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RADIATION EMITTED BY MOLECULES IN THE PRESENCE OF A STRONG HIGH-FREQUENCY FIELD

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A strong electromagnetic field of frequency ω and amplitude F induces radiation of lower frequency Ω_0 [Eq. (12)] in a molecular gas. The intensity of this radiation is computed. Quantum-electrodynamical considerations are presented which corroborate the applicability of the correspondence principle in the investigation of this phenomenon.

1. INTRODUCTION

THE phenomenon of radiation by molecules in the presence of a strong high-frequency field has been examined by the author.[1] In the present paper we develop a more detailed analysis of this phenomenon.

Let E_1 and E_2 be two non-degenerate energy levels of a molecule, μ_{11} and μ_{22} the dipole moments (electric or magnetic) of the molecule in the states with energies E_1 and E_2, and μ_{12} the dipole moment of the transition $1 \rightarrow 2$. Thus E_1 and E_2 can be components of the Stark splitting of the levels, whence μ_{11} and μ_{22} are electric dipole moments. Furthermore, let a strong electromagnetic field act at a frequency ω, close to the resonant frequency of the molecule $\omega_{12} = (E_1 - E_2)/\hbar \equiv \omega_0$. As is known, such a field excites transitions between the states 1 and 2 of the molecule. As a result of such transitions a change of the dipole moment of a molecule takes place from μ_{11} to μ_{22} and conversely. This change takes place with the frequency of transitions between the states 1 and 2. The number of such transitions per unit time has the order of magnitude

$$\Omega_0 \approx |\mu_{12}| F / \hbar, \tag{1}$$

where F is the amplitude of the field of frequency ω. Every change of dipole moment, however, must give rise to emission of energy. It is evident that such emission must have the frequency Ω_0. The experimental determination of this frequency permits very accurate evaluation of the product of the dipole moment of the transition μ_{12} by the amplitude of the high-frequency field.

By such a method, in principle, with a known dipole moment, a precise measurement of high-frequency fields is possible. On the other hand, if the intensity of the high-frequency field is known, there is the possibility of direct determination of the dipole moment μ_{12}.

We note that the effect described here is to a certain extent analogous to the Stark and Zeeman effects. In fact, the Stark effect gives the possibility of observing radiation of a frequency proportional to the product of the intensity of the constant electric field by the electric dipole moment in a given energy state (in our case μ_{11} or μ_{22}); the Zeeman effect gives the possibility of observing a frequency proportional to the product of the intensity of the constant magnetic field by the magnetic dipole moment (diagonal element of the magnetic dipole-moment operator). In the presence of a strong high-frequency field, however, there appears a radiation of frequency Ω_0, proportional to the product of the amplitude of this field by the magnitude of the dipole moment μ_{12} of the transition.

We shall first calculate the effect described here with the aid of the correspondence principle and then indicate quantum-electrodynamic considerations that confirm the existence of this effect.

2. ANALYSIS BASED ON THE CORRESPONDENCE PRINCIPLE

Based on the correspondence principle, we shall describe a molecule by means of quantum mechanics and the radiation by means of classical electrodynamics.

We shall assume that the following conditions are fulfilled:[2-4]

(a) $T_0 \ll 1/\omega \ll \bar{\tau}$, where T_0 is the duration of a molecular collision and $\bar{\tau}$ is the mean time between collisions;

(b) $$| \omega - \omega_0 | \equiv | \omega - \omega_{12} | \lesssim 1/\bar{\tau} \text{ and } | \omega - \omega_{mn} | \gg 1/\bar{\tau},$$

where m, n $\neq$ 1, 2;

(c) A molecular collision returns a molecule to the state with energy E_1 or E_2;

(d) $\omega_0 \gg \Omega_0$.

Let an isolated molecule have levels E_i which are characterized by the eigenfunctions $\Psi_i \exp(iE_i t/\hbar)$. Then

$$H_0 \Psi_i = E_i \Psi_i, \tag{2}$$

where H_0 is the Hamiltonian of a free molecule. In the presence of interaction with an electromagnetic field of frequency ω, the Hamiltonian of a molecule in an external field will have the form

$$H = H_0 - \mu F(t) = H_0 + V \sin \omega t, \tag{3}$$

where $F(t) = F \sin \omega t$ and $\boldsymbol{\mu}$ is the dipole moment operator.

