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SENSITIZED FLUORESCENCE IN PURE ALKALI METAL VAPORS

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Collisions that induce transitions between the doublet sublevels in pure alkali metal vapors are considered. The corresponding effective cross sections are calculated. The characteristics of the sensitized radiation are investigated. The results are compared with the experimental data.

INTRODUCTION

WHEN alkali-metal vapors are exposed to light of frequency close to the frequency of the transition of one of the levels of the doublet to the ground state, the scattered radiation contains also a frequency-shifted component, i.e., one corresponding to the transition from the other level of the doublet. This phenomenon, called sensitized fluorescence, is due to collisions. Indeed, the incident radiation excites atoms to one of the doublet levels. The collisions between the excited atom and the surrounding atoms can lead to a transition of the atom to the other doublet level. The change of the internal energy of the colliding atoms occurs in this case at the expense of their kinetic energy of relative motion. The emission of the atom excited to the other doublet level leads indeed to the phenomenon under consideration.

The transition of an atom from one doublet level to the other can occur both as a result of collisions with the same atoms, which are in the ground state, or as a result of collisions with extraneous atoms. We consider only collisions of the former type, i.e., we investigate sensitized fluorescence in pure alkali-metal vapors. This phenomenon was investigated in detail recently by Krause and co-workers[1-5] and Seiwert and co-workers[6,7], who determined the effective cross section of collisions with transitions between the doublet levels from the measured intensity of the sensitized fluorescence. In this paper we calculate this cross section and determine the main quantities characterizing the sensitized fluorescence in the system under consideration.

The cross section of the transition between the components of the doublet $P_{3/2}$ and $P_{1/2}$ due to collisions with like atoms was calculated by Ovchinnikova[8] under the assumption that the region of the transition is determined by taking the exchange integrals into account. The effective distances R to the transition point (point of pseudointersection of the terms) turned out in this case to be of the order of 15 for sodium (in the atomic system of units). We shall show that for alkali metals with a small distance ΔE between the sublevels of the doublet, the transition region lies at much larger distances, where the contribution of the exchange integrals is negligibly small. Thus, for example, for transitions between the first excited states of sodium ($\Delta E = 17\ \text{cm}^{-1}$), the effective distances R are of the order of 50. With increasing ΔE, the effective distances decrease and allowance for the overlap integrals apparently becomes necessary.

The transitions between the levels of the doublet due to collisions with extraneous atoms were considered in[9-14]. The dielectric constants of pure alkali-metal vapors at the resonant frequency was determined in an earlier paper by the author[15].

1. MATRIX ELEMENT

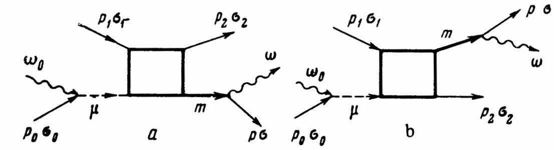
Let us write down the matrix element M of this process. Graphically this matrix element is shown in the figure, where a wavy line represents a photon, a thin solid line an atom in the ground state $S_{1/2}$, and a dashed line an atom in the state $P_{1/2}$, and a heavy line an atom in the state $P_{3/2}$. For concreteness, we assume here that the atom is initially excited in the $P_{1/2}$ state. The rectangle in the figure denotes the effective four-pole, i.e., the aggregate of diagrams describing the interaction between the excited and unexcited atoms, leading to a transition of the atom to the state $P_{3/2}$ ($P_{1/2} \to P_{3/2}$). The process can have either an exchange (b) or a non-exchange (a) character. On the mass shell or near it, the effective four-pole reduces to the amplitude of the corresponding process[16]. The situation here is perfectly analogous to that considered by us[17] in an investigation of resonant collisions. The amplitudes of the non-exchange and exchange processes will be denoted by f_1 and f_2. The analytic expression for the matrix element M is (we use, unless otherwise stipulated, the atomic system of units)

$$M^{\sigma\sigma_2\lambda}_{\sigma_0\sigma_1\lambda_0} = -\frac{2\pi}{V}\sqrt{\omega\omega_0}(\mathbf{e}_\lambda\mathbf{d})_{\sigma m'}(\mathbf{e}_{\lambda_0}\mathbf{d})_{\mu\sigma_0}\frac{4\pi}{MV}[f^{m\sigma_2}_{1\mu'\sigma_1}(\mathbf{q},\mathbf{q}_0) + f^{m\sigma_2}_{2\mu'\sigma_1}(\mathbf{q},\mathbf{q}_0)]\,G_{\mu'\mu}(p_0+k_0)\,\overline{G}_{m'm}(p+k), \tag{1}$$

