SOVIET PHYSICS JETP VOLUME 1, NUMBER 3 NOVEMBER, 1955

Absorption and Emission of Light by a Gray Substance

B. I. STEPANOV
Institute of Physics and Mathematics of the Academy of Sciences of the Belorussian SSR, Minsk

(Submitted to JETP editor April 13, 1954)
J. Exper. Theoret. Phys. USSR **28**, 559-566 (May, 1955)

A phenomenological theory of the spectroscopic properties of a gray substance is constructed. The Einstein coefficients for absorption and for forced and spontaneous radiation are determined. An expression is obtained for the energy level distribution function. It is shown that a gray substance possesses properties closely resembling those of a classical electrodynamic system. A solution of the problem considered is essential for the explanation of the laws of absorption and emission of light by complex molecules.

1. From the point of view of the absorption and emission of light, complex molecules such as the molecules of dyes form an intermediate link between simple diatomic molecules and complex condensed systems, the radiation of which approximates in character that of a black body. The spectra of diatomic molecules are basically discrete and, what is especially important, strictly individual. The spectra of complex molecules also possess a certain individuality: the positions of the absorption and fluorescence bands are different for the various molecules. However, this individuality is extremely limited, since the intensity distribution in the long wave length absorption bands and in the fluorescence bands is the same in many molecules. Complex molecules also possess other important special characteristics. In them the laws of mirror symmetry of the absorption and emission bands are followed, the positions and forms of the emission bands are independent of the wave length of the existing light, and so forth[1,2].

The absence of specificity in the spectra of complex molecules is connected with the presence in such molecules of a very large number of oscillational degrees of freedom and with the very intimate interaction between them and the transfer of oscillational energy within the molecule. Nevertheless, there is conserved in them the basic division of the energy into electronic and oscillational, and also the specificity of the discrete electronic levels which is manifested in the existence of definite bands in the absorption and emission spectra.

The class of compounds to be treated here is different in principle, and consists of highly condensed systems, so-called gray bodies. In their absorption and thermal emission spectra there is no selectivity whatsoever; all wave lengths of incident radiation are absorbed equally, and the spectral composition of the radiation is just that of the equilibrium radiation, differing from it only in rate[3]. Fluorescence is absent in such bodies, since absorbed energy is quickly transformed into thermal energy. These features are connected with the very strong interaction between the electrons and the nucleus, as a consequence of which a division of the energy of the system into electronic and oscillational is completely inadmissible. We may speak only of the total energy of the system as a whole. In the present work we treat of the spectroscopic characteristics of a gray body --- the distribution function for the energy levels and the transition probabilities between them for absorption and emission of light. The solution of this problem will make possible the determination of these quantities in processes of emission and absorption of light by complex molecules.

2. We first consider a condensed substance (not necessarily gray) with a complex spectrum of allowed energy values and in thermal equilibrium. In view of the strong interaction of the various elements, it is impossible to distinguish in it isolated centers of absorption and emission --- it appears uniform. The Einstein coefficients must be related not to the atoms or molecules, but to a certain small volume v_0 of the substance under investigation. Let there be n such volumes in 1 cm^3. If the density of radiant energy within the substance

---

[1] B. S. Neporent, J. Exper. Theoret. Phys. USSR **21**, 172 (1951); Izv. Akad. Nauk SSSR, Ser. Fiz. **15**, 533 (1951)

[2] B. S. Neporent and B. I. Stepanov, Usp. Fiz. Nauk **43**, 380 (1951)

[3] Sh. Fabri, *Obshchee Vvedenie v Fotometriiu (General Introduction to Photometry),* ONTI, 1934

under investigation is equal to $u(\nu)$, then the number of quanta $h\nu$ in the frequency interval $d\nu$ that are absorbed in one second in the volume $d\tau$, with transitions from the levels E (in the interval dE) to the levels $E + h\nu$, is equal to

$$n\rho(E, T)\,dE\,B_{\text{abs}}(E, \nu)\,u(\nu)\,d\nu\,d\tau.$$

Here $B_{\text{abs}}(E, \nu)$ is the Einstein coefficient of the volume v_0 for the pair of levels E and $E + h\nu$, and $n\rho(E, T)\,dE$ is the number of volumes with energies in the interval from E to $E + dE$. The distribution function $\rho(E)$ has the usual form

$$\rho(E, T) = C(T)\,g(E)\,e^{-E/kT}, \tag{1}$$

where $g(E)$ is the statistical weight and $C(T)$ is a normalized constant. The total number of quanta absorbed during transitions from all levels E is equal to

$$nu(\nu)\,d\nu\,d\tau\int_0^\infty \rho(E, T)\,B_{\text{abs}}(E, \nu)\,dE.$$

The corresponding energy absorbed is

$$dE_{\text{abs.}} = nu(\nu)\,h\nu\,d\nu\,d\tau\int_0^\infty \rho(E, T)\,B_{\text{abs}}(E, \nu)\,dE. \tag{2}$$

