ELECTRONIC AND VIBRATIONAL LEVELS OF THE NAPHTHALENE CRYSTAL AND MOLECULE

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The studies by I.V. Obreimow and collaborators of the spectra of crystals were based upon the following simple considerations. Since the interaction forces in molecular crystals are weak, the corresponding spectra—especially at low temperatures—should reproduce the gas spectrum with the following modifications: 1) the lines of purely electron transitions can be shifted, 2) the rotational structure of gas bands should disappear completely, and 3) low frequencies inherent to the crystal can appear instead.

These speculations can be verified by comparing the gas and crystal spectra directly. We did it for a typical molecular crystal, naphthalene. For this purpose, we had to photograph the naphthalene vapor spectrum once again.

By comparing the naphthalene crystal spectrum obtained at the liquid hydrogen temperature with the gas spectrum, we unexpectedly arrived at the following result. The crystal spectrum turned out to contain new line series, as well as single lines and bands which have no analogs in the gas spectrum, in addition to all those lines present in the vapor spectrum. The first two of three electron transitions at 29941, 31062, and 31960 cm^{-1}, which were definitely established by the coincidence of absorption and fluorescence lines [1], and the first of two electron transitions expected to exist at 31630 and 33736 cm^{-1} (according to some indirect considerations [1, 2]) have no counterparts in the gas spectrum.

Vapor Spectrum

We recorded the absorption spectrum of naphthalene vapor once again. The absorbing layer thickness was 17 or 100 cm. The spectrum features turned out to be different from those of the spectrum obtained by Henri and Laslo [3], and this fact deserves a different interpretation. In the range under examination, the spectrum is formed by two electron transitions from the ground state into excited ones: $\nu'_{\mathrm{I}} = 32455$ cm^{-1} and

$\nu'_{\mathrm{II}} = 35900$ cm^{-1}. Each of them combines with its own set of vibrational frequencies:

a) ν'_{I} combines with frequencies of 473, 703, 1002, 1181, 1415 (703 × 2), 1449, and 1603 cm^{-1}; the Raman scattering frequencies, which are close to them, are weakly intense, and they have no clearly defined recurrences in the spectrum;

b) only two frequencies combine with ν'_{II}: 500 and 1397 cm^{-1}; the adjacent Raman scattering frequencies are intense; both frequencies have clearly defined recurrences and combinations.

The rotational structure of vibrational bands cannot be resolved into separate lines even in the photographs obtained with high dispersion (a Hilger E$_1$ spectrograph). One can observe only the intensity beats formed by the aggregates of individual rotational lines. The bands are "red-tinted", which means an increase of the molecule's moment of inertia when the molecule is excited by light.

Classification of Crystal Spectrum Lines

The classification of lines in the crystal spectrum is more complicated, and it can be carried out by several signs such as 1) line polarization, 2) the presence of lines in the absorption and fluorescence spectra, 3) comparison with the gas spectrum, and 4) general line attributes such as width, intensity, *etc.*

Naphthalene crystals are monoclinic (Fig. 1). They are sublimated from vapor in the form of leaflets which can be very thin (fractions of micron). Two crystallographic axes lie in the leaflet plane: b is the monoclinic axis of the crystal, and a is the axis perpendicular to b. When light passes through the crystal transversely to the leaflet plane, there can propagate two oscillations, along the a-axis and along the b-axis. These two oscillations correspond to two polarized spectral components: a and b. Some spectral lines are observed only in the a-component, these are a-lines; others are observed only in the b-component, these are b-lines and
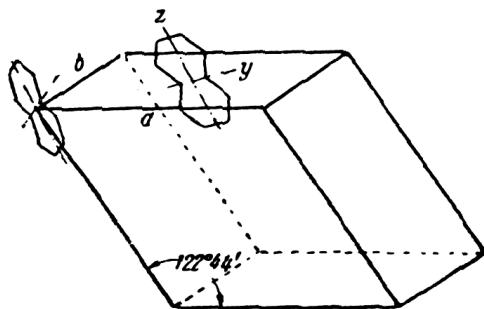
Fig. 1. Scheme of a naphthalene crystal

B-bands. Finally, some spectral lines are observed simultaneously in both components, these are weakly polarized lines. As a rule, the *b*-lines are more intense than the *a*-lines.

The comparison of the crystal and gas spectra shows, first of all, that the crystal spectrum has no rotational structure at all, and the bands are not "red-tinted". The crystal spectrum has a specific shape which is due to the following reasons: a part of crystal spectrum lines can be classified into certain series, whereas other lines, which are much more numerous, do not form series, but they group together around the serial lines. These satellite lines lie not only on the short-wave side from the main serial line, but also on the long-wave side. Satellite lines can easily be classified by their general attributes. They are very narrow, they are less intense than the main lines, and their polarization is rather strong. In addition to satellite lines which can be associated only with crystal lattice vibrations, the crystal spectrum also demonstrates a continuous absorption background, which is more intense near the serial lines. The corresponding intensification range is confined by satellite lines and low-frequency lines.

