Proc. Indian Acad. Sci. **A55** 36–41 (1962)

The infra-red absorption by diamond and its significance—Part VIII. Dynamical theory

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

Received December 12, 1961

1. Introduction

In the sixth part of this memoir, it was shown by dynamical reasoning of a very simple and general character that the structure of diamond possesses eight distinct monochromatic frequencies of free vibration. These modes were fully described and exhibited in figures. They were also listed in a table in the descending order of their frequencies in so far as such arrangement could be inferred from the geometry of the modes and its relation to the tetrahedral configuration of the valence-bonds of carbon.

In the foregoing or seventh part of the memoir, the actual values of the eight characteristic frequencies were determined by a study of the spectrographic records of the infra-red absorption by diamond. It is clear, however, that the association of these frequencies with the respective normal modes indicated by the dynamical theory requires further justification. It is necessary, in the first place, to show by further development of the dynamical theory that the normal modes do possess the frequencies actually exhibited in the spectrographic records. It would further be necessary to justify the individual assignments by considering the activity of the respective modes in the absorption of infra-red radiation and comparing it with the facts of observation. Reserving the latter task for the next part of the memoir, we shall proceed to consider the theoretical evaluation of the frequencies of the normal modes.

2. The first approximation

The dynamical problem with which we are concerned is very simple. We have only to write down the equations of motion of one single nucleus in the crystal, taking into account its interactions with the surrounding nuclei. The nucleus considered and the interacting nuclei have all the same amplitude and direction of movement, while the phases of movement are all either the same or opposite. The

solution of the equations of motion for the nucleus considered gives the frequency of the normal mode. The different modes differ in their frequencies by reason of the differences in the direction in which the nuclei oscillate in relation to the structure of the crystal, as also by reason of the phases of movement being different. The evaluation of the forces acting on any particular nucleus by reason of its displacements relative to the surrounding nuclei is the essence of the problem. If the resultant of these forces is known, the frequency of vibration can be written down immediately.

The interactions between two nuclei may be defined by considering the components of the relative displacement of the two nuclei and of the force of interaction between them resolved along the cubic axes of the structure and specifying the ratios of the components of force and displacement, otherwise known as the force-constants. The most important internuclear forces are evidently those arising from the displacement of the nucleus under consideration relative to the four nuclei with which it is bonded in a tetrahedral configuration by the valence forces.

The high symmetry of the structure of diamond results in all cases in a very considerable reduction in the number of force-constants appearing in the equations of motion. For instance, only two force-constants are needed to express the interactions with the four nearest neighbours. We may denote them by α and β respectively; α refers to the case in which the force and the displacement are both along the same cubic axis, while β refers to the case in which they are mutually perpendicular. The equations of motion in which α and β and the mass m of the carbon nucleus appear may be readily written down and solved. As the procedure is very simple, it will be sufficient here to set out the formulae giving the eight distinct frequencies thus obtained.

Mode I	$4\pi^2\nu_1^2c^2m$	$=4\alpha$
Mode II	$4\pi^2\nu_2^2c^2m$	$=(3\alpha+\beta)$
Mode III	$4\pi^2\nu_3^2c^2m$	$=(2\alpha+2\beta)$
Mode IV	$4\pi^2\nu_4^2c^2m$	$=(\alpha+2\beta)$
Mode V and VI	$4\pi^2\nu_{5,6}^2c^2m$	$=2\alpha$
Mode VII	$4\pi^2\nu_7^2c^2m$	$=(3\alpha-2\beta)$
Mode VIII	$4\pi^2\nu_8^2c^2m$	$=(2\alpha-2\beta)$
Mode IX	$4\pi^2\nu_9^2c^2m$	$=(\alpha-\beta)$

The formulae can be simplified further if the ratio α/β is regarded as known. For example, we may take α/β equal to 2, which is a reasonable assumption. All the eight frequencies can then be expressed in terms of a single constant. To find this, we may base ourselves on the frequency of mode I which is known to be $1332\,\mathrm{cm}^{-1}$ and then proceed to evaluate the other frequencies. We thus obtain the results shown in table 1. The calculated frequencies are all of the right order of magnitude. But they are systematically smaller than the observed values. The

Table 1. Mode and frequencies
$\alpha = 3{\cdot}14 \times 10^5$ dynes/cm $\beta = 1{\cdot}57 \times 10^5$ dynes/cm

Modes	Frequency (cm^{-1}) Calculated	Frequency (cm^{-1}) Observed
I	1332	1332
II	1246	1273
III	1153	1219
IV	942	1176
V & VI	942	1087
VII	942	1010
VIII	666	746
IX	471	624

reason for this is clearly to be found in our neglect of the interactions of each nucleus with its more distant neighbours.

