

In all the four figures reproduced with this part of the memoir, a small but clear and sharply defined minimum of transmission appears between the $4.2\ \mu$ and $4.3\ \mu$

ordinates on the recording sheet. We may locate it as 4.25μ or 2352 cm^{-1} . This is very clearly the octave of the fourth characteristic mode which was located at 8.5μ or 1176 cm^{-1} in the first-order absorption, thus confirming the latter determination.

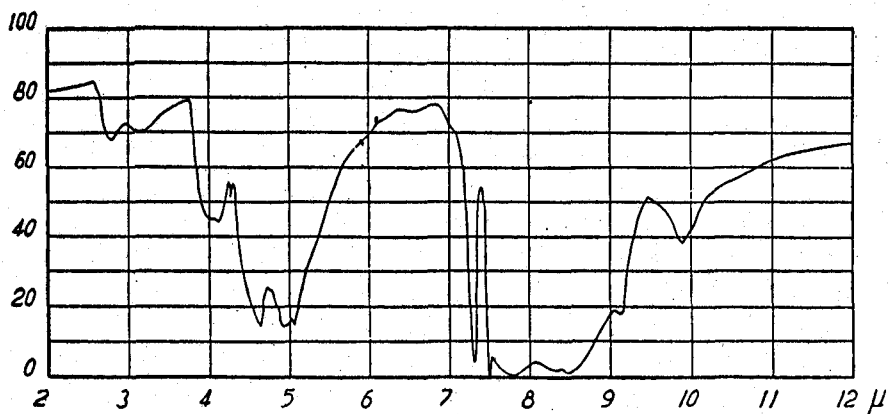


Figure 3. Percentage transmission by diamond; plate thickness 1.44 mm.

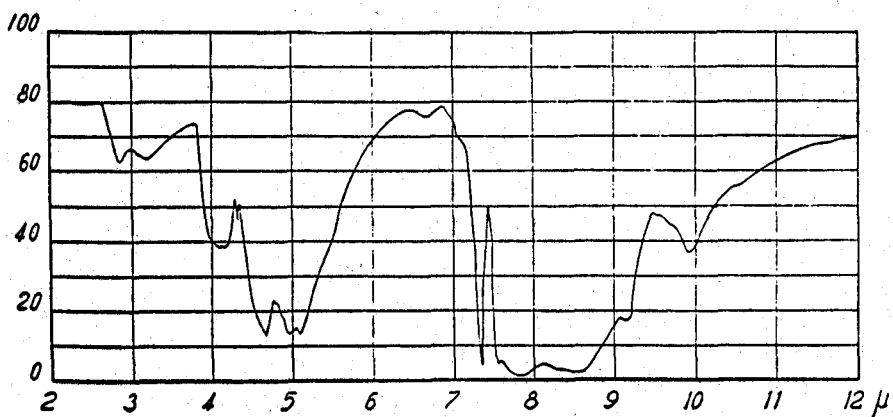


Figure 4. Percentage transmission by diamond; plate thickness 1.49 mm.

The sharply defined peak, located at 4.6μ , is the most striking feature in the records of the absorption spectra of all diamonds. Expressed in wave-numbers, this is 2173 cm^{-1} , half of which is 1087 cm^{-1} or 9.2μ when expressed as a wavelength. The wavelength at which the record of the first-order absorption has an inflexion point and exhibits its steepest fall is also 9.2μ . We are, therefore, justified in ascribing these features to the same normal mode which is responsible

for the extremely pronounced and sharp absorption peak located at 4.6μ in the second-order absorption. We accordingly recognise 1087 cm^{-1} as the fifth characteristic vibration frequency of diamond.

Another feature of the second-order absorption spectrum of diamond, quite as prominent as that considered above, is the minimum of transmission located at 4.95μ . Expressed in wave-numbers, this is 2020 cm^{-1} . This is clearly the octave of the sixth characteristic mode with its wavelength at 9.9μ or 1010 cm^{-1} already recognised in the first-order absorption. The sixth characteristic frequency of diamond of 1010 cm^{-1} is thus firmly established.

We may sum up the foregoing by the statement that the first six characteristic frequencies of diamond expressed in wave-numbers are 1332, 1273, 1219, 1176, 1087 and 1010 cm^{-1} respectively. They appear as fundamentals in the first-order absorption and with doubled frequencies in the second-order, thereby confirming the existence of the respective normal modes and enabling their frequencies to be specified with precision.

4. The seventh and eighth normal modes

In the preceding part of this memoir it was shown that the seventh and eighth normal modes would have frequencies distinctly lower than those of the other six modes by reason of the circumstance that they do not involve any changes in the length of the valence-bonds between the carbon atoms. For the same reason also, their activity in infra-red absorption should be low. Thus, it becomes a question whether any evidence would be forthcoming for the existence of these modes in the records of infra-red absorption.

The manifestation of the first six characteristic frequencies in the transmission curves is accompanied by a rapid decrease in absorption as we proceed from 7.5μ towards longer wavelengths. Indeed, the absorption at 12μ is quite small. Hence, if the seventh and eighth characteristic frequencies are lower than 850 cm^{-1} it is scarcely to be expected that their presence would be detectable in the first-order absorption spectrum. It is thus in the second-order absorption and not in the first that we should look for evidence of their presence.

Referring to the region between 6μ and 7μ in the four spectrographic records reproduced in figures 1 to 4 above, one finds in each case a small but quite definite dip in the curve of absorption of a few per cent which is located at 6.7μ , in other words at 1492 cm^{-1} . Since all the higher characteristic frequencies appear doubled in the second-order absorption, we may reasonably assume that this dip also represents the seventh characteristic mode appearing in absorption with doubled frequency. Accordingly, we recognise 746 cm^{-1} as the seventh fundamental frequency of vibration of diamond.

Recognising 746 cm^{-1} as the seventh fundamental, it becomes possible to give an acceptable explanation for other features noticed in the spectrographic

records. In the absorption spectra of all diamonds, we find that the peak at $5\ \mu$ appears doubled. The major component appearing at $4.95\ \mu$ or $2020\ \text{cm}^{-1}$ has already been recognised above as the double of the sixth characteristic frequency. The other component of the peak located at $5.09\ \mu$, in other words at $1965\ \text{cm}^{-1}$, receives a reasonable explanation as a summation of the third and seventh characteristic frequencies ($1219\ \text{cm}^{-1} + 746\ \text{cm}^{-1} = 1965\ \text{cm}^{-1}$). The appearance of this summation is clearly the result of its close approximation in frequency to the octave of the sixth fundamental which is strongly active in the second-order absorption.

Finally, we come to the explanation of the amazingly strong and sharp absorption peak at $7.3\ \mu$ noticed in all the four spectrographic records reproduced above. Recognising this absorption located at $1370\ \text{cm}^{-1}$ as a summation of the seventh and eighth fundamental frequencies, the latter comes out as $624\ \text{cm}^{-1}$. The exceptional characters of this absorption are clearly the result of its close approximation in frequency to the fundamental at $1332\ \text{cm}^{-1}$ which exhibits similarly surprising characters.

5. Summary

The absorption spectra of four exceptionally large plates of diamond which were recorded in the NaCl range of the infra-red spectrograph have been critically studied and analysed. From the study it emerges that the structure of diamond has eight characteristic frequencies of free vibration which are respectively 1332, 1273, 1219, 1176, 1087, 1010, 746 and $624\ \text{cm}^{-1}$.