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Abstract

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ON THE CLASSIFICATION OF SECONDARY LUMINESCENCE

1. As a result of interaction with atoms and molecules, the primary light flux is transformed into secondary luminescence, which to one degree or another bears the imprint of the properties of the substance under study. In some cases (complex molecules in solution, uranyl compounds, etc.) the properties of the secondary luminescence are completely determined by the properties of the substance transforming the light; in other cases (atoms, vapors of simple molecules) the properties of the secondary luminescence depend on the properties of the incident radiation.

According to their observed properties, all transformed light is divided into photoluminescence, Rayleigh scattering, and combination scattering. According to Vavilov (^{1}), luminescence is such luminescence as has a duration greater than the period of light oscillations and, consequently, is capable of being quenched. Conversely, scattering disappears (or arises) practically instantaneously after the cessation (or beginning) of the action of the exciting force. In accordance with this, it is also assumed that scattering is not quenched.

Vavilov’ s criterion, applied by him in two cases (by the capacity for quenching), made it possible to classify nonequilibrium emissions correctly (^{1}). This served as an experimental confirmation of the criterion. However, the literature contains no theoretical substantiation of Vavilov’ s classification; nowhere is it clarified how deeply this criterion reflects the essence of the process of light transformation.

2. Within the framework of classical theory, the question of the transformation of light is reduced to the analysis of the solution of the dipole equation (^{2})

$$\ddot{x} + 2(\gamma \quad + \gamma \quad)\dot{x} + \omega_0^2 x = \frac{e}{m} E_0 \cos \omega t. \qquad (1)$$

Here ω_0 is the natural frequency of the dipole, and γ and γ are damping coefficients due to radiative braking and interaction with the medium. If, at the moment the external field is switched on, the dipole was at rest, then, independently of the frequency of the irradiating light, the luminescence of the stationary regime is established not immediately, but after a time $t > 1/(2\gamma \quad +$

$2\gamma\ )$. In the stationary regime the dipole transforms light without change of frequency according to the law

$$I(\omega) \sim \frac{\omega^4 I_0(\omega)}{(\omega_0^2-\omega^2)^2+4(\gamma\quad+\gamma\ )^2\omega^2}, \tag{2}$$

where $I_0(\omega)$ and $I(\omega)$ are the intensities of the primary and secondary fluxes. It follows from this that the position and contour of the line of the transformed light depend strongly on the spectral composition of the irradiating line. If irradiation is carried out with a narrow line ($\Delta\omega \ll \gamma\quad+\gamma\ $), then the secondary line coincides with the primary one both in frequency and in contour ($I(\omega) \sim I_0(\omega)$). The ratio of emitted to absorbed energy determines the energy yield of dipole emission (^{2}):

$$B = \frac{\gamma}{\gamma\quad+\gamma}. \tag{3}$$

With increasing γ_{tr}, the yield decreases. However, this affects the intensity of the luminescence only near resonance; for $|\omega_0-\omega| \gg \gamma_{\mathrm{rad}}+\gamma_{\mathrm{tr}}$, according to (2), the intensity of the secondary luminescence does not depend on γ_{tr}, i.e., on the action of the quencher.

After the irradiation is stopped, the stationary luminescence described by (2) vanishes instantaneously ($I_0(\omega)=0$); instead, afterglow is observed, with duration $\tau = 1/(2\gamma_{\mathrm{rad}}+2\gamma_{\mathrm{tr}})$ and a spectrum of the form

$$S(\omega) \sim \frac{1}{(\omega_0-\omega)^2+(\gamma_{\mathrm{rad}}+\gamma_{\mathrm{tr}})^2}. \tag{4}$$

Here $S(\omega)$ is the energy of frequency ω emitted by the dipole during the entire time of afterglow. From comparison of (2) and (4) it follows that, in the general case, the spectrum of the stationary regime does not coincide with the afterglow spectrum. Only when irradiation is carried out with a broad line ($\Delta\omega \gg \gamma_{\mathrm{rad}}+\gamma_{\mathrm{tr}}$) and the frequency ω_0 falls inside the irradiating line do both spectra have one and the same form. But even in this special case the transformation of light proceeds essentially in the same way as in all other cases.