Secondly, the serial lines of the crystal spectrum form series of two categories: 1) the series belonging to the first category resemble gas series and 2) the series belonging to the second category have no analogs in the gas spectrum.

Indeed, only two of all the crystal spectrum series can be easily and unambiguously confronted with the two above-mentioned series of the vapor spectrum. One of them starts from the line of a purely electron transition at $\nu'_I = 31955$ cm^{-1} which can be found in the fluorescence spectrum as a weak double line at 31960–31965 cm^{-1}; the other starts from the line at $\nu'_{II} = 33736$ cm^{-1} which is absent in the fluorescence spectrum.

The frequency ν'_I combines with vibrational frequencies of 455, 718, 992, 1143, 1191, 1393, 1431 (718×2), and 1577 cm^{-1}; the adjacent Raman scattering frequencies are not intense, except for a frequency of 1384 cm^{-1}. These vibrations have no pronounced recurrences.

The frequency ν'_{II} combines only with two vibrations, at 518 and 1389 cm^{-1} which have pronounced recurrences and combinations. The adjacent Raman scattering frequencies are quite intense.

In the crystal, the transition ν'_I is red-shifted by 500 cm^{-1}, as compared to that in the gas, and the transition ν'_{II} is red-shifted by 2164 cm^{-1}.

The similarity between the gas and crystal spectra is confined only to the two above-described series. The other lines and bands in the crystal spectrum have no analogs in the gas spectrum, being *characteristic of the crystal state.*

The crystal's serial lines of this second category can be subdivided into three series. The most intense series is associated with the shortest-wave transition in the crystal, the frequency of the first line in this long series being $\nu'_3 = 33441$ cm^{-1}. It combines with many frequencies of intramolecular vibrations, the most distinct frequencies being 212, 408, 518, 658, 909, and 1383 cm^{-1}. These vibrations have pronounced recurrences and combinations, especially those at 518 and 1383 cm^{-1} which are close to the intense Raman scattering lines at 512 and 1384 cm^{-1}.

The serial lines of this category also include the first two purely electron transitions in the crystal, $\nu'_1 = 29941$ cm^{-1} and $\nu'_2 = 31062$ cm^{-1}, which were mentioned above. In fact, their structure is more complicated. In the fluorescence spectrum, the transition at 29941 cm^{-1} is represented by a weak double line at 29941–29936 cm^{-1}. In the absorption spectrum, the both lines are visible, but in different components: the a_1-line ($\nu = 29931$ cm^{-1}) is very weak, while the b_1-line ($\nu = 29944$ cm^{-1}) is sharp and distinct. They are both observed only in the thick crystal (1–1.5 mm), being therefore weak. This transition is accompanied by weak lines of intramolecular vibrations which are visible only in the *b*-component. The most intense of them are the lines at 400, 724, 1282, and 1383 cm^{-1}.

The transition at 31062 cm^{-1} is the main transition in the fluorescence spectrum, where it is accompanied by numerous intramolecular vibration frequencies with excellent recurrences and combinations. Its lines are also strongly polarized in the absorption spectrum: the b_2-line ($\nu = 31063$ cm^{-1}) is visible only in the *b*-component,

whereas the a_2-line ($\nu = 31050$ cm^{-1}) can be observed only in the a-component. This transition is more intense than the transition $\nu_1' = 29944$–29931 cm^{-1} but is still classified as a weak one. The relevant frequencies of intramolecular vibrations are absent in the spectrum.

A-lines and B-bands

Two groups of lines and bands observed only in either of the components (i.e., those with very strong polarization) should be classified into the second category as well. These are the A-lines and B-bands of the crystal spectrum. The B-bands are distinguished among other crystal lines by their polarization, shape, and very high intensity. They are continuous bands (within the adopted limits of dispersion) with sharp edges. These bands and their complex structure are clearly seen in the crystals thicker than fractions of a micron. Neither A-lines nor B-bands have analogs in the fluorescence spectrum. In the absorption spectrum, they stand apart and are not related to one another by means of usual intramolecular vibration frequencies. Their origin can be associated only with certain electron states of the crystal. The A-lines have the following frequencies: $\nu = 31474$ cm^{-1} (A_1-line) and $\nu = 32227$ cm^{-1} (A_2-line). The edge frequencies of B-bands in the thinnest crystal are 31603 and 31638 cm^{-1} (the red edge and the blue edge of the B_1-band, respectively), and 32241 and 32270 cm^{-1} (the red edge and the blue edge of the B_2-band, respectively).