The wave function of a molecule in an external field satisfies the Schrödinger equation

$$i\hbar\, \partial\Psi/\partial t = (H_0 + V \sin \omega t)\, \Psi. \tag{4}$$

We shall seek the solution of this equation satisfying the conditions (a) through (d) by a method given in the book by Landau and Lifshitz.[5]

In the presence of interaction, we seek a solution of Eq. (4) in the form

$$\Psi(t) = a_1 \Psi_1 + a_2 \Psi_2. \tag{5}$$

Here we have used condition (b). At the instant of collision, $t = t_0$, according to condition (c), let*

$$a_1 = 0; \quad a_2 = 1. \tag{6}$$

Using conditions (b) and (d), we obtain upon transformation the following equations for a_1 and a_2:

$$i\hbar \frac{da_1}{dt} = -\frac{V_{12}}{2i} e^{i\delta t} a_2; \quad i\hbar \frac{da_2}{dt} = \frac{1}{2i} V_{21} e^{-i\delta t} a_1, \tag{7}$$

where $\delta = \omega_0 - \omega$. We make the substitutions

$$D = | a_2 |^2 - | a_1 |^2; \quad c_{12} = a_1^* a_2; \quad c_{21} = a_2^* a_1 \tag{8}$$

and obtain the equations

$$\dot{D} = -[V_{12} c_{21} e^{i\delta t} + V_{21} c_{12} e^{-i\delta t}]/\hbar, \tag{9a}$$
$$\dot{c}_{12} = (V_{12}/2\hbar)\, D e^{i\delta t}, \quad \dot{c}_{21} = (V_{21}/2\hbar)\, D e^{-i\delta t}. \tag{9b}$$

Equations (9) can be solved exactly. Differentiation of Eq. (9a) and substitution in Eq. (9b) gives

$$\ddot{D} = -\hbar^{-2} | V_{12} |^2 D - (i\delta/\hbar)\, [V_{12} c_{21} e^{i\delta t} - V_{21} c_{12} e^{-i\delta t}].$$

Again differentiating and using Eqs. (9a, b) we obtain

$$D = -\{(| V_{12} |/\hbar)^2 + \delta^2\}\, \dot{D}. \tag{10}$$

The general integral of this equation is

$$D = \alpha \cos \Omega_0 (t - T) + \beta, \tag{11}$$

where

$$\Omega_0^2 = (| V_{12} | / \hbar)^2 + \delta^2 \tag{12}$$

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*One could choose the other possible initial condition $a_2 = 0$, $a_1 = 1$. The final result, as is clear from physical considerations, does not depend on which of these conditions is assumed.

and α, β and T are real constants. The initial conditions [Eq. (6)] can be rewritten in the new notation in the form

$$c_{12} = c_{21} = 0, \quad D = 1 \ \text{for} \ t = t_0. \tag{13}$$

If the first two conditions are substituted in Eq. (9a) we obtain $\dot{D} = 0$ when $t = t_0$; whence $T = t_0$ in Eq. (11). Analogously we find the constants α and β. As a result we obtain

$$D = (\hbar\Omega_0)^{-2} \{ |V_{12}|^2 \cos\Omega(t - t_0) + (\hbar\delta)^2 \}. \tag{14}$$

Let us now determine the mean dipole moment of a molecule at an instant of time t. Using Eq. (5), we find

$$\langle\mu\rangle = \int \Psi^*(t)\,\mu\,\Psi(t)\,dq = |a_1|^2 \mu_{11} + |a_2|^2 \mu_{22} + c_{12}\mu_{12} e^{-i\omega_0 t} + c_{21} e^{i\omega_0 t} \mu_{21}. \tag{15}$$