where ω_0, $\mathbf{k}_0$, $\mathbf{e}_{\lambda_0}$ and ω, $\mathbf{k}$, and $\mathbf{e}_\lambda$ are respectively the frequencies, wave vectors, and polarization vectors of the absorbed and emitted photons, M is the mass of the atom, V is the volume of the system, and $\mathbf{q}_0$ and $\mathbf{q}$ are the relative momenta of the atoms before and after the collision:

$$\mathbf{q}_0 = {}^1\!/_2(\mathbf{p}_0 + \mathbf{k}_0 - \mathbf{p}_1), \quad \mathbf{q} = {}^1\!/_2(\mathbf{p} + \mathbf{k} - \mathbf{p}_2),$$

G and $\overline{G}$ are the Green's functions of the excited atoms.



The indices σ, μ, and m characterize the projections of the total angular momentum of the atom in the states $S_{1/2}$, $P_{1/2}$, and $P_{3/2}$ respectively. Summation over repeated indices is implied. The interaction between the excited and unexcited atoms is via resonant dipole-dipole interaction and is characterized by large effective cross sections. These collisions determine also the Green's functions of the excited atoms. As shown in[17], these Green's functions, accurate to small correction terms, are

$$G_{\mu\mu'}(p_0+k_0)=\frac{\delta_{\mu\mu'}}{\omega_0-\omega_1-\mathbf{p}_0\mathbf{k}_0/M+i\Gamma_1},$$
$$\bar{G}_{mm'}(p+k)=\frac{\delta_{mm'}}{\omega-\omega_2-\mathbf{pk}/M+i\Gamma_2}, \tag{2}$$

where we have used the condition $|\mathbf{k}| \ll |\mathbf{p}|$. By ω_1 and ω_2 we denote the frequencies corresponding to the transitions from the excited levels $P_{1/2}$ and $P_{3/2}$ to the ground state $S_{1/2}$. The widths Γ_1 and Γ_2 of the excited levels were determined in[15]:

$$\Gamma_1=\gamma_1/2+2{,}73n\lambda\!\!\!^{-3}\gamma_1,$$
$$\Gamma_2=\gamma_2/2+4{,}38n\lambda\!\!\!^{-3}\gamma_2, \tag{3}$$

where γ_1 and γ_2 denote the radiative lifetimes of the states $P_{1/2}$ and $P_{3/2}$, $\gamma_1 \approx \gamma_2 \approx \gamma$, $\lambda\!\!\!^{-} = c/\omega_1 \approx c/\omega_2$, and n is the density of the atoms. For a rarefied medium, when $n\lambda\!\!\!^{-3} \ll 1$, the widths Γ_1 and Γ_2 reduce to the radiative vertices of the doublet levels. Averaging over the momenta of the colliding particles, we write the differential effective cross section of the process under consideration in the form

$$d\sigma=\frac{2\pi nV}{cV^{-1}}\int d\mathbf{p}_0\,d\mathbf{p}_1\varphi(\mathbf{p}_0)\varphi(\mathbf{p}_1)\int\frac{d\mathbf{p}_2\,d\mathbf{p}}{(2\pi)^3}V\overline{|M|^2}\delta(\mathbf{p}_0$$
$$+\mathbf{k}_0+\mathbf{p}_1-\mathbf{p}_2-\mathbf{k}-\mathbf{p})\delta(\omega_0+\varepsilon_{\mathbf{p}_0}+\varepsilon_{\mathbf{p}_1}-\omega-\varepsilon_{\mathbf{p}_2}-\varepsilon_{\mathbf{p}})\frac{\omega^2d\omega\,d\Omega V}{(2\pi c)^3} \tag{4}$$

where $\varphi(\mathbf{p})$ is a normalized Maxwellian distribution, $\epsilon_p = p^2/2M$, the bar over M denotes summation and averaging over the spin indices. The density n is the result of the fact that the process is a three-particle one.

For the subsequent calculation of the effective cross section of sensitized fluorescence (4), it is necessary to know the amplitude f or the effective cross section of collision with transition between the doublet levels.

