

SCATTERING OF ELECTROMAGNETIC WAVES BY DIPOLE MOLECULES

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Scattering of an electromagnetic wave by molecules possessing dipole moments is considered by classical and quantum methods. Expressions are obtained for the total elastic and inelastic scattering cross sections. Frequency shifts are found which depend on the intensity of the incident wave.

THE spectrum of a system located in the field of a strong electromagnetic wave undergoes an appreciable change. This leads to various observed effects. The intensities and frequencies of the absorption lines change.^[1-3] In the Raman spectrum^[4] the frequency shifts relative to the frequency of the incident wave and the corresponding scattering cross sections will depend on the intensity of the incident wave.

In this paper we consider the motion of a molecule possessing a dipole moment in a strong radiation field. It is assumed that the electric field intensity E of the wave is small compared with the atomic field and the frequency ω_0 is considerably larger than the eigenfrequencies of the rotation of the molecules, but small compared with the vibrational frequencies. The change in the dipole moment d is due to the precession of the molecule (this change, as will be shown below, is $\sim d^2E/J\omega_0^2$) and to the polarizability (this change is $\sim \kappa E$, where the polarizability $\kappa \sim 10^{-24} \text{ cm}^3$). Therefore, for sufficiently low frequencies $\omega_0 \ll d\sqrt{JK} \sim 0.3 \text{ eV}$ one can ignore the polarizability and consider the molecule as a rigid rotator with a moment of inertia J and a dipole moment d of constant magnitude, whose interaction with the wave is of the form

$$U = -dE_0 \cos \omega_0 t. \tag{1}$$

The dipole moment will execute rapid precessional oscillations (of frequency ω_0), and the average kinetic energy of these oscillations will play the role of a potential energy for the slow rotation. If the field is sufficiently large, so that this potential energy is not small compared with the energy of free rotation, then the spectrum will change appreciably.

Let us begin with the classical treatment. The equations of motion of a rigid rotator in the field (1) are of the form

$$\varphi' = \frac{M_z}{J \sin^2 \theta}, \quad \theta'' = \frac{M_z^2 \cos \theta}{J^2 \sin^3 \theta} - \frac{dE_0}{J} \cos \omega_0 t \cos \theta, \tag{2}$$

where θ is the angle between d and E_0 , φ is the azimuthal angle, M_z is the conserved projection of the momentum on E_0 , and the primes denote time derivatives of the corresponding quantities.

We write $\theta(t)$ in the form

$$\theta(t) = \theta_0(t) + \frac{dE_0}{J\omega_0^2} \cos \omega_0 t \sin \theta_0(t), \tag{3}$$

where $\theta_0(t)$ changes with a frequency small compared with ω_0 . In addition we assume that the condition

$$dE_0/J\omega_0^2 \ll 1 \tag{4}$$

is satisfied. Substituting (3) in the second of Eqs. (2), and averaging over the rapid oscillations (of frequency ω_0), we obtain for θ_0 an equation with an effective potential energy^[5]

$$\theta_0'' = -\frac{1}{J} \frac{dU_{\text{eff}}}{d\theta_0}, \quad U_{\text{eff}} = \frac{M_z^2}{2J \sin^2 \theta_0} + \frac{1}{4} \frac{d^2 E_0^2}{J\omega_0^2} \sin^2 \theta_0, \tag{5}$$

which can be integrated in elementary fashion:

$$t = \int d\theta_0 \left\{ \frac{2}{J} (\varepsilon - U_{\text{eff}}) \right\}^{-1/2}. \tag{6}$$

The constant ε entering in (6) represents the energy of the motion of the rotator in the field of the wave averaged over the rapid oscillations. With the aid of an adiabatic invariant it can be related to the energy of the rotator for $t = -\infty$ if it is assumed that $E_0(t = -\infty) = 0$. The form of the effective potential energy depends on the relationship between $\alpha = d^2 E_0^2 / 4J\omega_0^2$ and $\beta = M_z^2 / 2J$. If $\alpha < \beta$, then U_{eff} has at the point $\pi/2$ a minimum

$$U_0 = \alpha + \beta. \tag{7}$$

If, on the other hand, $\alpha > \beta$, then U_{eff} has at the point $\pi/2$ a maximum equal to U_0 and two symmetrically placed minima

$$U_1 = 2\sqrt{\alpha\beta}. \tag{8}$$

For $\varepsilon > U_0$ the "slow" motion is given by the following equations:

$$\begin{aligned} \cos \theta_0 &= \sqrt{1 - a^2} \text{cn}(u_1, k_1), & \varphi &= \frac{b}{a\sqrt{b^2 - a^2}} \Pi(\text{am } u_1, n_1, k_1), \\ u_1 &= \frac{dE_0}{\sqrt{2}J\omega_0} \sqrt{b^2 - a^2} t & k_1 &= \sqrt{\frac{1 - a^2}{b^2 - a^2}}, \quad n_1 = \frac{1 - a^2}{a^2} \\ a^2 &= \frac{\varepsilon}{2\alpha} \left[1 - \sqrt{1 - \frac{4\alpha\beta}{\varepsilon^2}} \right], & b^2 &= \frac{\varepsilon}{2\alpha} \left[1 + \sqrt{1 - \frac{4\alpha\beta}{\varepsilon^2}} \right]. \end{aligned} \tag{9}$$