Using the corresponding principle as a basis, we can now find the emission and absorption of the molecule. The last two terms in Eq. (15) give the contribution to absorption of electromagnetic radiation of frequency ω.[2, 3] Therefore, we shall be interested in the first two terms in Eq. (15):

$$\langle\mu_1\rangle = |a_1|^2 \mu_{11} + |a_2|^2 \mu_{22} = {}^1/_2 [\mu_{11} + \mu_{22} + (\mu_{22} - \mu_{11}) \Omega_0^{-2}\delta^2] + {}^1/_2 (\hbar\Omega_0)^{-2} (\mu_{22} - \mu_{11}) |V_{12}|^2 \cos\Omega_0 (t - t_0). \tag{16}$$

Here we have used Eq. (14) and the fact that $|a_1|^2 + |a_2|^2 = 1$. The contribution to the emission is given by the variable part of the moment

$$\langle\tilde{\mu}\rangle = \mu_0 \cos\Omega_0 (t - t_0), \tag{17}$$

where*

$$\mu_0 = {}^1/_2 (\mu_{22} - \mu_{11}) (\hbar\Omega_0)^{-2} |V_{12}|, \tag{18}$$

in the case of strict resonance $\delta = 0$ and

$$\mu_0 = {}^1/_2 (\mu_{22} - \mu_{11}); \quad \Omega_0 = |V_{12}| / \hbar. \tag{19}$$

Taking into account that the times τ between collisions are distributed according to the law

$$w(\tau)\,d\tau = (1/\bar{\tau}) \exp(-\tau/\bar{\tau})\,d\tau \tag{20}$$

(this occurs for a sufficiently rarefied gas), one can find that the spectral intensity of the emission of a molecule has the form

$$I(\Omega) \backsim [(\Omega_0 - \Omega)^2 + \bar{\tau}^{-2}]^{-1}. \tag{21}$$

The total intensity of the emission is equal to

$$I_{\text{total}} = (\Omega_0^4/3c^3)\,\mu_0^2. \tag{22}$$

This emission is essentially a non-equilibrium process. It proceeds only under the influence of an external driving field (in our case the strong field of frequency ω). Therefore Kirchhoff's law does not apply here and the absorption by a molecule of a field of frequency Ω_0 will not bear the resonance character of Eq. (21).

In fact, in addition to the strong field of frequency ω, let a weak field of frequency Ω close to the frequency Ω_0 act on a molecule. Then the Hamiltonian of a molecule in an external field can be written

$$H = H_0 + V \sin\omega t + W \sin\Omega t. \tag{23}$$

In this case in place of Eqs. (9) we obtain

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*In Ref. 1 in the expression for μ_0 there is an additional factor $D_0 = \rho_{22}^0 - \rho_{11}^0$ or, in the notation of the present work, $D_0 = (|a_2|^2 - |a_1|^2)_{t = t_0}$. This quantity, however, has a modulus of unity (see the preceeding footnote) and we therefore omit it here.

$$\dot{D} = -\frac{1}{\hbar}[V_{12}c_{21}e^{i\delta t} + V_{21}c_{12}e^{-i\delta t}] + \frac{2\sin\Omega t}{i\hbar}[W_{21}e^{i\omega_{21}t}c_{12} - c_{21}W_{12}e^{i\omega_{12}t}];$$

$$\dot{c}_{12} = \frac{1}{2\hbar}V_{12}De^{i\delta t} + \frac{1}{i\hbar}\sin\Omega t\,[W_{12}e^{i\omega_{12}t} + c_{12}(W_{11} - W_{22})]; \quad \dot{c}_{21} = \frac{1}{2\hbar}V_{21}De^{i\delta t} - \frac{\sin\Omega t}{i\hbar}[W_{21}e^{i\omega_{21}t} + c_{21}(W_{11} - W_{22})].$$

If we discard the non-resonance terms of these equations we obtain

$$\dot{D} = -\frac{1}{\hbar}[V_{12}c_{21}e^{i\delta t} + V_{21}c_{12}e^{-i\delta t}]/\hbar; \tag{24a}$$

$$\dot{c}_{12} = (V_{12}/2\hbar)\,De^{i\delta t} + \frac{\sin\Omega t}{i\hbar}(W_{11} - W_{22})\,c_{12}, \quad \dot{c}_{21} = (V_{21}/2\hbar)De^{-i\delta t} - \frac{\sin\Omega t}{i\hbar}(W_{11} - W_{22})\,c_{21}. \tag{24b}$$