If the substance is being acted on by radiant energy, then besides absorption there will always be forced emission. The energy of the forced emission is equal to

$$dE_{\text{em}}^{\text{forced}} = nu(\nu)\,h\nu\,d\nu\,d\tau\int_0^\infty \rho(E + h\nu, T) \times B_{\text{em}}(E, \nu)\,dE. \tag{3}$$

Here $B_{\text{em}}(E, \nu)$ is the Einstein coefficient for forced emission for transitions from the level $E + h\nu$ to the level E (the magnitude E referring always to the lower level). Since

$$B_{\text{em}}(E, \nu) = B_{\text{abs}}\,g(E)/g(E + h\nu), \tag{4}$$
$$\rho(E + h\nu, T) = C(T)\,g(E + h\nu)\,e^{-(E+h\nu)/kT},$$

then Eq. (3) is equal to

$$dE_{\text{em}}^{\text{forced}} = e^{-h\nu/kT}\,dE_{\text{abs}}. \tag{5}$$

For large values of $h\nu/kT$ the role of forced emission is insignificant, whereas for small values of $h\nu/kT$ it is very essential. During forced radiation the corresponding quantum is emitted in the direction of propagation of the incident quantum. As Frish[4] has emphasized, this circumstance allows one to consider forced emission as a special kind of "negative absorption". Experimentally, one measures not the magnitude dE_{abs} but the magnitude

$$dE'_{\text{abs}} = dE_{\text{abs}} - dE_{\text{em}}^{\text{forced}} \tag{6}$$
$$= (1 - e^{h\nu/kT})\,nu(\nu)\,h\nu\,d\nu\,d\tau\int_0^\infty C \times (T)\,g(E)\,e^{-E/kT}B_{\text{abs}}(E, \nu)\,dE.$$

The coefficient of proportionality a between the quantity of absorbed energy and the quantity of light energy $u(\nu)\,d\nu\,d\tau$ in the volume $d\tau$ is called, in accordance with the terminology of Frish, the absorption capacity. Thus

$$a(\nu, T) = \frac{dE'_{\text{abs}}}{u(\nu)\,d\nu\,d\tau} = n\left(1 - e^{-h\nu/kT}\right) \times h\nu\int_0^\infty C(T)\,g(E)\,e^{-E/kT}B_{\text{abs}}(E, \nu)\,dE. \tag{7}$$

Analogously to Eqs. (2) and (5) we can write an expression for the energy of spontaneous emission per second

$$dE_{\text{em}}^{\text{spont}} = nh\nu\,d\nu\,d\tau\int_0^\infty \rho(E + h\nu, T)\,A(E, \nu)\,dE = w(\nu, T)\,d\nu\,d\tau. \tag{8}$$

Here $w(\nu, T)$ is the (spontaneous) emissive power of the substance under investigation. Since

$$A = B_{\text{abs}}\,\frac{8\pi h\nu^3}{v^3}\,\frac{g(E)}{g(E + h\nu)},$$

then

$$w(\nu, T) = nh\nu\int_0^\infty \rho(E + h\nu, T)\,A(E, \nu)\,dE = a(\nu, T)\,\frac{8\pi h\nu^3}{v^3}\,\frac{1}{e^{h\nu/kT} - 1}. \tag{9}$$

---

[4] S. E. Frish, Usp. Fiz. Nauk **43**, 512 (1951); Vestn. Leningrad State Univ. **8**, 130 (1953)

3. We now consider a gray substance. We shall call a gray substance any substance whose absorption capacity is the same for all frequencies and whose radiation power is proportional to the radiation power of a black body*. From this it follows that

$$a(\nu, T) = n\left(1 - e^{-h\nu/kT}\right) \tag{10}$$

$$h\nu \int_0^\infty C(T)\, g(E)\, e^{-E/kT} B_{\text{abs.}}(E, \nu)\, dE = P,$$

where P is a certain constant. This equation, together with the normalization condition

$$\int_0^\infty C(T)\, g(E)\, e^{-E/kT} dE = 1 \tag{11}$$

can serve for the determination of the unknown function $B_{\text{abs}}(E, \nu)$. Making the substitution

$$B_{\text{abs}}(E, \nu) = P \frac{1}{nh\nu} B'(E) \tag{12}$$

in Eq. (10), we obtain

$$\left(1 - e^{-h\nu/kT}\right) \int_0^\infty C(T)\, g(E)\, e^{-E/kT} B'(E) = 1. \tag{13}$$