2. EFFECTIVE CROSS SECTION FOR THE TRANSITION BETWEEN THE DOUBLET LEVELS

The Hamiltonian of a system of two colliding atoms, one excited and the other not, is

$$H=H_0(1)+H_0(2)+V(\mathbf{R}),$$

where $V(\mathbf{R})$ is the interaction operator. At distances large compared with atomic, it has the form of the dipole-dipole interaction operator:

$$V(\mathbf{R})=\frac{\mathbf{d}_1\mathbf{d}_2}{R^3}-\frac{3(\mathbf{d}_1\mathbf{R})(\mathbf{d}_2\mathbf{R})}{R^5}, \tag{5}$$

where R is the distance between atoms, and $\mathbf{d}_1$ and $\mathbf{d}_2$ are the operators of the dipole moments of the colliding atoms. For resonant collisions, distances of the order of the Weisskopf radius ρ_0 are significant: $\rho_0 \sim g/\sqrt{v}$, where v is the relative velocity of the atoms and $g^2 = d_{3/2}^2/4 = d_{1/2}^2/2$, where d_j is the reduced matrix element of the dipole transition $P_j \rightarrow S_{1/2}$.

We shall assume that the velocity of the atoms is small compared with the electron velocity, $v \ll 1$. In the opposite case, the employed approximations, particularly the assumption that the principal role is played by distances that are large compared with the atomic distances, will be violated. At the same time, we assume that the temperature T of the gas is sufficiently high, so that the condition $T \gg \Delta E$ is satisfied. If the distance between the levels of the doublet ΔE is such that $\Delta E \gg g^2/\rho_0^3$, then the effective distances for such collisions are $R \sim (g^2/\Delta E)^{1/3} \ll \rho_0$, and the condition for the applicability of the adiabatic perturbation theory is satisfied

$$\frac{g^2}{R^3}\gg\frac{1}{\tau_{\text{coll}}}\sim\frac{v}{R}. \tag{6}$$

This condition is satisfied only for the lightest of the alkali metals—lithium.

On the basis of the adiabatic perturbation theory, we should construct, to obtain the transition probability, the electronic terms of the quasimolecule made up of the excited and unexcited atom. If the corresponding electronic terms intersect then, as is well known[13], the transition from one term to the other occurs at the intersection point.

Knowing the atomic wave functions ψ_{jm} (excited states) and χ_σ (the ground state) and the perturbation operator V(5), it is easy to find in first approximation of perturbation theory the electronic terms $\epsilon(R)$ and the corresponding wave functions Φ of the quasimolecule made up of the colliding atoms. It is also possible to carry over to the perturbation operator the spin-orbit interaction operators of the atoms causing the occurrence of the fine structure (states $P_{1/2}$ and $P_{3/2}$). Since like atoms in different states take part in the collision, an additional degeneracy arises in the system, connected with the possible exchange of excitation between the like atoms. Accordingly, all the possible states of the quasimolecules break up into two classes—even and odd. A transition from one class of solutions to the other corresponds to a change of the sign in the secular equation of the matrix elements of the operator V (5).

It is convenient to perform the calculations in a coordinate system with z axis parallel to the vector $\mathbf{R}$. Each term of the quasimolecule is characterized by the projection Ω of the total angular momentum J. The states corresponding to different signs of Ω belong to the same energy. The value $\Omega = 0$ corresponds to four terms, $\Omega = 1$ to three terms, and $\Omega = 2$ to one term.

We are particularly interested in those terms of the quasimolecule, which intersect in the approximation under consideration at some value $R = R_0$. In the region of the intersection point, the conditions for the applicability of the adiabatic approximation are violated, and the transition from one term to the other had a maximum probability. The transition between terms of unequal parity is forbidden, so that to find the points of intersection it is necessary to investigate terms of different parity independently. We shall henceforth consider mainly odd terms, since they turn out to make the main contribution

An investigation of the solutions of the secular equation, which we do not present here, shows that actually there exists two intersecting terms $\epsilon_0(R)$ and $\epsilon_1(R)$, corresponding to values $\Omega = 0$ and $\Omega = 1$ respectively:

$$\varepsilon_0 = E_{3/2} - {}^1/_2\Delta E - {}^3/_2 U + {}^1/_2[(\Delta E)^2 + U^2 - {}^2/_3 U\Delta E]^{1/2}, \tag{7}$$

where $U = g^2/R^3$, and the term ϵ_1 is determined from the solution of the cubic equation