Conclusions

Figure 2 shows the level diagrams for the naphthalene crystal and a naphthalene molecule in a gas. The diagrams were plotted by analyzing the corresponding spectra. Thin horizontal bars, which correspond to the vibrational states of the given level, are drawn above thick horizontal bars, which correspond to electron transitions. The states peculiar to the both gas spectrum and crystal spectrum are connected by oblique lines. All other levels are observed only in the crystal spectrum. Figure 2 also demonstrates the polarization of these levels.

The spectrum formed by the transitions from the normal state of the crystal into various excited states shown in the diagram consists of series of two types:

1) The series belonging to the first category are formed by weakly polarized lines which have close
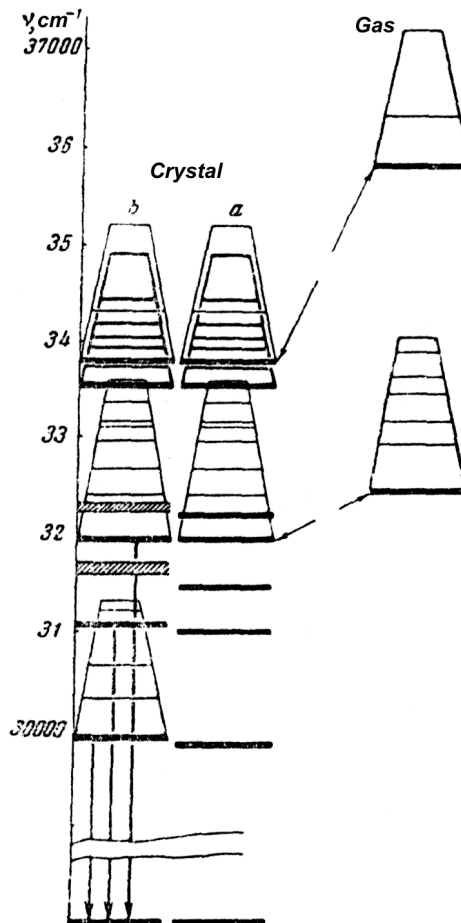

Fig. 2. Level diagrams for the naphthalene crystal and a naphthalene molecule in a gas

resemblance to the corresponding gas series. Such a similarity and a weak polarization imply that these lines are determined by the *symmetry of a naphthalene molecule*. The ratio of their intensities in the crystal can be obtained by projecting the molecule polarization vectors $\mathbf{p}_x$ and $\mathbf{p}_y$ on the a- and b-axes of the crystal.

2) The series belonging to the second category are formed by purely crystal lines which have no analogs in vapor. The lines of these series are polarized very strongly, except for the short-wave series, whose polarization is not evident. These lines are determined by the *symmetry of the crystal*.

The classification of lines on the basis of their polarization can be made not only for a special case of naphthalene but also for other crystals of aromatic series. Hence, it represents a general phenomenon for the crystals of this type. That is why this fact can probably be taken as a foundation for determining the crystal

structure and the arrangement of molecules in crystals on the basis of spectral data.

The possibility of the splitting of molecular levels into strongly polarized components in the crystal was considered by A.S. Davydov [4] and in our study on the light dispersion in anthracene crystals.

1. I.V. Obreimow and C.G. Shabaldas, J. Phys. **7**, 168 (1943).
2. A. Prikhotjko, J. Phys. **8**, 257 (1944).
3. V. Henri and H. Laslo, Proc. Roy. Soc. **105**, 662 (1924).
4. A.S. Davydov, Zh. Eksp. Teor. Fiz. **18**, 210 (1948).

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In the 20-th century, a new direction in solid state physics, the physics of excitons in nonmetallic crystals, was discovered and substantiated. The merit of creation and development of this new direction belongs to the author of the paper given above, Antonina Fedorivna Prikhot'ko. In 1944–1948, when studying the low-temperature spectra of naphthalene single crystals in polarized light, she observed the doublets of highly polarized absorption bands which were absent from the spectra of free molecules (see the text of the paper). It was the first experimental confirmation of the existence of collective currentless excited states in molecular crystals, excitons. The concept of exciton was introduced by Ya.I. Frenkel in his theoretical works in 1931. The large cycle of experimental (by A.F. Prikhot'ko) and theoretical (by A.S. Davydov) researches allowed a complete picture of elementary excitations (excitons) in molecular crystals to be created. They play an important role not only in solid state physics, but also in chemistry, biology, and so on.

Antonina Fedorivna Prikhot'ko was Academician of the NAS of Ukraine, the Hero of Socialist Labor, and the winner of the Lenin's Prize and the State's Prize of Ukraine.