Examining, solely for simplicity, the case of strict resonance $\delta = 0$, differentiation of Eq. (24a) yields

$$\ddot{D} + \hbar^{-2}|V_{12}|^2 D = \frac{1}{i\hbar}\sin\Omega t\,(W_{11} - W_{22})\,[V_{12}c_{21} - V_{21}c_{12}]. \tag{25}$$

In the absence of a field of frequency Ω, the right side of Eq. (25) is zero. If absorption of the frequency Ω exists, it is caused by the term on the right side of Eq. (25). It is easy to see, however, that in our approximation the right side is zero. As a matter of fact, one can substitute Eqs. (9b) for c_{12} and c_{21} in the right side. But from these equations we have (for $\delta = 0$):

$$(d/dt)\,[V_{12}c_{21} - V_{21}c_{12}] = 0.$$

At the initial moment $t = t_0$; $c_{12} = c_{21} = 0$ and consequently for all time

$$V_{12}c_{21} - V_{21}c_{12} = 0.$$

Thus a weak external field of frequency $\Omega \approx \Omega_0$ does not change the character of the motion of a molecule and consequently, resonance absorption at the frequency Ω_0 does not exist. This also follows from the physical considerations presented above.

Let us now examine the question of the coherence of the radiation from the individual molecules of a gas. Let for example, E_1 and E_2 be components of the Stark splitting and μ_{11} and μ_{22} be effective dipole moments in the states 1 and 2. (In this case it is necessary to assume that the effect of a constant electric field is taken into account in the Hamiltonian of the "free" molecule H_0.) Then μ_0 [see Eq. (18)] will have one and the same value for all molecules and consequently, the amplitudes of the radiation fields of all molecules will have one and the same value.* The phase of the radiation however, is random and depends on the time of the last collision for each molecule. The total field intensity of the radiation of all the molecules will be:[6]

$$\mathbf{E} = \sum_i \mathbf{A}_i \cos\Omega\,(t - t_{i0}) = \mathbf{A}\sum_i \cos(\Omega t - \varphi_i) = \mathbf{E}_0\cos(\Omega t + \varphi), \tag{26}$$

$$\mathbf{E}_0^2 = A^2\Big[\Big(\sum_i \cos\varphi_i\Big)^2 + \Big(\sum_i \sin\varphi_i\Big)^2\Big]; \tag{27}$$

$$\tan\varphi = \sum_i \sin\varphi_i \Big/ \sum_i \cos\varphi_i. \tag{28}$$

Equation (27) can be rewritten in the form

$$E_0^2 = A^2\Big[n + 2\sum_{i,\,k}\cos(\varphi_i - \varphi_k)\Big], \tag{29}$$

where n is the number of molecules and the summation is carried out over the cosines of the $n(n-1)/2$ phase differences between the separate molecules.

Let us estimate the possible values of the phase differences $\epsilon_{ik} = \varphi_i - \varphi_k$. For all $\epsilon_{ik} \ll 1$, $E_0^2 \approx n^2A^2$ and the radiation is coherent; for ϵ_{ik}, which take all possible values from 0 to 2π and higher, the sum in Eq. (29) is equal to zero and the radiation is incoherent. In our case

$$\varepsilon_{ik} = \Omega\,(t_{i0} - t_{k0}).$$

For an estimate one can assume that $t_{i0} - t_{k0}$ varies from 0 to $\bar{\tau}$ —the mean time between collisions. But

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*In the example under discussion it is supposed that the molecules are separated by distances much smaller than the wavelength of the emitted radiation.