$$\lambda^3 - 2U\lambda^2 - \lambda({}^1/_3\Delta E^2 + U^2) + 2U^3 + {}^2/_9\Delta EU + {}^2/_{27}\Delta E^3 = 0, \tag{8}$$

where $\epsilon_1 = E_{1/2} + (2/3)\Delta E + \lambda$, $\epsilon_1 = E_{1/2}$ at $R \to \infty$. The point of intersection of the terms is determined by the relation

$$g^2 / R_0^3 = 1.04\Delta E. \tag{9}$$

The wave functions corresponding to these terms are of the form

$$\begin{gathered}\Phi_0 = b_0(R)\overline{\Psi}^{(1)}_{1.0} + c_0(R)\overline{\Psi}^{(2)}_{1.0},\\ \Phi_{\pm1} = a_1(R)\overline{\Psi}_{2,\pm1} + b_1(R)\overline{\Psi}^{(1)}_{1,\pm1} + c_1(R)\overline{\Psi}^{(2)}_{1,\pm1},\end{gathered} \tag{10}$$

and at $R \to \infty$ we get $b_0 = c_1 = 1$ and $a_1 = b_1 = c_0 = 0$.

We have denoted by $\overline{\Psi}_{J\Omega}$ the wave functions of the system of two non-interacting atoms ($V = 0$), having a total angular momentum J and its projection Ω. The functions $\overline{\Psi}^{(1)}_{1\Omega}$ and $\overline{\Psi}^{(2)}_{1\Omega}$ correspond to states with energies $E_{3/2}$ and $E_{1/2}$. At the intersection point we have

$$\begin{gathered}b_0(R_0) = 0.87, \quad c_0(R_0) = 0.49,\\ b_1(R_0) = 0.31, \quad c_1(R_0) = 0.74, \quad a_1(R_0) = 0.61.\end{gathered} \tag{11}$$

Bearing in mind that the main contribution to the cross section of a transition from one term to the other is made by states corresponding to intersecting terms, we represent the wave function Ψ of the system in the form of a superposition

$$\Psi = \alpha\Phi_0 + \beta\tilde{\Phi}_1 + \beta'\tilde{\Phi}_1', \tag{12}$$

where we have introduced in lieu of the functions $\Phi_{\pm1}$, for convenience, their linear superpositions

$$\tilde{\Phi}_1 = \frac{1}{\sqrt{2}}(\Phi_1 + \Phi_{-1}), \quad \tilde{\Phi}_1' = \frac{1}{\sqrt{2}}(\Phi_1 - \Phi_{-1}). \tag{13}$$

The state connected with Φ_0 is $\tilde{\Phi}_1$ and not $\tilde{\Phi}_1'$.

The functions Φ_0 and $\Phi_{\pm1}$ are expressed, in accordance with (10), in terms of the atomic functions $\Psi_{J\Omega}$, taken in a rotating system of coordinates (z axis along R). We should not transform these functions in a fixed coordinate system. Substituting then the wave function Ψ (12) in the Schrödinger equation, we obtain a system of equations for the amplitudes α and β.

Using the Landau-Zener approximation in the usual manner[18], we obtain an expression for the probability of transition $W(\rho)$ from one term to the other:

$$W(\rho) = \frac{4\pi}{v}\frac{V'^2(R_0)R_0}{(R_0^2 - \rho^2)^{1/2}}\left(\frac{d\varepsilon_0}{dR} - \frac{d\varepsilon_1}{dR}\right)^{-1}_{R=R_0}, \tag{14}$$

where

$$V' = -(b_1 b_0 + c_1 c_0)v\rho / R_0^2.$$

Using the results (9)—(11) and integrating the probability $W(\rho)$ with respect to the impact parameters ρ, we obtain finally an expression for the effective cross section with transition from one level to the other:

$$\sigma_v = 2\pi\int_0^{R_0}\rho d\rho W(\rho) = 1.25\frac{16\pi^2}{9}\frac{vg^{2/3}}{(\Delta E)^{4/3}} = 20\frac{v\lambda\!\!\!^-\gamma^{1/3}}{(\Delta E)^{4/3}}. \tag{15}$$

For transitions in which even states take part, the numerical coefficient turns out to be smaller by two orders of magnitude. We shall henceforth disregard the contribution of the even states.