Equation (13) in conjunction with Eq. (11) has a solution only for high frequencies ($h\nu \gg kT$). In this case the factor ($1 - e^{-h\nu/kT}$) is equal to unity. An exact calculation shows that the solution is perfectly well defined:

$$B' = 1. \tag{14}$$

This same result may be obtained from simple qualitative concepts. Actually it follows from Eq. (12) that B' is independent of the temperature. If, taking account of this fact, we attempt to solve Eq. (13) in conjunction with Eq. (11) by way of the function $B'(E)$, then any function $B'(E)$ chosen so as to satisfy Eq. (13) for one temperature will not satisfy Eq. (13) for any other temperature.

Thus the solution of Eq. (10) for $h\nu \gg kT$ has the form

$$B_{\text{abs}}(\nu) = P/nh\nu. \tag{15}$$

The dependence of B_{abs} on ν has a simple significance. Actually in the equation

$$nB_{\text{abs}}(\nu)\, u(\nu)\, d\nu = P \frac{u(\nu)\, d\nu}{h\nu} \tag{16}$$

the left side is the number of quanta absorbed per unit volume per second. In the right member $u(\nu)d\nu/h\nu$ is equal to the number of quanta of the given frequency per unit volume. Hence for a gray substance with $h\nu \gg kT$ the number of quanta absorbed is proportional to the total number of quanta --- the probability of absorption being equal for quanta of any frequency. Since B_{abs} is independent of E, the probability of absorption of a quantum is also independent of the state of the body (its energy) at the instant of its interaction with the photon. Thus, for a gray substance, the probability of absorption of a quantum depends neither on the properties of the substance (E), nor on the properties of the quantum. The conceptual limit of the complete absence of selectivity in the processes of interaction between light and matter is realized in the gray substance.

4. The solution of Eq. (10) has been obtained for $h\nu \gg kT$. It is not applicable for $h\nu \sim kT$ nor for $h\nu < kT$. Moreover, it may be shown that in general a solution of Eq. (10) valid for all temperatures does not exist. This means that Eq. (10) itself must be invalid, that is, that the absorption capacity $a(\nu, T)$ cannot be constant for all ranges of frequency. If $a(\nu, T)$ is constant for $h\nu \gg kT$, then for $h\nu < kT$ it depends in one degree or another on ν, and this in turn means that a gray substance, in the sense in which we have defined it, does not exist in nature. This last assertion is not contradicted by the known experimental facts. Actually the usual definition of a gray substance is based on the study of absorption capacity in a wide range of wavelengths --- the ultraviolet, visible and near infra-red regions. In all these regions a is constant. Only by going over into the region of the far infra-red and the region of radio waves can we observe first a small, and then a more notable, deviation from this law.

The deviation from the law a = const on going over into the region $h\nu \sim kT$ is connected with the appearance of forced emission, the energy of which depends on the frequency and the temperature even for gray substances. If we assume that the coefficient B_{abs} retains the value of Eq. (15) even for small ν, then the absorption capacity of a gray body with account being taken of forced emission is equal to

$$a(\nu, T) = \left(1 - e^{-h\nu/kT}\right) P. \tag{17}$$

---

* In what follows we shall speak of a gray substance rather than of gray bodies, since we are not interested in the dimensions nor in conditions on their boundaries.

In the limiting cases of very small ν ($\nu \to 0$) and very high temperatures ($T \to \infty$), the absorption capacity is negligibly small, and, consequently, a gray substance, as, indeed, any other, loses its ability to absorb incident radiation. The absorption that does occur is completely balanced by forced emission.