it is obvious that the condition $\Omega \overline{\tau} > 2\pi$ is essential for the existence of the spectral line Ω_0. Thus we can rewrite Eq. (26) in the form:

$$\mathbf{E} = \mathbf{A}\sqrt{n}\cos(\Omega t + \varphi),$$

and the intensity of radiation of all the molecules is obtained as the product of the intensity of radiation of a single molecule [Eq. (22)] by the number of molecules n:

$$J_s = (\Omega_0^4 / 3c^3)\mu_0^2 n. \tag{30}$$

Reabsorption of radiation at the frequency Ω_0 can be disregarded because there is no resonance absorption at the frequency Ω_0. We note that, in contrast to the intensity of spontaneous emission, which is proportional to the number of active molecules $n_{act} = n_2 - n_1$ (see, e.g., Refs. 7 — 9), where n_1 and n_2 are the numbers of molecules in the upper and lower levels, it is the total number of molecules which enters in Eq. (30). This is related to the circumstance that the intensity of radiation at the frequency Ω_0 does not depend on whether a molecule is found in the upper or lower level at the instant of collision.

The effect described here of radiation in the presence of a strong high-frequency field occurs only in a case where the difference $(\mu_{22} - \mu_{11})$ is not zero. Generally speaking, a check of this condition is not necessary in each specific case. One can say at once, however, that the indicated difference does not vanish for the case where $E_1 - E_2 = \hbar\omega_0$ depends on a constant electric (Stark effect) or magnetic (Zeeman effect) field.

As a matter of fact in this case the energy of interaction with the constant field F_c is included in the Hamiltonian of the "free" molecule

$$H_0' = H_0 - \mu_z F_c$$

(the steady field F_c is directed along the z axis). Further, since

$$(\partial H_0' / \partial F_c)_{nn} = -(\mu_z)_{nn} = \partial E_n / \partial F_c$$

(see, e.g., Ref. 5), we have

$$(\mu_z)_{22} - (\mu_z)_{11} = -\partial(E_2 - E_1) / \partial F_c.$$

Let us introduce the appropriate matrix elements for diatomic molecules and symmetric-top type molecules.

We examine first the diatomic molecule. If the molecule consists of different atoms (or of different isotopes), it has a constant dipole moment $\mu\mathbf{n}$, where $\mathbf{n}$ is a unit vector directed along the axis of the molecule. It will be necessary for us to determine the matrix elements $\mu_z = \mu n_z$.

In Hund's case a (see Ref. 5)

$$E(J, M_J, \Omega) = U_e + A_e\Omega + \hbar\omega_e(v + {}^1/_2) + B_e[J(J+1) - 2\Omega^2] - F_c\mu M_J\Omega / J(J+1).$$

Here E is the energy level of a molecule in the presence of an electric field F_c; $\Omega = \Lambda + \Sigma$ is the projection of the sum of the orbital and spin moments of a molecule on the axis of the molecule, J is the total moment of the number of motions of the molecule, and M_J is its projection on the z axis. If a high-frequency field F is directed along the z axis, the selection rules $\Delta J = \pm 1$; and $\Delta M_J = 0$ apply.

The difference of the energy levels is

$$E(J+1, M_J, \Omega) - E(J, M_J, \Omega) = 2B_e(J+1) - F_c\mu\frac{2M_J\Omega}{J(J+1)(J+2)};$$

whence

$$(\mu_z)_{22} - (\mu_z)_{11} = 2\mu M_J\Omega / J(J+1)(J+2).$$

We note that in the absence of an electric field there is degeneracy over the quantum numbers M_J which is completely removed by the linear Stark effect. Thus in our case the presence of an electric field is necessary since in the absence of the field the mean value of $(\mu_z)_{22} - (\mu_z)_{11}$ over all the degenerate sublevels of M_J is zero.

The matrix elements $(\mu_Z)_{12}$ in the present case have the form[5]

$$(\mu_z)_{J,\,M_J,\,\Omega}^{J+1,\,M_J,\,\Omega} = \mu\sqrt{(J+1)^2 - M_J^2}\,\frac{1}{J+1}\sqrt{\frac{(J+1)^2-\Omega^2}{4(J+1)^2-1}}\,.$$

In an analogous way one can find matrix elements for Hund's case b. In this case the energy of the Stark splitting is

$$-F_c(\mu_z)_{nn} = \Delta E_{M_J} = -F_c\mu M_J\Lambda\frac{J(J+1)-S(S+1)+K(K+1)}{2K(K+1)J(J+1)}\,.$$

Here Λ is the projection of the orbital moment of the electrons on the axis of the molecule, S is the total spin of all the electrons of the molecule, and K is the sum of the orbital moment of the electrons and of the rotational moment of the nuclei.