We obtain also an expression for the cross section averaged over the relative velocity of the colliding particles and the polarization. Let us consider first the transition $P_{3/2} \to P_{1/2}$. Recognizing that the transition occurs only from one state out of 16 possible ones (see (10)), we find the averaged cross section

$$\bar{\sigma}_{12} = 1.25\frac{\bar{v}\lambda\!\!\!^-\gamma^{1/3}}{(\Delta E)^{4/3}}, \tag{16}$$

where $\bar{v} = 4\sqrt{T/\pi M}$. For the inverse process $P_{1/2} \to P_{3/2}$, the transition occurs in one out of eight possible states. Accordingly we have

$$\bar{\sigma}_{21} = 2\bar{\sigma}_{12} = 2.50\frac{\bar{v}\lambda\!\!\!^-\gamma^{1/3}}{(\Delta E)^{4/3}}. \tag{17}$$

We shall show below that although the effective cross section determined in experiments with sensitized fluorescence are close to the obtained averaged cross sections, they are somewhat different nonetheless.

3. EFFECTS OF CROSS SECTION OF SENSITIZED FLUORESCENCE

Let us calculate the sensitized-fluorescence cross section (4), using the obtained expression for the effective cross section σ_v(15). The amplitudes of the non-exchange and exchange processes f_1 and f_2 will be expressed in terms of the amplitudes of scattering in the even and odd states, f_+ and f_-:

$$\begin{gathered}f_1(\mathbf{q}, \mathbf{q}_0) = {}^1/_2[f_+(\mathbf{q}, \mathbf{q}_0) + f_-(\mathbf{q}, \mathbf{q}_0)],\\ f_2(\mathbf{q}, \mathbf{q}_0) = {}^1/_2[f_+(-\mathbf{q}, \mathbf{q}_0) - f_-(-\mathbf{q}, \mathbf{q}_0)].\end{gathered} \tag{18}$$

Since the main contribution is made by transitions in the odd state, we shall henceforth retain only the amplitude f_-.

When the atom is irradiated at a frequency close to ω_1 the transition during the collision occurs from the state $P_{1/2}$ to the state $P_{3/2}$:

$$(\Psi^{(2)}_{1,1} + \Psi^{(2)}_{1,-1})/\sqrt{2} \to \Psi^{(1)}_{1,0},$$

(see (8) and (13)). Since

$$\Psi^{(2)}_{1,\pm1} = \chi_{\pm1/2}\psi_{1/2,\pm1/2},$$

$$\Psi^{(1)}_{1,0} = \frac{1}{\sqrt{2}}(\chi_{1/2}\psi_{3/2,-1/2} - \chi_{-1/2}\psi_{3/2,1/2}),$$

it follows that the amplitude $f^{m\sigma_2}_{-\mu\sigma_1}$ is given by

$$f^{m\sigma_2}_{-\mu\sigma_1}(\mathbf{q}, \mathbf{q}_0) = {}^1/_2 f_-(\mathbf{q}, \mathbf{q}_0)\delta_{\mu\sigma_1}\delta_{m\sigma_2}(\delta_{\sigma_2,1/2} - \delta_{\sigma_2,-1/2})(\delta_{\mu,1/2} + \delta_{\mu,-1/2}), \tag{19}$$

where the function $f_-(\mathbf{q}, \mathbf{q}_0)$ no longer depends on the spin indices. When taken on the mass shell, the amplitude f_- is connected in the usual manner with the effective cross section σ_v(15):

$$\int |f_-(\mathbf{q}, \mathbf{q}_0)|^2 d\Omega = \sigma_v,$$

where the integration is over all the directions of the vector $\mathbf{q}$, with

$$\frac{\mathbf{q}^2}{M}-\frac{\mathbf{q}^2_0}{M}=-\Delta E.$$

Using relations (18) and (19), we obtain for the average square of the matrix element (1) the following expression (the summation is carried out over the indices of the matrix element M):

$$\overline{|M|^2}=\frac{1}{8}\sum|M^{\sigma\sigma_2\lambda}_{\sigma_0\sigma_1\lambda_0}|^2$$
$$=\frac{4\pi^2}{V^2}\frac{5}{32}\gamma^2\bar{\lambda}^4\left(1-\frac{3}{5}\cos^2\theta\right)\frac{\pi^2}{M^2V^2}|f_-(\mathbf{q},\mathbf{q}_0)-f_-(-\mathbf{q},\mathbf{q}_0)|^2\cdot$$
$$\times\frac{\Gamma_1}{(\bar{\omega}_1-\mathbf{p}_0\mathbf{k}_0/M)^2+\Gamma_1^2}\frac{\Gamma_2}{(\bar{\omega}_2-\mathbf{pk}/M)^2+\Gamma_2^2},\tag{20}$$

where γ denotes the radiative lifetime of one of the levels of the doublet. The difference between these lifetimes for the states $P_{1/2}$ and $P_{3/2}$ will be neglected. We shall also neglect, where possible, the difference between the frequencies ω_0, ω_1, ω_2, and ω, denoting them by ω, $\bar{\lambda} = c/\omega$, $\overline{\omega}_2 = \omega - \omega_2$, $\overline{\omega}_1 = \omega_0 - \omega_1$. By θ we denote the angle between the $\mathbf{k}$ and $\mathbf{q}_0$.

