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Abstract

Full Text

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DETERMINATION OF THE NATURE OF AN ELEMENTARY EMITTER FOR ABSORPTION AND EMISSION OSCILLATORS WHOSE DIRECTIONS DO NOT COINCIDE

Investigations of polarized luminescence, carried out at various angles to the direction of the exciting light and for various directions of oscillation of the electric vector of the exciting light, make it possible, as was shown by S. I. Vavilov ([1]), to determine the nature of the elementary acts of absorption and emission of light by a substance; subsequently this method was developed in the works of P. P. Feofilov ([2], [3]). The method can be applied not only to determine the nature of absorption and emission oscillators arranged parallel to one another, but also to those rotated relative to one another by some angle α.

If we introduce a coordinate system XYZ such that the electric vector of the exciting light beam coincides in direction with the axis OZ, then the degree of polarization when observed along the axis OY will be

$$P = \frac{I_z - I_x}{I_z + I_x}.$$

The subscripts on I indicate the direction of oscillation of the electric vector in the corresponding components of the luminescence flux.

Let us rotate the electric vector of the exciting light beam together with the coordinate system relative to the line of observation through an angle η. Then the observed degree of polarization as a function of the angle η is represented in the form

$$P = \frac{I_z \cos^2 \eta + I_y \sin^2 \eta - I_x}{I_z \cos^2 \eta + I_y \sin^2 \eta + I_x}. \tag{1}$$

The components I_x, I_y, and I_z are different for different multipoles.

A straightforward, but rather cumbersome, calculation gives the expression for the degree of polarization as a function of the angles α and η for the case of absorbing and emitting electric dipoles

$$e \to e: \qquad P = \frac{3\cos^2\alpha - 1}{3 + \cos^2\alpha} \frac{\cos^2\eta}{1 + \dfrac{3\cos^2\alpha - 1}{3 + \cos^2\alpha}\sin^2\eta}. \tag{2}$$

Similarly, for the cases: electric dipole–quadrupole

$$e \to q: \qquad P = \frac{3\cos^2\alpha - 1}{5 - \cos^2\alpha} \frac{\cos^2\eta}{1 + \dfrac{3\cos^2\alpha - 1}{5 - \cos^2\alpha}\sin^2\eta}; \tag{3}$$

electric quadrupole–dipole

$$q \to e: \qquad P = -\frac{3\cos^2\alpha - 1}{5 - \cos^2\alpha} \frac{\sin^2\eta}{1 + \dfrac{3\cos^2\alpha - 1}{5 - \cos^2\alpha}\cos^2\eta}; \tag{4}$$

electric quadrupole–quadrupole

$$q \to q: \qquad P = -\frac{5\cos^4\alpha - 3\cos^2\alpha}{4\cos^4\alpha - 3\cos^2\alpha + 3} \frac{\sin^2\eta}{1 + \dfrac{5\cos^4\alpha - 3\cos^2\alpha}{4\cos^4\alpha - 3\cos^2\alpha + 3}\cos^2\eta}; \tag{5}$$

magnetic dipole–dipole

$$m \to m: \qquad P = -\frac{3\cos^2\alpha - 1}{3 + \cos^2\alpha} \frac{\sin^2\eta}{1 - \dfrac{3\cos^2\alpha - 1}{3 + \cos^2\alpha}\cos^2\eta}; \tag{6}$$

magnetic dipole–electric dipole

$$m \to e: \qquad P = \frac{3\cos^2\alpha - 1}{3 + \cos^2\alpha} \frac{\sin^2\eta}{1 - \dfrac{3\cos^2\alpha - 1}{3 + \cos^2\alpha}\cos^2\eta}; \tag{7}$$

electric dipole–magnetic dipole

$$e \to m: \qquad P = -\frac{3\cos^2\alpha - 1}{3 + \cos^2\alpha} \frac{\cos^2\eta}{1 - \dfrac{3\cos^2\alpha - 1}{3 + \cos^2\alpha}\sin^2\eta}. \tag{8}$$

Putting in formulas (2), (3), and (8) $\eta = 0$, and in formulas (4), (5), (6), and (7) $\eta = \pi/2$ (the usual conditions for measuring the degree of polarization), we obtain

$$e \to e: \ P_0 = \frac{3\cos^2\alpha - 1}{3 + \cos^2\alpha}, \tag{2'}$$

$$e \to q: \ P_0 = \frac{3\cos^2\alpha - 1}{5 - \cos^2\alpha}; \tag{3'}$$

$$q \to e: \ P_0 = -\frac{3\cos^2\alpha - 1}{5 - \cos^2\alpha}; \tag{4'}$$

$$q \to q: \ P_0 = -\frac{5\cos^4\alpha - 3\cos^2\alpha}{4\cos^4\alpha - 3\cos^2\alpha + 3}. \tag{5'}$$

The formula for $m \to e$ is the same as $(2')$, while the formulas for $m \to m$ and $e \to m$ differ from $(2')$ only in sign.

Expression $(2')$ is the well-known formula obtained by F. Perrin [(6)] and V. L. Levshin [(5)], relating the observed degree of polarization to the angle between the absorbing and emitting electric dipoles. Formulas $(3')$, $(4')$, and $(5')$ express the same dependence for the cases dipole–quadrupole, quadrupole–dipole, and quadrupole–quadrupole. These formulas make it possible, from the limiting polarization, to calculate the angles between the oscillators; however, it is first necessary to determine the nature of the oscillator, which, as far as we know, has not previously been done (this is especially important when, under the usual conditions of observing polarization, the degree of polarization is close to zero, since in this case it is possible that a quadrupole is responsible for absorption).