For non-linear molecules of the symmetric-top type it is easy to find[5]

$$(\mu_z)_{22} - (\mu_z)_{11} = 2\mu M_J k/J(J+1)(J+2); \quad (\mu_z)_{J,\,M_J,\,k}^{J+1,\,M_J,k} = \mu\sqrt{(J+1)^2-M_J^2}\,\frac{1}{J+1}\sqrt{\frac{(J+1)^2-k^2}{4(J+1)^2-1}}\,,$$

where J is the moment of the top, M_J its projection on the z axis and k the projection on the moving axis connected to the molecule. One should note that the matrix element $(\mu_Z)_{12}$ which determines the transition probability between the levels E_1 and E_2, generally speaking is different from the matrix element $(\mu_Z^0)_{12}$ which corresponds to the transition between the levels E_1^0 and E_2^0, where the index 0 denotes levels of the Hamiltonian H_0 (without a constant field). In case, however, the energy of the Stark splitting is much less than the difference of the levels of the non-perturbed Hamiltonian (only under this condition are all the formulas written down here correct), the difference of these elements is rather small.

With the aid of the formulas written down here for the matrix elements one can estimate the value of the intensity of the radiation Eq. (30). Let $\delta = 0$, then, according to Eq. (19)

$$\Omega_0 = F(\mu_z)_{12}/\hbar; \quad \mu_0 = {}^1/_2\,[(\mu_z)_{22} - (\mu_z)_{11}]$$

and for the symmetric-top we have*

$$J_s = \frac{F^2\mu^6}{3c^3\hbar^4}\,n\,\frac{[(J+1)^2 - M_J^2\,]^2[(J+1)^2 - k^2\,]^2 M_J^2 k^2}{J^2(J+1)^6(J+2)^2\,[4(J+1)^2-1]^2}\,.$$

Let $k = 1$, $M_J = 1$ and $J = 1$, then

$$J_s = 7.7\cdot 10^{-43}\,n\mu^6F^4\ \mathrm{w}\,.$$

Here μ is in Debye units and F is cgs units. If we take $\mu = 12$ (for the CsI molecule, see Ref. 10), $n = 10^{17}$ and F = 5 statvolts/cm = 1.5 kv/cm, then $J_S = 1.4 \times 10^{-16}$ w.

The intensity of radiation can be substantially raised by means of a molecular beam in which all of the molecules are in a single energy state. If a high-frequency field begins to act on a molecule in such a molecular beam, then in the first instant the system will radiate coherently with an intensity proportional to n^2, the square of the number of molecules in the beam. The dipole moment of the entire system will be equal to $n\mu_0 \cos\Omega_0(t-t_0)$. Newly arriving molecules, however, will decrease the dipole moment of the system since the sum of the dipole moments of these molecules is close to zero.

Actually, let the field begin to act at the time t_0. Then the dipole moment of the entire system at the time t is equal to

$$\mathbf{P} = n_1(t)\,\mu_0\cos\Omega_0(t-t_0) + \sum_{i=1}^{n_2(t)}\mu_0\cos\Omega_0(t-t_0-z_i/v_i),$$

where $n_2(t)$ is the number of molecules newly arrived in the time $t-t_0$ $[n_2(t_0)=0]$ and $n_1(t)$ is the number of molecules still remaining of those which in the initial moment filled the entire region in which the field was acting, $[n_1 = n - n_2]$; z_i and v_i are the coordinates and velocity of the i-th molecule.