3. The results of the calculation obtained for the classical dipole are also contained in quantum electrodynamics. Along with this, quantum electrodynamics makes it possible easily to investigate other possibilities of the transformation of light. Consider, for example, an atom possessing three energy levels and interacting with the surrounding medium. The light transformed by such an atom in the stationary regime consists of three lines $^{(3)}$. In Fig. 1 the arrows denote the most probable processes. The length of the arrow indicates the frequency of the photon taking part in the given process. The direction of the arrow and the symbols attached

Fig. 1

Figure 1: Fig. 1

to it denote the transition of the atom (absorption of one photon of a given frequency may be associated with a transition to both the second and the third state). One of the lines of secondary light is obtained as the result of a transformation occurring without a change in the photon frequency: $\omega'' = \omega'$, where ω' is the frequency of the incident photon. The energy distribution in this line is described by the expression

Fig. 1

$$I_p(\omega'') \sim \left| \sum_{j=2,3} \left[\frac{d_{1j}^{(2)} d_{j1}^{(1)}}{-(\gamma_j^{(\text{rad})} + \gamma_j^{(\text{tr})}) + (\omega_{j1} - \omega'')} + \frac{d_{1j}^{(1)} d_{j1}^{(2)}}{\omega_{j1} + \omega''} \right] \right|^2 \omega''^4 I_0(\omega''), \quad (5)$$

where $d_{j1}^{(1)}$ and $d_{j1}^{(2)}$ are the matrix elements of the projections of the dipole moment onto the polarization direction of the incident and secondary photons, and $\gamma_j^{(\text{rad})}$ and $\gamma_j^{(\text{tr})}$ are the constants of radiative and nonradiative damping of the j-th level.

This line is characterized by properties almost coinciding with the properties of the classical line (2). Only such a line exists for a system with two levels.

The second line gives a transformation of light in which the frequencies of the secondary and primary photons differ by the atom’ s proper frequency:

$\omega'' = \omega' - \omega_{21}$. If the width of level 2 is small (the level is metastable), then the intensity of this line is determined by the formula

$$I_k(\omega'') \sim \left| \frac{d_{23}^{(2)} d_{31}^{(1)}}{-i(\gamma_3^{(\text{rad})} + \gamma_3^{(\text{tr})}) + (\omega_{32} - \omega')} + \frac{d_{23}^{(1)} d_{31}^{(2)}}{\omega_{31} + \omega''} \right|^2 \omega''^4 I_0(\omega'' + \omega_{21}). \quad (6)$$

As is seen from (5) and (6), the positions and contours of both lines depend strongly on the frequency and contour of the irradiating line. If the irradiating line is narrow ($\Delta\omega \ll \gamma_3^{(\text{rad})} + \gamma_3^{(\text{tr})}$), then, independently of the degree of resonance ($\omega' \simeq \omega_{31}$), their contour coincides with the contour of the primary line.

The third line (2 → 1) differs substantially from the first two. Its frequency and contour do not depend at all on the properties of the irradiating line and are determined only by the properties of the atom. The distribution of intensity within this line has the form:

$$I_l(\omega'') = \frac{D}{(\omega_2 - \omega'')^2 + (\gamma_2^{(\mathrm{rad})} + \gamma_2^{(\mathrm{tr})})^2}, \tag{7}$$

where D is, up to a factor, the integral intensity of the line (in general, depending on the excitation conditions). This line is a proper line of the atom.

After the irradiation is stopped, all the lines of the stationary regime (5), (6), and (7) disappear instantaneously (more precisely, at the rate at which the primary light is switched off). In their place, at the expense of the energy accumulated by the atom in the stationary regime, afterglow lines appear, which always belong to the proper lines of the atom. To each line of the stationary regime one may assign a definite share of the afterglow energy. In the general case, as in the classical theory, the afterglow spectrum corresponding to lines (5) and (6) does not coincide with the spectrum of the stationary regime. On the contrary, the afterglow corresponding to line (7) coincides exactly with it both in frequency and in the contour of the line. The integral intensity of line (7) decreases continuously according to an exponential law from its value in the stationary regime to zero.