As is known, the limiting value of the degree of polarization under horizontal observation, in the case of absorbing and emitting electric dipoles coinciding in direction, is $P_0 = 1/2$, and $P_0 = 1/3$ for mutually perpendicular dipoles. P_0 is always equal to zero under vertical observation of polarization. In other cases, as is seen from Table 1, the limits of variation of P_0 depending on the observation conditions are entirely different.

Table 1

P_0 for different multipoles at different values of the angle α

Fig. 1

Figure 1: Fig. 1

Observations	$e \to e$, $\alpha = 0$	$e \to e$, $\alpha = \frac{\pi}{2}$	$q \to q$, $\alpha = 0$	$q \to q$, $\alpha = \frac{\pi}{2}$	$e \to q$, $\alpha = 0$	$e \to q$, $\alpha = \frac{\pi}{2}$	$q \to e$, $\alpha = 0$	$q \to e$, $\alpha = \frac{\pi}{2}$	$m \to m$, $\alpha = 0$	$m \to m$, $\alpha = \frac{\pi}{2}$	$m \to e$, $\alpha = 0$	$m \to e$, $\alpha = \frac{\pi}{2}$	$e \to m$, $\alpha = 0$	$e \to m$, $\alpha = \frac{\pi}{2}$
Horizontal	$1/2$	$-1/3$	0	0	$1/2$	$-1/5$	0	0	0	0	0	0	$-1/2$	$1/3$
Vertical	0	0	$-1/2$	0	0	0	$-1/2$	$1/5$	$-1/2$	$1/3$	$1/2$	$-1/3$	0	0

The formulas obtained, (2)–(8), make it possible to extend S. I. Vavilov' s proposed method of polarization diagrams for determining the nature of elementary emitters to the case of absorption and emission oscillators whose directions do not coincide.

Fig. 1

It is known that unambiguous conclusions about the multipolarity of an emitting system can be drawn only when the limiting polarization is greater than 1/3. For absorbing oscillators there are no such restrictions. Since in complex molecules the transition with emission always occurs between one and the same pair of electronic levels, irrespective of the absorption band in which the excitation of luminescence is produced, the nature of the emitting system obviously remains unchanged, whether we excite the luminescence in the long-wavelength absorption band or in the short-wavelength bands. Therefore, when determining the nature of the elementary oscillator in different regions of the absorption spectrum, the absorbing system will change, while the emitting system will remain unchanged. Thus, in all cases unambiguous conclusions may be drawn about the nature of the oscillators.

In practice it is convenient to use the formulas obtained by representing them graphically. Indeed, formulas (2)–(8), if the first factor is denoted by P_0, may be represented in the form

$$e \to e: \qquad \frac{1}{P} = \frac{1}{P_0} + \left(\frac{1}{P_0} - 1\right) \operatorname{tg}^2 \eta; \tag{2”}$$

$$e \to q: \qquad \frac{1}{P} = \frac{1}{P_0} + \left(\frac{1}{P_0} + 1\right) \operatorname{tg}^2 \eta; \tag{3”}$$

$$q \to e: \qquad \frac{1}{P} = -\frac{1}{P_0} = \left(\frac{1}{P_0} + 1\right) \operatorname{ctg}^2 \eta; \tag{4”}$$

$$q \to q: \qquad \frac{1}{P} = -\frac{1}{P_0} - \left(\frac{1}{P_0} - 1\right) \operatorname{ctg}^2 \eta; \qquad (5")$$

$$m \to m: \qquad \frac{1}{P} = -\frac{1}{P_0} - \left(\frac{1}{P_0} - 1\right) \operatorname{ctg}^2 \eta; \qquad (6")$$

$$m \to e: \qquad \frac{1}{P} = \frac{1}{P_0} + \left(\frac{1}{P_0} - 1\right) \operatorname{ctg}^2 \eta; \qquad (7")$$

$$e \to m: \qquad \frac{1}{P} = -\frac{1}{P_0} - \left(\frac{1}{P_0} + 1\right) \operatorname{tg}^2 \eta. \qquad (8")$$

If the values of $\operatorname{tg}^2 \eta$ or $\operatorname{ctg}^2 \eta$ are plotted along the abscissa axis, and $1/P$ along the ordinate axis, then these formulas are represented by straight lines (Fig. 1) with strongly differing directions. These differences in direction are substantial even if the maximum observed polarization is small (in the figures it has been taken equal to 15%). For $P_0 = 1/2$, these straight lines are mutually perpendicular.

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CITED LITERATURE

[1] S. I. Vavilov, *ZhETF*, **10**, 1363 (1940); Collected Works, **2**, 1952. [2] P. P. Feofilov, *DAN*, **55**, 407 (1947). [3] P. P. Feofilov, *DAN*, **44**, 159 (1944). [4] V. L. Levshin, *Photoluminescence of Liquid and Solid Substances*, Moscow–Leningrad, 1951. [5] V. L. Levshin, *Proceedings of FIAN*, **1**, 19 (1955). [6] F. Perrin, *Ann. de phys.*, **12**, 169 (1929).

Note: Figure translations are in progress. See original paper for figures.