At the instant of time $t_0 + \tau$, where τ is the mean time of flight of a molecule through the condenser (in which the high-frequency field acts) $n_1(t_0+\tau) = 0$ and the dipole moment

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*The same is true for diatomic molecules in a state with spin equal to zero if one substitutes J, M_J and k for K, M_K and Λ.

$$\mathbf{P} = \sum_{i=1}^{n} \mu_0 \cos \Omega_0 (t - t_0 - z_i / v_i) \approx 0.$$

The radiation becomes completely incoherent. If the field is now switched off, then after a time $\geq \tau$, i.e., at an instant of time $t_0' \geq t_0 + 2\tau$, all of the molecules in the condenser will be newly found in a single energy state. If at this moment the field is again switched on, radiation $\sim n^2$ once more resumes which after a time τ completely goes over into non-coherent radiation $\sim n$.

Thus in order to attain coherent radiation of a frequency Ω_0 it is necessary to supply a high-frequency field in pulses of duration $t_1 \leq \tau$, where the time between pulses t_2 must satisfy the condition $t_2 \geq \tau$. Then in the time interval t_1 the radiation Ω_0 will be approximately proportional to n^2 while in the interval t_2 the intensity will be zero. Thus, for $n = 10^{10}$ (this is a fully attainable number of molecules in a molecular beam; cf. Ref. 11) $n^2 = 10^{20}$, this gives an intensity of radiation $\sim 10^3$ larger than that calculated earlier.

3. QUANTUM-ELECTRODYNAMIC ANALYSIS

The occurrence radiation at the frequency Ω_0 [Eq. (12)] can be explained on the basis of simple quantum-electrodynamic considerations.

Actually a system which consists of a molecule and of an electromagnetic field of frequency ω, is described by the Hamiltonian

$$\mathcal{H} = H_0 + H^0_\gamma + V/2, \tag{31}$$

where H_0 is the Hamiltonian of the free field of frequency ω and $V/2$ is the interaction energy [the coefficient $^1\!/_2$ is needed to retain conformity with Eq. (30)]. We shall seek a solution of the equation

$$\mathcal{H}\Psi = \mathcal{E}\Psi \tag{32}$$

in the form of a superposition of solutions of the equation

$$(H_0 + H^0_\gamma)\,\Psi^{(0)} = \mathcal{E}^{(0)}\Psi^{(0)}.$$

Let us write

$$\Psi = c_1\Psi^{(0)}_1 + c_2\Psi^{(0)}_2, \tag{33}$$

where

$$\Psi^{(0)}_1 = \Psi^{(0)}_{1m}\Phi_{N_0}(N);\;\; \Psi^{(0)}_2 = \Psi_{2m}\Phi_{N_0+}\,(N)$$

are wave functions which correspond to energy levels of the system molecule + field:

$$\mathcal{E}^{(0)}_1 = E_1 + N_0\hbar\omega;\;\; \mathcal{E}^{(0)}_2 = E_2 + (N_0 + 1)\,\hbar\omega,$$

Here $\mathcal{E}_1^{(0)} \approx \mathcal{E}_2^{(0)}$; $\Psi_{1m}^{(0)}$ and $\Psi_{2m}^{(0)}$ are wave functions of the free molecule, $\Phi_{N_0}(N)$ and $\Phi_{N_0+1}(N)$ are wave functions of the free field and N is the number of photons

Substituting Eq. (33) in Eq. (32), multiplying first by $\Psi_1^{(0)*}$ and then by $\Psi_2^{(0)*}$ and integrating, we obtain two equations

$$c_1(\mathcal{E}^{(0)}_1 - \mathcal{E}) + c_2V_{12}/2 = 0, \quad c_1V_{21}/2 + c_2(\mathcal{E}^{(0)}_2 - \mathcal{E}) = 0. \tag{34}$$

The condition for the existence of a non-trivial solution to these equations gives

$$\mathcal{E}_{1,2} = \frac{1}{2}(\mathcal{E}^{(0)}_1 + \mathcal{E}^{(0)}_2) \pm \frac{1}{2}\sqrt{(\mathcal{E}^{(0)}_1 - \mathcal{E}^{(0)}_2)^2 + |V_{12}|^2}. \tag{35}$$

Thus, transitions of the molecule + field system are possible with radiation of quanta of energy

$$\mathcal{E}_1 - \mathcal{E}_2 = \sqrt{\hbar^2(\omega_0 - \omega)^2 + |V_{12}|^2} = \hbar\Omega_0. \tag{36}$$

This is the same expression for the frequency of the emission which we obtained earlier [see Eq. (12)].