5. Knowing the Einstein coefficient (15) characterizing the probability of absorption of incident radiation, and using the general relation (4), we can readily write the expression for the Einstein coefficient for forced emission

$$B_{\mathrm{em}} = \frac{P}{nh\nu}\frac{g(E)}{g(E+h\nu)}\,. \qquad (18)$$

Expressions (18) and (15) contradict each other; the coefficient B_{abs} is independent of the energy of the initial level, while the coefficient B_{em} depends on it. Selectivity is not among the properties of absorption by a gray substance. At the same time, according to Eq. (18), selectivity is a very characteristic property of forced emission. This contradiction may be eliminated only if we make a supplementary specification regarding the properties of the function $g(E)$ and require that the ratio $g(E)/g(E+h\nu)$ be independent of E. Differentiating the relation

$$g(E + h\nu) = f(h\nu)\,g(E)$$

first with respect to E and then with respect to $h\nu$, and comparing the results obtained, one can readily show that the function $g(E)$ must have the form

$$g(E) = Ae^{-\alpha E}. \qquad (19)$$

There now arises the further question of the significance of the parameter α. At first sight we might suppose that it is arbitrary (positive) and that different gray substances have different values of α. However, this supposition also meets with a contradiction. Actually, according to Eq. (16), the probability of absorption of a quantum by a gray substance is independent of the frequency of the incident light. At the same time the probability of forced emission of a quantum, which is equal to

$$\frac{nB_{\mathrm{em}}u(\nu)\,d\nu}{u(\nu)\,d\nu/h\nu} = P\frac{g(E)}{g(E+h\nu)} = Pe^{\alpha h\nu}, \qquad (20)$$

will depend on ν. Consequently, for $\alpha \neq 0$ the well-known selectivity of the process of interaction between light and matter is still observed. This cannot be allowed for a gray body, and hence $\alpha = 0$, $g(E) = 1$ for arbitrary E, and the distribution function has the form

$$\rho(E) = Ce^{-E/kT}. \qquad (21)$$

6. The result obtained is, at first sight, somewhat paradoxical. In considering questions of chemical kinetics it is customary to suppose that in complex molecules the statistical weight $g(E)$ is equal to E^{L-1}, where L is the number of oscillational degrees of freedom. The corresponding distribution function then takes the ususal form

$$\rho(E) = CE^{L-1}e^{-E/kT}. \qquad (22)$$

In the application of this equation it is often forgotten that it is a rough approximation. Actually the expression (22) can be obtained if we assume that the energy of a molecule can be represented as the sum of $2L$ quadratic terms, that is, if we completely disregard the anharmonicity of the potential function, which includes also the interaction of the separate degrees of freedom. In actual complex molecules, and even more so in gray substances, these conditions are never realized. We recall that a characteristic property of the objects we are here considering is a strong interaction of the separate degrees of freedom and an interchange of energy among them. The degree of complexity of a molecule is characterized not only by the number of oscillational degrees of freedom L, but also, and primarily, by the magnitude of the interaction between them. From our point of view, a gray substance represents a case of extreme complexity. Hence a function $\rho(E)$ of the type of Eq. (22) is absolutely inapplicable. Calculations based on the optical properties of a gray substance (absence of selectivity) show that the form of the distribution function is given by Eq. (21), that is, that the simple distribution function for a gray substance is very simple --- it coincides with the distribution function for a classical harmonic oscillator with one degree of freedom. Consequently, in the presence of a very strong interaction between the separate degrees of freedom the form of the distribution function ceases to depend on their number. The whole object --- the gray substance --- acts as a single system. In such systems the entire energy of the whole system cannot in principle be represented in the form of a sum of energies localized in the separate degrees of freedom. In the given case the statistical weight, which for weakly interacting degrees of freedom is determined by the number of possible means of distribution of the energy is equal to unity*.

We could also have arrived at just this result in another manner. Let us suppose that, on solving the problem in the zeroth approximation and neglecting certain forms of interactions, we determine that the energy levels are completely degenerate. It is well-known that taking account of interactions always leads to a removal of degeneracy, to a splitting of levels. If this interaction is very great, then the degeneracy will always be removed, even in the case of a complex spectrum of energy values.

7. The Einstein coefficients for a gray substance are equal to

$$B_{\mathrm{abs}}(\nu) = B_{\mathrm{em}}(\nu) = \frac{P}{nh\nu}, \quad A(\nu) = \frac{8\pi\nu^2}{v^3}\frac{P}{n}. \tag{23}$$

From Eq. (23) it follows that the probability of spontaneous radiation of a gray substance, A_{em}, depends only on the frequency and, further, that the dependence itself is very simple ($A \sim \nu^2$). An analogous dependence does not exist in simple quantum mechanical systems (A depends on the properties of both of the combining levels of energy). At the same time it occurs in classical electrodynamics even for the simple dipole. The oscillational energy of the dipole is proportional to ν^2, the energy radiated per second by the dipole is proportional to ν^4, and the ratio of the radiated energy to the self energy is ν^2. An exact calculation shows (see, for example, reference 5) that this ratio is equal to

$$\gamma = \frac{8\pi^2 e^2}{3m}\frac{\nu^2}{c^3}.$$

The magnitude of γ determines the rate at which the radiation intensity falls off, and corresponds to the transition probability in quantum theory. Thus from the point of view of the laws of light emission a gray substance is notably closer to a classical object than to a quantum mechanical one. The quantum properties of an object are washed out in proportion to its complexity, to the increase in its number of degrees of freedom and to the growth of the interaction between them: a discrete spectrum of allowed energy values is converted into a continuous one, and the transition probabilities between all levels spaced at equal intervals from each other become equal.