3. The second and third approximations

The agreement between the calculated and observed frequencies can be improved by taking into account the interactions between the particular nucleus and the twelve other nuclei which are its next nearest neighbours and are all situated at the same distance from it. All these twelve neighbours are located at the points of the same rhombohedral lattice as the nucleus under consideration. They move together with it in mode I and hence in the expression for the frequency of that mode, their interactions do not appear. The position is different with regard to the other modes listed in table 1. In every one of the latter modes, the nuclei in the alternate cubic or octahedral layers of the structure oscillate in opposite phases and hence the interactions between the nuclei located in the same lattice necessarily appear in the equations of motion. A single additional constant γ suffices to express these interactions, but it appears multiplied by different numerical factors (2 or 4 or 8) for the different modes. The formulae for the frequencies as thus corrected are given below:

Mode I	$4\pi^2\nu_1^2 cm$	$= 4\alpha$
Mode II	$4\pi^2\nu_2^2 cm$	$= 3\alpha + \beta + 2\gamma$
Mode III	$4\pi^2\nu_3^2 cm$	$= 2\alpha + 2\beta + 4\gamma$
Mode IV	$4\pi^2\nu_4^2 cm$	$= \alpha + 2\beta + 8\gamma$
Modes V and VI	$4\pi^2\nu_{5,6}^2 cm$	$= 2\alpha + 8\gamma$
Mode VII	$4\pi^2\nu_7^2 cm$	$= 3\alpha - 2\beta + 8\gamma$
Mode VIII	$4\pi^2\nu_8^2 cm$	$= 2\alpha - 2\beta + 4\gamma$
Mode IX	$4\pi^2\nu_9^2 cm$	$= \alpha - \beta - 2\gamma$

The interactions of each nucleus with the twelve other still more distant neighbours can be similarly taken care of by introducing still another constant which now appears (multiplied by a numerical factor which may be 1 or 2 or 3 or 4 as the case may be) in all the equations of motion and the formulae for the frequencies derived therefrom. These formulae are:

Mode I	$4\pi^2\nu_1^2c^2m$	$= 4\alpha + 4\delta$
Mode II	$4\pi^2\nu_2^2c^2m$	$= 3\alpha + \beta + 2\gamma + \delta$
Mode III	$4\pi^2\nu_3^2c^2m$	$= 2\alpha + 2\beta + 4\gamma + 2\delta$
Mode IV	$4\pi^2\nu_4^2c^2m$	$= \alpha + 2\beta + 8\gamma + 3\delta$
Modes V and VI	$4\pi^2\nu_{5,6}^2c^2m$	$= 2\alpha + 8\gamma + 2\delta$
Mode VII	$4\pi^2\nu_7^2c^2m$	$= 3\alpha - 2\beta + 8\gamma + \delta$
Mode VIII	$4\pi^2\nu_8^2c^2m$	$= 2\alpha - 2\beta + 4\gamma + 2\delta$
Mode IX	$4\pi^2\nu_9^2c^2m$	$= \alpha - \beta + 2\gamma + 3\delta$

4. Comparison of the calculated and observed frequencies

Whereas table 1 shows the frequencies calculated on the basis of a single constant, table 2 exhibits the results of the calculation with three constants and table 3 with four. The values of α used are the same in tables 1 and 2 and also the same as the value of $(\alpha + \delta)$ in table 3. The constants β and γ used in the three tables are also not very different. Hence, the improved agreement which is apparent between the calculated and observed frequencies is very clearly the result of taking the interactions with 4, 16 and 28 neighbours into account respectively in the three cases. It is worthy of special remark that whereas the calculated frequencies of modes IV, V, VI and VII are all the same in table 1, they show a small progressive

Table 2. Modes and frequencies
($\alpha = 3{\cdot}14 \times 10^5$ dynes/cm; $\beta = 1{\cdot}64 \times 10^5$ dynes/cm and $\gamma = 0{\cdot}26 \times 10^5$ dynes/cm)

Modes	Frequency (cm^{-1}) Calculated	Frequency (cm^{-1}) Observed
I	1332	1332
II	1279	1273
III	1224	1219
IV	1096	1176
V & VI	1087	1087
VII	1077	1010
VIII	746	746
IX	534	624

Table 3. Modes and frequencies
($\alpha = 2{\cdot}78 \times 10^5$; $\beta = 1{\cdot}75 \times 10^5$; $\gamma = 0{\cdot}25 \times 10^5$;
$\delta = 0{\cdot}36 \times 10^5$ dynes/cm)

Modes	Frequency (cm^{-1}) Calculated	Frequency (cm^{-1}) Observed
I	1332	1332
II	1244	1273
III	1233	1219
IV	1150	1176
V & VI	1081	1087
VII	1008	1010
VIII	731	746
IX	607	624

fall in table 2, but only in table 3 do they actually fall into line with the observed frequencies.

We are thus fully justified in inferring from the results of these calculations that the characteristic frequencies determined by a study of the spectroscopic records are actually the frequencies of the normal modes of vibration of the structure of diamond deduced from the dynamical theory.

5. Summary

The eight characteristic frequencies of vibration of the structure of diamond are theoretically evaluated in the first, second and third approximations, taking successively into account the interactions of each nucleus with its 4, 16 and 28 neighbours. A satisfactory agreement emerges between the calculated frequencies and those observed spectroscopically.