We substitute (20) and (4), in which it is convenient to change to integration with respect to the momenta $\mathbf{p}_0$, $\mathbf{p}_1$, $\mathbf{p}_2$, and $\mathbf{p}$ to integration over the summary momentum $\mathbf{P}$ and the relative momenta $\mathbf{q}$ and $\mathbf{q}_0$. We shall henceforth assume that the Doppler widths are much larger than the widths Γ_1 and Γ_2. Under these conditions, the dispersion functions which enter in (20) can be approximately replaced by δ functions. We neglect here the contribution of the virtual processes. Estimates show that when $\Gamma_1 \sim \Gamma_2 \sim \gamma$ the virtual processes yield a correction not exceeding 10^{-3}.

Neglecting where possible the momentum of the photon compared with the thermal momenta of the atoms, we rewrite the expression for the effective cross section in the form

$$d\sigma_{21}(\omega_0,\omega)=\frac{5\pi}{2^8}\frac{n\bar{\lambda}^2}{M^2}\frac{\gamma^4}{\Gamma_1\Gamma_2}\frac{d\Omega d\omega}{(2\pi MT)^3}\int d\mathbf{P}\,d\mathbf{q}\,d\mathbf{q}_0$$
$$\times\exp\left\{-\frac{1}{MT}\left(\frac{\mathbf{P}^2}{4}+\mathbf{q}_0^2\right)\right\}\left(1-\frac{3}{5}\cos^2\theta\right)\delta\left(\bar{\omega}_1-\frac{\mathbf{k}_0\mathbf{P}}{2M}-\frac{\mathbf{q}_0\mathbf{k}_0}{M}\right)$$
$$\times\delta\left(\bar{\omega}_2-\frac{\mathbf{kP}}{2M}-\frac{\mathbf{qk}}{M}\right)|f_-(\mathbf{q},\mathbf{q}_0)-f_-(-\mathbf{q},\mathbf{q}_0)|^2\delta\left(\frac{\mathbf{q}^2}{M}-\frac{\mathbf{q}_0^2}{M}+\Delta E\right),\tag{21}$$

where the subscripts of the cross section denote the fact that the irradiation is at a frequency close to ω_1. If the irradiation is at a frequency close to ω_2, the cross section $d\sigma_{12}$ is written in similar fashion.

The amplitude f_- differs from zero only in the region of sufficiently small angles. We shall use this circumstance and neglect the interference terms. We also take into account that $\Delta E \ll T$. We denote by ϑ the angle between the vectors $\mathbf{k}$ and $\mathbf{k}_0$. In the angle region $\vartheta \gg \Delta E/T$ and $\pi-\vartheta \gg \Delta E/T$, the effective cross section is given by

$$d\sigma_{21}(\omega_0,\omega)=\frac{5}{2^7}\sqrt{\frac{\pi}{2}}\frac{n\bar{\lambda}^3\gamma^2}{\Gamma_1\Gamma_2}\bar{\sigma}_{21}\frac{d\Omega d\omega}{ku}$$
$$\times\exp\left(-\frac{\bar{\omega}_2^2}{k^2u^2}\right)\left\{\frac{1}{\sin\vartheta}\exp\left(-\frac{\tilde{\omega}^2}{k_0^2u^2\sin^2\vartheta}\right)\left[\frac{17}{20}+\frac{1}{5}\frac{\bar{\omega}_2^2}{k^2u^2}\right.\right.$$
$$\left.\left.-\frac{3}{10}\frac{\bar{\omega}_1^2}{k^2_0u^2}\cos^2\vartheta-\frac{3}{20}\sin^2\vartheta-\frac{2}{5}\frac{\bar{\omega}_1\bar{\omega}_2}{k_0ku^2}\cos\vartheta\right]\right\},$$
$$+\frac{1}{2}\frac{\tilde{\omega}^2}{k_0^2u^2\sin^2\vartheta}\Big]+\exp\left(-\frac{\bar{\omega}_1^2}{k^2u^2}\right)\left[1+\frac{\bar{\omega}_1^2}{2k_0^2u^2}+\frac{1}{5}\frac{\bar{\omega}_2^2}{k^2u^2}-\right.\tag{22}$$