If, on the other hand, $U_0 < \varepsilon < U_1$ (under the condition $\alpha > \beta$), then the motion is given by the relations

$$\begin{aligned} \cos \theta_0 &= \sqrt{1 - a^2} \text{dn}(u_2, k_2), & \varphi &= \frac{b}{a\sqrt{1 - a^2}} \Pi(\text{am } u_2, n_2, k_2), \\ u_2 &= \frac{dE_0}{\sqrt{2}J\omega_0} \sqrt{1 - a^2} t, & k_2 &= \sqrt{\frac{b^2 - a^2}{1 - a^2}}, \quad n_2 = \frac{b^2 - a^2}{a^2}. \end{aligned} \tag{10}$$

The following notation^[6] has been used in (9) and (10): $\text{cn}(u, k)$, $\text{sn}(u, k)$, and $\text{dn}(u, k)$ are elliptic Jacobi func-

tions, am is the amplitude of u , and $\Pi(x, n, k)$ is an elliptic integral of the third kind. The components of the dipole moment are of the form

$$d_x \pm id_y \cong de^{\pm i\varphi} \sin \theta_0 + \frac{d^2 E_0}{J\omega_0^2} \cos \omega_0 t e^{\pm i\varphi} \sin \theta_0 \cos \theta_0,$$

$$d_z \cong d \cos \theta_0 - \frac{d^2 E_0}{J\omega_0^2} \cos \omega_0 t \sin^2 \theta_0.$$

Let us calculate the intensity of the dipole radiation. Differentiating in these equations only the second terms, we obtain the following expressions for the total scattering cross sections:

$$\sigma = \frac{8\pi}{3c^4} \frac{d^4}{J^2} \left\{ a^2 + (1-a^2) \left[1 - \frac{E(k_2)}{K(k_2)} \right] \right\}, \quad (11)$$

when $\alpha > \beta$ and $U_0 > \varepsilon > U_1$, and

$$\sigma = \frac{8\pi}{3c^4} \frac{d^4}{J^2} \left\{ a^2 + (b^2 - a^2) \left[1 - \frac{E(k_1)}{K(k_1)} \right] \right\}, \quad (12)$$

when $\varepsilon > U_0$. Here K and E are complete elliptic integrals of the first and second kind.

The usual expression for the total cross section for scattering by a rigid rotator (see, for example, [7]) is obtained from (11) and (12) if one replaces in the latter the curly brackets by $\frac{2}{3}$.

We present expressions for the cross sections which correspond to radiation of a given frequency. For $\alpha > \beta$ and $U_0 > \varepsilon > U_1$ they are of the form (the scattered frequencies are indicated in parentheses):

$$\sigma_n^{(1)} = \frac{8\pi}{3c^4} \frac{d^4}{J^2} A_n^2 \quad (\omega = \omega_0 + n\Omega_1),$$

$$\sigma_n^{(2)} = \frac{8\pi}{3c^4} \frac{d^4}{J^2} \frac{B_n^2}{2} \quad (\omega = \omega_0 + \Omega_2 + n\Omega_1),$$

$$\sigma_n^{(3)} = \frac{8\pi}{3c^4} \frac{d^4}{J^2} \frac{B_{-n}^2}{2} \quad (\omega = \omega_0 - \Omega_2 + n\Omega_1),$$

where

$$A_0 = a^2 + (1-a^2) \left[1 - \frac{E(k_2)}{K(k_2)} \right],$$

$$A_n = A_{-n} = -(1-a^2) \frac{\pi^2}{K^2(k_2)} \frac{n\lambda^n}{1-\lambda^{2n}}, \quad \lambda = \exp \left\{ -\pi \frac{K'(k_2)}{K(k_2)} \right\}, \quad n \geq 1,$$

$$B_n = \frac{a\sqrt{1-a^2}}{K(k_2)} \int_0^{K(k_2)} \cos \left\{ \frac{b}{a\sqrt{1-a^2}} \left[\Pi(\text{am } x, n_2, k_2) - \frac{\Pi(n_2 k_2)}{K(k_2)} x \right] - \frac{n\pi}{K(k_2)} x \right\} \text{dn}(x, k_2) \sqrt{1+n_2 \text{sn}^2(x, k_2)} dx, \quad (14)$$

$$\Omega_1 = \frac{\pi}{K(k_2)} \frac{dE_0}{\sqrt{2}J\omega_0} \sqrt{1-a^2}, \quad \Omega_2 = \frac{M_z}{Ja^2} \frac{\Pi(n_2, k_2)}{K(k_2)},$$

$$\Pi(n, k) \equiv \Pi(\pi/2, n, k),$$

and $K'(k)$ is $K(\sqrt{1-k^2})$.

