

THEORETICAL REMARKS ON ABSORPTION AND EMISSION BANDS IN CRYSTALS AT LOW TEMPERATURES

BY

P. EHRENFEST

The absorption and fluorescence bands of compounds of the UO_2 radical and of crystals containing the rare earths provide typical examples of the simplification which physical phenomena so often undergo when the thermal motion of the molecules is decreased. While these bands are broad and blurred at room temperature, they are resolved on cooling, as is well known, into a number of lines which at the temperature of liquid hydrogen sometimes become narrower than, for example, the D-lines.¹⁾

If one now considers several details which appear, from the viewpoint of modern ideas on the radiation and absorption of light on the one hand and on thermal vibrations of crystal lattices on the other hand, problems arise which cannot indeed be satisfactorily solved at the moment, but which even without being solved can still provide points of view for further study of the details mentioned above. I may, consequently, offer several remarks about them here.²⁾

1. According to Bohr every optical phenomenon (absorption, fluorescence, phosphorescence, etc.) is connected with the transition of a system from one quantized motion to another. In our case the magnitude of the energy change which appears, $\varepsilon'' - \varepsilon'$, and consequently also the frequency of the monochromatic radiation belonging to the phenomenon,

$$\nu = (\varepsilon'' - \varepsilon')/h, \quad (1)$$

will be influenced by the fact that the optically active electron is in the middle of a crystal lattice. It is desirable for the time being to consider two sorts of influences as separate, although it is also possible to unite both kinds under a single viewpoint:

A. The Stark effect arising from the electric fields of neighboring atoms (compare in this connection the explanation of the "pressure-broadening" of spectral lines in gases).

B. The possibility that energy is taken up from the thermal vibrations of the crystal lattice in the absorption and fluorescence phenomenon (compare the explanation of the band spectra of gases).

Effect B already deserves our particular attention because it may be

¹⁾ Jean Becquerel, *Le Radium* 4 (1907), p. 328; Jean Becquerel and H. Kamerlingh Onnes, *Comm. No. 103, Versl. Ak. Amsterdam*, Febr. 1908; Henri and Jean Becquerel and H. Kamerlingh Onnes, *Comm. No. 110, Versl. Ak. Amsterdam*, April 1909.

²⁾ I should like to refer here to the beautiful and interesting exposition by P. Pringsheim: "Fluoreszenz und Phosphoreszenz im Lichte der neueren Atomtheorie", Chapter VIII.

that with its help one can succeed in investigating the vibrations of the crystal lattice and their connection with quantum theory in much more detail than is possible by means of the dependence of the specific heat on temperature.

2. Influence A must always lead to a broadening of the lines whenever the various electrons are in statistically different fields of neighboring atoms at the moment they participate in the optical phenomenon.

Since the thermal motion means a disturbance of the order of the lattice, this sort of line broadening must appear in every crystal if only the temperature is raised sufficiently high; one can expect it even at low temperatures in solutions and glassy substances.

3. So far as influence B is concerned one can say that the vibrational energy of essentially any arbitrary fundamental vibration of the crystal lattice can be absorbed in the optical transition. In agreement with this the formula for the frequency ν of all possible absorption and emission phenomena should read:

$$h\nu = E'' - E' + \sum_i (p_i'' - p_i') h\omega_i. \quad (2)$$

$E'' - E'$ here signifies the energy difference of the electronic motions before and after the transition; ω_i is the frequency of an arbitrary fundamental vibration of the crystal lattice; p_i'' and p_i' are the quantum numbers of this vibration before and after the optical phenomenon occurs.³⁾

We have not taken account of certain complications in this formula for the frequencies ν of the various lines in order to have a result which can be easily surveyed; namely we have omitted terms which contain products or squares of the p 's or which describe an interaction between crystal vibrations and electronic motion which depends on the intensity of the motion. These terms are, however, of importance for the *intensity* of the lines. For the existence and the relative intensity of the various "combination tones" in the Fourier expansion of the electronic motion are based on the non-linearity of the forces and on the interaction mentioned, and according to Bohr's correspondence principle it is just the presence or absence of these combination tones which determines whether the quantum jumps, i.e. the lines, corresponding to them are present or not.

An absorption or emission line given by formula (2) corresponds to a combination tone

$$\cos \{ \Omega t + \sum_i (p_i'' - p_i') \omega_i t \} \quad (3)$$

in the Fourier expansion of the electronic motion.

In order to avoid too many details we have assumed here that, apart from lattice vibrations, the electron simply carries out a periodic motion of frequency Ω , and that its quantum number changes by no more than one. Otherwise more Ω 's should appear in (3) and indeed multiplied by various

³⁾ We quantize the fundamental vibrations in the usual way here, although it is to be hoped that this formal treatment can soon be replaced by a more natural one.

integers, namely by the differences in the quantum numbers associated with them.