On the basis of the correspondence principle we have found that the intensity of radiation is proportional to $|\mu_{11}-\mu_{22}|^2$. A quantum electrodynamic examination must lead to the conclusion that the matrix elements of the operator of the energy of interaction with the electromagnetic field of frequency Ω_0 which correspond to the transition $\mathcal{E}_1 \to \mathcal{E}_2$, are proportional to $|\mu_{11}-\mu_{22}|$. We shall demonstrate that this actually occurs.

The operator for the energy of interaction with the field of the emission can be written as

$$\hat{W} = \hat{W}_0(q) \sum_k{}' (a_k + \overset{+}{a}_k) = B\hat{\mu} \sum_k{}' (a_k + \overset{+}{a}_k); \tag{37}$$

Here $\hat{W}_0(q)$ depends only on the coordinates of the molecule, B is a constant and a_k and $\overset{+}{a}_k$ are operators of absorption and creation of photons of frequency $\Omega = ck$. The prime on the summation sign denotes that terms with frequency close to ω_0 are dropped from the sum, these terms being taken into account in Eq. (31) in the interaction energy V/2 with the external field of frequency ω. The matrix elements of the operator Eq. (37) have the form:

$$\left(\Psi_{\mathcal{E}_1} \Phi_{N_\Omega^0}(N_\Omega),\ \hat{W}_0(q) \sum_k{}' (a_k + a_k^+) \Psi_{\mathcal{E}_2} \Phi_{N_\Omega^0+1}(N_\Omega) \right). \tag{38}$$

Let further

$$\Psi_{\mathcal{E}_1} = c_1 \Psi_{1m} \Phi_{N_0}(N) + c_2 \Psi_{2m} \Phi_{N_0+1}(N), \quad \Psi_{\mathcal{E}_2} = c_1' \Psi_{1m} \Phi_{N_0}(N) + c_2' \Psi_{2m} \Phi_{N_0+1}(N). \tag{39}$$

Then the matrix element which corresponds to the appearance of a photon of frequency Ω, is

$$(\mathcal{E}_1, 0 \,|\, \hat{W} \,|\mathcal{E}_2, 1_\lambda) = \overset{*}{c}_1 c_1 ((\hat{W}_0 q))_{11} + \overset{*}{c}_2 c_2' (\hat{W}_0(q))_{22} = B(\overset{*}{c}_1 c_1' \mu_{11} + \overset{*}{c}_2 c_2' \mu_{22}). \tag{40}$$

Here we have taken into account the orthogonality of the functions Φ_{N_0} and Φ_{N_0+1}. The probability of a transition with the emission of a photon with frequency Ω is proportional to the square of the modulus of the matrix element Eq. (40) and is essentially different from zero under the condition that $\mathcal{E}_1 = \mathcal{E}_2 + \hbar\Omega$. This condition coincides with Eq. (36).

It is still necessary for us to find the coefficient c_1, c_1', c_2 and c_2'. From Eqs. (34) and (35) we find

$$c_1/c_2 = V_{12}/[\mathcal{E}_2^{(0)} - \mathcal{E}_1^{(0)} + \sqrt{(\mathcal{E}_1^{(0)} - \mathcal{E}_2^{(0)})^2 + |V_{12}|^2}], \quad \overset{*}{c}_1/\overset{*}{c}_2 = -c_2'/c_1' \quad \text{or} \quad \overset{*}{c}_1 c_1' = -\overset{*}{c}_2 c_2'. \tag{41}$$

Using Eqs. (40) and (41) we find

$$(\mathcal{E}_1 \,|\, \hat{W} \,|\, \mathcal{E}_2 + \hbar\Omega) = B\overset{*}{c}_1 c_1' (\mu_{11} - \mu_{22}). \tag{42}$$

Here under μ_{11} and μ_{22} it is necessary to understand the projection of the vectors μ_{11} and μ_{22} in the direction of polarization of the emitted quantum $\hbar\Omega$.

Thus the quantum electrodynamic approach justifies the application of the correspondence principle in our case.

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