Analogous expressions are also obtained for the case $\varepsilon > U_0$:

$$\sigma_n^{(4)} = \frac{8\pi}{3c^4} \frac{d^4}{J^2} C_n^2 \quad (\omega = \omega_0 + n\Omega_3),$$

$$\sigma_n^{(5)} = \frac{8\pi}{3c^4} \frac{d^4}{J^2} \frac{D_n^2}{2} \quad \left(\omega = \omega_0 + \Omega_4 + \frac{2n+1}{2} \Omega_3 \right),$$

$$\sigma_n^{(6)} = \frac{8\pi}{3c^4} \frac{d^4}{J^2} \frac{D_{-n}^2}{2} \quad \left(\omega = \omega_0 - \Omega_4 + \frac{2n+1}{2} \Omega_3 \right),$$

where

$$C_0 = a^2 + (b^2 - a^2) \left[1 - \frac{E(k_1)}{K(k_1)} \right],$$

$$C_n = C_{-n} = -(b^2 - a^2) \frac{\pi^2}{K^2(k_1)} \frac{n\lambda^n}{1-\lambda^{2n}}, \quad \lambda = \exp \left\{ \right.$$

$$D_n = \frac{a\sqrt{1-a^2}}{2K(k_1)} \int_0^{2K(k_1)} \cos \left\{ \frac{b}{a\sqrt{b^2-a^2}} \left[\Pi(\text{am } x, n_1, k_1) - \frac{\Pi(n_1, k_1)}{K(k_1)} x \right] - \frac{(n+1/2)\pi}{K(k_1)} x \right\} \text{cn}(x, k_1) \sqrt{1+n_1 \text{sn}^2(x, k_1)} dx;$$

$$\Omega_3 = \frac{\pi}{K(k_1)} \frac{dE_0}{\sqrt{2}J\omega_0} \sqrt{b^2-a^2}, \quad \Omega_4 = \frac{M_z}{Ja^2} \frac{\Pi(n_1, k_1)}{K(k_1)}. \quad (16)$$

In formulas (14) and (16) $\Omega_1, \Omega_2, \Omega_3$, and Ω_4 are frequencies of the "slow" motion of the rotator which depend on the intensity of the incident wave. Let us investigate these quantities in certain limiting cases. If $\alpha < \beta$ and $\varepsilon \approx U_0$,

$$\Omega_3 = 2 \frac{M_z}{J} \sqrt{1 - \frac{d^2 E_0^2}{2M_z^2 \omega_0^2}}, \quad \Omega_4 = \frac{M_z}{J},$$

and when $\varepsilon \gg U_0$, the energy dependence is the same as in the absence of the field:

$${}_{1/2}\Omega_3 = \Omega_4 = \sqrt{2\varepsilon/J}.$$

If $\alpha > \beta$ and the energy ε is close to the minimum $\varepsilon \approx U_1$,

$$\Omega_1 = 2 \frac{dE_0}{\sqrt{2}J\omega_0} \sqrt{1 - \sqrt{2} \frac{M_z \omega_0}{dE_0}}, \quad \Omega_2 = \frac{dE_0}{\sqrt{2}J\omega_0}.$$

For $\varepsilon \rightarrow U_0$ the frequency Ω_1 vanishes as $1/\ln(1-\varepsilon/U_0)^{-1}$, and $\Omega_2 = M_z/J$.

Let us consider the scattering cross sections for certain special cases. If the strong inequality

$$\alpha \gg \beta \sim \varepsilon_0 = M^2/2J, \quad (17)$$

holds, where ε_0 is the energy of the rotator in the absence of the wave, then the energy ε in the field of the wave is

$$\varepsilon = \frac{MdE_0}{\sqrt{2}J\omega_0} \approx U_1 \ll U_0. \quad (18)$$

In this case inelastic scattering occurs principally

$$\sigma_{\text{inel}}(\omega_0 + \Omega_2) = \sigma_{\text{inel}}(\omega_0 - \Omega_2) \approx \frac{\pi}{3c^4} \frac{d^4}{J^2} \frac{\varepsilon}{U_0} \left(1 + \frac{U_1}{\varepsilon} \right),$$

$$\sigma_{\text{inel}}(\omega_0 + \Omega_2 - \Omega_1) = \sigma_{\text{inel}}(\omega_0 - \Omega_2 + \Omega_1)$$

$$\approx \frac{\pi}{3c^4} \frac{d^4}{J^2} \frac{\varepsilon}{U_0} \left(1 - \frac{U_1}{\varepsilon} \right), \quad (19)$$

$$\Omega_2 \approx \frac{dE_0}{\sqrt{2}J\omega_0} \left(1 - \frac{\varepsilon - U_1}{4\alpha} \right), \quad \Omega_1 - \Omega_2 = \frac{dE_0}{\sqrt{2}J\omega_0} \left(1 - \frac{\varepsilon + U_1}{4\alpha} \right).$$