4. The displacements of neighboring atoms in the crystal lattice with respect to each other are much smaller, other things being equal, for slow vibrations than for the fastest ones whose wavelength is already about as small as the lattice spacing. The following are therefore to be expected only for these fastest vibrations:

- a. large deviations from Hooke's law and
- b. intense mutual combination tones, in particular with
- c. the frequency Ω of the electronic motion.⁴⁾

According to the correspondence principle, however, it follows from this that

α . in equation (2), quantum jumps for which $p''_i - p'_i$ is considerably greater than one occur only for lattice vibrations of the highest frequencies,

β . and only for these vibrations do the quantum numbers change jointly in the same optical phenomenon, or

γ . do they change simultaneously with the quantum number of the electron.

The quantum number of the electron must undergo a change in every case when one is concerned with lines in the visible or the ultraviolet spectrum. According to γ however, $p''_i - p'_i$ is then equal to zero in equation (2) for all but the fastest lattice vibrations; moreover, α and β lead to still further simplifications of (2).

5. Effect B, i.e. the absorption of energy from the lattice vibrations in optical phenomena, is particularly clear for the fluorescence spectra of crystalline compounds of the uranyl radical UO_2 . One sees the characteristic details in these spectra recur again and again with a constant frequency difference $\Delta\nu$, where this $\Delta\nu$ has approximately the same value for all UO_2 compounds (850 cm^{-1} in round numbers). This reminds one very clearly of the corresponding phenomenon in the band spectra of gases, and one can indeed assert with certainty that one is concerned here with the participation of *the vibrations within the UO_2 radical* in the optical transition.

At low temperatures it appears that that which repeats again and again with a spacing $\Delta\nu$ is a group of different lines whose spacing (from each other) is approximately $\delta\nu \cong 180 \text{ cm}^{-1}$.

One probably needs more observational material in order to attain a more reliable explanation of the origin of these lines. These groups of lines are very similar to one another in related UO_2 compounds, apart from a systematic displacement.⁵⁾ A change in the percentage of water of crystal-

⁴⁾ Joint translational vibrations of neighboring atoms with a frequency which is small with respect to the frequency of revolution of the electrons give rise to no appreciable combination tones with the latter. One easily sees this by remembering an analogous case: suppose that the sun is moved to and fro with a frequency which is small compared to the frequency of revolution of a planet. Here too the combination tones will be missing in the planet's motion.

⁵⁾ E. L. Nichols and H. L. Howes, Phys. Rev. 11 (1918) p. 285.

lization, on the other hand, already causes considerable deviations.⁶⁾

6. Little is known yet about the question of whether a line which one sees recur repeatedly over the whole fluorescence spectrum with a spacing $\Delta\nu \cong 850 \text{ cm}^{-1}$ also recurs with this same interval in the region of the absorption spectrum.

Nichols thinks he has found ⁷⁾ that this recurrence of mutually analogous lines in the absorption spectrum takes place with a spacing $\Delta\nu \cong 710 \text{ cm}^{-1}$. Such a contrast between absorption spectra and fluorescence spectra will surely not be easy to explain. And yet this important question must be cleared up before one can try with any chance of success to give an explanation of several other interesting details such as, for example, the course of the relative intensities of the various lines in their successive repetitions in the fluorescence spectrum. It is to be hoped that one will be able to demonstrate a connection with the very important fact ⁸⁾ that the absorption and the anomalous dispersion of various absorption lines in the spectra of rare earths first increase as the temperature is decreased and then decrease again after passing through a maximum, the temperature of this maximum being different for different lines.

The following remark is obvious: a definite absorption line can appear only when electrons are in a definite quantum state initially. The relative populations depend on the temperature. One or another definite quantum state whose energy is not too small will be missing at $T = 0$, and then appear as the temperature is increased, and finally become rarer at still higher temperatures (in favor of states with still higher energy).

7. Bohr's correspondence principle puts us in a position to formulate especially sharply the conditions under which the situation appears in its simplest form; namely, when the "combination tones" with the lattice vibrations occur in as simple and transparent a way as possible in the Fourier expansion of the electronic motion. The factors favorable to this are, first, as simple and fully analyzable a crystal structure as possible; further, that the optically active electrons of the absorbing atoms be not on the surface of the atoms but more to their interior (according to Bohr, atoms with incomplete inner shells of electrons, typical examples of which are just the rare earth ions characterized by strong paramagnetism and ionic absorption in the visible spectral region); and finally, naturally, temperatures as low as possible.

One can expect that, particularly at low temperatures, the different series of fluorescence lines can be excited by monochromatic irradiation to some extent independently of each other, and in this way the most reliable analysis and explanation of the phenomena will become possible.

⁶⁾ E. L. Nichols and E. Merritt, *Phys. Rev.* **9** (1917) p. 113.

⁷⁾ See Reference (5), p. 295.

⁸⁾ Jean Becquerel and H. Kamerlingh Onn l.c. § 4. "Intensity maximum of each band for a definite temperature."