where $u = \sqrt{2T/M}$, $\tilde{\omega} = \overline{\omega}_1 - \cos\vartheta\,\omega_2$, and $\overline{\sigma}_{21}$ is given by expression (17). The cross section $d\sigma_{12}(\omega_0, \omega)$ is obtained from (22) by making the substitutions $\omega_1 \to \omega$ and $\omega \to \omega_0$.

From (22) with allowance for (3) it follows that when the density of the medium n changes, the effective cross section of the sensitized fluorescence reaches a maximum at $n\bar{\lambda}^3 \sim 1$.

We present now expressions for the absorption line shape $d\sigma(\omega_0)$ and the emission line shape $d\sigma(\omega)$ of the sensitized fluorescence

$$d\sigma_{21}(\omega_0)=\int d\sigma_{21}(\omega,\omega_0)\,d\omega$$
$$=\frac{11\pi}{2^7\sqrt{2}}\frac{\gamma^2}{\Gamma_1\Gamma_2}n\bar{\lambda}^3\bar{\sigma}_{21}e^{-\nu_0^2}\,d\Omega\left(1+\frac{5}{11}\nu_0^2-\frac{3}{11}\nu_0^2\cos^2\vartheta-\frac{3}{22}\sin^2\vartheta\right),$$
$$d\sigma_{21}(\omega)=\frac{1}{ku}\int d\sigma_{21}(\omega_0,\omega)\,d\omega_0$$
$$=\frac{11\pi}{2^7\sqrt{2}}\frac{\gamma^2}{\Gamma_1\Gamma_2}\frac{n\bar{\lambda}^3}{ku}\bar{\sigma}_{21}e^{-\nu^2}\left(1+\frac{2}{11}\nu^2\right)d\omega\,d\Omega,\tag{23}$$

where

$$\nu_0=\frac{\omega_0-\omega_1}{ku},\qquad\nu=\frac{\omega-\omega_2}{ku}.$$

In the case of irradiation at a frequency close to ω_2, we have for the absorption line shape

$$d\sigma_{12}(\omega_0)=\frac{11\pi}{2^6\sqrt{2}}\frac{\gamma^2}{\Gamma_1\Gamma_2}n\bar{\lambda}^3\bar{\sigma}_{12}\,e^{-\nu_0'^2}\left(1+\frac{2}{11}\nu_0'^2\right)d\Omega\tag{24}$$

and analogously for the emission line shape

$$d\sigma_{12}(\omega)=d\sigma_{21}(\omega_0)\tag{25}$$

with the substitution $\omega_2 \to \omega_1$.

As follows from (22)–(25), the effective widths of the frequency distributions are of the order of the Doppler widths. Integrating these distributions over the frequencies, we obtain

$$d\sigma_{21}=\frac{3\pi^{3/2}}{2^{11/5}}n\bar{\lambda}^3\frac{\gamma^2}{\Gamma_1\Gamma_2}\bar{\sigma}_{21}\,d\Omega,$$
$$d\sigma_{12}=\frac{3\pi^{3/2}}{2^{9/2}}n\bar{\lambda}^3\frac{\gamma^2}{\Gamma_1\Gamma_2}\bar{\sigma}_{12}\,d\Omega.\tag{26}$$

It follows from (26) that the effective cross section of the sensitized fluorescence, integrated over the frequencies, is isotropic.

In an experimental investigation of the sensitized fluorescence one usually registered radiation scattered through an angle $\pi/2$, and the ratio of the intensities of the frequency-shifted and frequency-unshifted radiation is determined, i.e., the ratio of the intensity of the sensitized and resonant fluorescence. In the case when this ratio is small, it is assumed equal to $nQ\overline{v}/\gamma$, where Q stands for the effective cross section of a collision with transition between the levels of the doublet, and $\overline{v}$ is the average relative velocity.