By determining the quantum yields of lines (5), (6), and (7), one can show that an increase of $\gamma_j^{(\mathrm{tr})}$ leads to a decrease of the quantum yields, i.e., all lines of secondary light are quenched. However, there is a certain difference between the quenching of line (7) and the quenching of lines (5) and (6). A decrease of the quantum yield of line (7) is always associated with a decrease of its intensity. A change in the quantum yields of lines (5) and (6), however, as in the classical theory, is reflected in their intensities only in the case of resonance ($|\omega_{31} - \omega'|$ less than or comparable with $\gamma_3^{(\mathrm{rad})} + \gamma_3^{(\mathrm{tr})}$).

4. Theoretical analysis of the transformation of light by atoms (and simple molecules) shows that classification of this phenomenon according to the criterion of quenching is impossible if by quenching, as usual, one understands a decrease of the yield. Classification according to the duration of afterglow is ambiguous and can sometimes lead to incorrect results. If this criterion is understood literally, then every secondary luminescence should be assigned to photoluminescence, since every luminescence of a stationary regime has a definite afterglow corresponding to it. True, the afterglow spectrum does not always coincide (is well stitched) with the spectrum of the stationary regime. The "stitching" of the spectra may be used in classifying the phenomenon of light transformation.

As already noted, the properties of lines (7) differ substantially from the properties of lines (5) and (6). The frequency and contour of line (7) are determined only by the properties of the atom, as a result of which the corresponding afterglow line is well stitched with it. On the contrary, the spectral composition of lines (5) and (6) depends strongly on the frequency and contour of the irradiating line and, consequently, in the general case differs from the spectral composition of the afterglow. This difference

properties is the external expression of the fact that these lines arise as the result of processes that differ in their mechanism. In the formation of lines (5) and (6), no intermediate processes are interposed between the acts of absorption of the primary photon and emission of the secondary photon. Therefore both acts occur independently of one another, which is reflected in the strong connection between the primary and secondary photons. Conversely, the act of emission of the photons belonging to line (7) is separated from the act of absorption by the transition $3 \rightarrow 2$, accompanied by the emission of photons with the combination frequency $\omega' - \omega_{21}$. As a result of this intermediate process, any dependence of the properties of the secondary light on the properties of the primary light is lost.

Taking this into account, the phenomenon of light conversion may be classified as follows. Line (7) should be assigned to photoluminescence, and lines (5) and (6) to Rayleigh and combination scattering. Under nonresonant irradiation, the luminescence described by formulas (5) and (6) is undoubtedly scattering. In the case of resonance it becomes very intense. In this case line (5) is usually called "resonance radiation" or "resonance fluorescence," and line (6) "fluorescence" (4,5). It seems to us that the light conversion described by (5) and (6), in the case of resonance, should be called resonance scattering, since in essence (in the mechanism of the phenomenon) it differs in no way from light conversion in the nonresonant case. There are only external differences between them. The transition of resonance radiation into specular reflection with increasing vapor pressure (4,5) confirms the correctness of such a classification.

The properties of light converted by a classical dipole are analogous to the properties of the luminescence described by formula (5). Therefore the classical dipole makes it possible to describe only Rayleigh scattering.

5. As a result of interaction with the surrounding medium, atoms and simple molecules can change their state without losing the ability to emit light. Such intermediate processes lead to quenching of scattering and to a corresponding increase in the intensity of some photoluminescence lines. In complex molecules, along with this, there also occurs a rapid redistribution of the vibrational-rotational energy of the molecule over the degrees of freedom (2). Calculations show that, as a result of this, scattering is practically completely quenched, and therefore only photoluminescence is always observed.

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