It is evident that a gray substance cannot be compared to a single classical dipole. A classical dipole radiates only one frequency (within the limits of the natural line width), whereas a gray body radiates all frequencies. A gray body can be compared only with an infinite assembly of dipoles of all frequencies, that is a system of charges moving according to some aperiodic laws. In this last case a solution in a Fourier series will contain all frequencies.

We note that the magnitude

$$\frac{nA(\nu)\,d\nu}{P} = \frac{8\pi\nu^2}{v^3}\,d\nu \tag{24}$$

has a very simple physical interpretation. The right side coincides with the number of independent natural oscillations of the equilibrium radiation in the frequency interval $d\nu$ and in unit volume. The numerator of the left side represents the number of quanta $h\nu$ in the interval $d\nu$ emitted (spontaneously) by unit volume of the substance. Thus the number of quanta emitted by a gray substance is proportional to the number of frequencies which the equilibrium radiation must contain. This again shows that the probabilities are determined to a significant extent by purely classical considerations.

8. It must be emphasized that the definition of a gray substance is different in principle from the definition of a black body. A body which absorbs all the energy incident on it, that is, transmits none and reflects none, is called a black body. A body which is not black in small volumes (thicknesses) may become practically black in large volume. A black body need not necessarily be made up of gray material. Different frequencies may be absorbed differently. It is only necessary that the thickness of the body be large and that the energy of all frequencies be absorbed completely. Moreover, the definition of a black body is connected in principle with the properties of the medium. A body which is black with respect

---

[5] F. A. Korolev, *Spectroscopy of High Resolving Power*, GITTL, 1953, Eq. (4)

[*] An analogous result is obtained in the quantum mechanical treatment of the electrons of complex atoms. The energy of the entire atom cannot be represented in the form of a sum of energies of the separate electrons. In just this way only the orbital moment of the entire atom has a definite significance, whereas the orbital moments of the separate electrons do not. If by introduction of an external field we eliminate the degeneracy connected with the various orientations of the vector **L** in space, then the statistical weights of all the energy levels will equal unity.

to one medium may cease to be black in another medium. In the former case both the body and the medium must have the same index of refraction. A change in the index of refraction of the medium leads to the appearance of reflected waves. We have defined the nature of a gray substance differently. Its properties are not connected with the medium nor, moreover, with the dimensions of a body, but are determined exclusively by the properties of its own structure, by the large interaction of atoms and molecules. At the same time a black body may be very simple in composition but very large in volume.

It must be kept in mind that the absorption capacity (7) cannot be set equal to unity, although this mistake has sometimes occurred in the literature. Actually the absorption capacity (7) is the absorption of light per unit volume per unit time and consequently involves the dimension of time. The emissive power $w(\nu, T)$ involves the dimension of time in the same way, and only their ratio is independent of time. It is impossible to define the concept of a black body from Eq. (9).

9. The results obtained above for the laws of absorption and emission of light by a gray substance should aid in the clarification of the laws of absorption and emission of light by complex molecules. From the point of view of the structure of the oscillational energy levels and the transitions between them, these objects are clearly quite close to a gray substance. From the point of view of the structure of the electronic energy levels and the transitions between them, they are near to simple molecules. They retain, at least approximately, the division of the total energy of the system into electronic energy and energy of nuclear motion. On analyzing the experimental material, Neporent[1,2] came to the conclusion that the probabilities of transitions between oscillational levels of higher and lower electronic states are almost independent of the magnitude of the oscillational energy in the initial state. In the opinion of Neporent they depend only on the frequency. These experimental facts indicate that many properties characteristic of a gray substance are present also in complex molecules. Of course, for the complete explanation of the spectroscopic properties of complex molecules it is necessary to take into account specifically the interactions of the electronic and oscillational energies. This question is open to further development.

Translated by Brother Simon Peter, F.S.C.
97