If the density n is sufficiently small, then the dragging of the radiation[19,20], can be neglected, and then the intensity ratio reduces to the ratio of the corresponding effective cross sections. The effective cross sections of resonant fluorescence $d\sigma_{11}$ (at the level $P_{1/2}$) and $d\sigma_{22}$ (at the level $P_{3/2}$) can be readily calculated (see, for example[21]). When the Doppler width is much larger than all the other widths, these cross sections are given by

$$d\sigma_{11} = \frac{\pi}{8}\lambdabar^2 \frac{\gamma^2}{\Gamma_1 k u}\, d\Omega,$$
$$d\sigma_{22} = \frac{5\pi}{16}\left(1 - \frac{3}{10}\sin^2\vartheta\right)\frac{\lambdabar^2\gamma^2}{\Gamma_2 k u}\, d\Omega. \tag{27}$$

These cross sections, like the cross sections (26), were obtained by integrating with respect to the emitted quantum and averaging over the frequency of the incident quantum. The ratio of the cross sections at $\vartheta = \pi/2$ and $n\lambda^3 \ll 1$, when $\Gamma_1 = \Gamma_2 = \gamma/2$ (see (3)), are respectively

$$\eta_{21} = \frac{d\sigma_{21}}{d\sigma_{11}} = \frac{3\pi}{8}\frac{n\bar{v}\bar{\sigma}_{21}}{\gamma},$$
$$\eta_{12} = \frac{d\sigma_{12}}{d\sigma_{22}} = \frac{3\pi}{7}\frac{n\bar{v}\bar{\sigma}_{12}}{\gamma}. \tag{28}$$

In[1-7] the measured values of η_{12} and η_{21} were used to determine the cross sections

$$Q_{12} = \frac{\eta_{12}\gamma}{n\bar{v}}, \quad Q_{21} = \frac{\eta_{21}\gamma}{n\bar{v}}$$

and their ratio Θ. From (28) it follows that

$$Q_{21} = \frac{3\pi}{8}\bar{\sigma}_{21}, \quad Q_{12} = \frac{3\pi}{7}\bar{\sigma}_{12}. \tag{29}$$

Taking into account also the connection between the cross sections $\bar{\sigma}_{12}$ and $\bar{\sigma}_{21}$ (17), we obtain

$$\Theta = \frac{Q_{21}}{Q_{12}} = \frac{7}{8}\frac{\bar{\sigma}_{21}}{\bar{\sigma}_{12}} = \frac{7}{4}. \tag{30}$$

The appearance of the factor $7/4$ in place of 2 is connected with the angular dependence of the cross section of the resonance fluorescence at the level $P_{3/2}$.

Using the relations (29) and (16), and (17), we can compare the results of the calculations with the experimental data. Under the conditions of the experiment, the inequality $\Delta E \ll T$ is not satisfied for sodium and worse for potassium. In[6] for transitions between the first excited states of sodium ($\Delta E = 17\ \text{cm}^{-1}$) the values obtained were

$$Q_{21} = 1.7\cdot 10^{-14}\,\text{cm}^2 \quad Q_{12} = 1.0\cdot 10^{-14}\,\text{cm}^2; \quad \Theta = 1.7.$$

The obtained value of Θ is in good agreement with (30). From the Q_{12} and Q_{21} given in (29) it follows that

$$\bar{\sigma}_{21} = 1.44\cdot 10^{-14}\,\text{cm}^2, \quad \bar{\sigma}_{12} = 0.74\cdot 10^{-14}\,\text{cm}^2$$

Calculations by means of formulas (16) and (17) yield ($T = 280°\text{C}$)

$$\bar{\sigma}_{21} = 1.94\cdot 10^{-14}\,\text{cm}^2, \quad \bar{\sigma}_{12} = 0.97\cdot 10^{-14}\,\text{cm}^2,$$

i.e., the agreement is perfectly satisfactory.

Transitions connected with allowance for the exchange integrals lead for sodium, in accordance with[8], to the cross section $\sigma_{21} \sim (0.5-1.0)\times 10^{-14}\ \text{cm}^2$. In[1] they observed for sodium a cross section $Q_{12} = 2.83 \times 10^{-14}\ \text{cm}^2$, from which it follows that $\bar{\sigma}_{12} = 2.1 \times 10^{-14}\ \text{cm}^2$. This is approximately twice the calculated value. The cross section observed in[7] for transitions between first excited states of potassium ($\Delta E = 57\ \text{cm}^{-1}$) is approximately three times the calculated value. Even larger cross sections were observed in[2]. In this case apparently it is already necessary to take into account in the calculation the contribution from the exchange integrals.

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