The total cross section is

$$\sigma \approx \frac{4\pi}{3c^4} \frac{d^4}{J^2} \frac{\varepsilon}{U_0}, \quad (20)$$

whereas the elastic cross section is small

$$\sigma_{\text{el}} \approx \frac{2\pi}{3c^4} \frac{d^4}{J^2} \left(\frac{\varepsilon}{U_0} \right)^2. \quad (20')$$

If the parameters α and β satisfy the condition

$$\alpha \sim \beta \ll \varepsilon_0, \quad (21)$$

then the energy in the wave $\varepsilon \approx \varepsilon_0 \gg U_0$, and the cross sections are of the form

$$\begin{aligned} \sigma_{\text{sey,up}}(\omega_0 \pm \Omega) &= 1/4\sigma, \quad \sigma_{\text{el}} = 1/2\sigma, \\ \sigma &= \frac{4\pi}{3c^4} \frac{d^4}{J^2}, \quad \Omega \approx 2 \sqrt{\frac{2\varepsilon}{J} \left(1 - \frac{\alpha}{4\varepsilon}\right)}. \end{aligned} \quad (22)$$

Finally, for a sufficiently weak field when

$$\alpha \ll \beta \lesssim \varepsilon_0, \quad (23)$$

we have $\varepsilon \approx \varepsilon_0 \sim U_0$, and

$$\begin{aligned} \sigma_{\text{el}} &= \frac{2\pi}{3c^4} \frac{d^4}{J^2} \left(1 + 3 \frac{U_0}{\varepsilon}\right), \\ \sigma_{\text{inel}}(\omega_0 \pm \Omega) &= \frac{\pi}{3c^4} \frac{d^4}{J^2} \left(1 - \frac{U_0}{\varepsilon}\right), \\ \sigma &= \frac{4\pi}{3c^4} \frac{d^4}{J^2} \left(1 + \frac{U_0}{\varepsilon}\right), \quad \Omega \approx 2 \sqrt{\frac{2\varepsilon}{J}}. \end{aligned} \quad (24)$$

Actually cases (21) and (23) correspond to classical perturbation theory.

Let us go over to the quantum mechanical calculation. In the Schrödinger equation for the wave function of a rigid dipole in the field of an electromagnetic wave

$$\left\{ \frac{\hbar^2}{2J} \mathbf{M}^2 - d\mathbf{E}_0 \cos \omega_0 t \right\} \Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

we carry out a change of variable

$$\theta = \theta_0 + \frac{dE_0}{J\omega_0^2} \cos \omega_0 t \sin \theta_0. \quad (25)$$

Assuming condition (4) satisfied, we seek Ψ in the form

$$\begin{aligned} \Psi &= \left\{ \sin \theta \left(1 + \frac{dE_0}{J\omega_0^2} \cos \omega_0 t \cos \theta_0\right) \right\}^{-1/2} \\ &\times \exp \left\{ i \frac{dE_0}{\hbar\omega_0} \sin \omega_0 t \cos \theta_0 \left(1 + \frac{1}{2} \frac{dE_0}{J\omega_0^2} \cos \omega_0 t \cos \theta_0\right) \right\} e^{im\varphi} u(t, \theta_0) \end{aligned} \quad (26)$$

In the equation for the "slow" function u we average over fast oscillations (of frequency ω_0). u can then be represented in the form

$$u = \exp\{-iet/\hbar\} w(\theta_0), \quad (27)$$

where w satisfies an equation with the effective potential energy

$$\frac{d^2 w}{d\theta_0^2} + \left\{ \frac{2J\varepsilon}{\hbar^2} + \frac{1}{4} - \frac{m^2 - 1/4}{\sin^2 \theta_0} - \frac{1}{2} \left(\frac{dE_0}{\hbar\omega_0} \right)^2 \sin^2 \theta_0 \right\} w = 0. \quad (28)$$

We consider the solutions of this equation (this is Hill's equation) for low-lying states in the case when $m \sim 1$, and

$$\mu \equiv dE_0 / \sqrt{2}\hbar\omega_0 \gg 1. \quad (29)$$

This condition is equivalent to (17). It is convenient to express w in the following form:

$$w = (\sin \theta_0)^{|m|+1/2} z(\theta_0), \quad (30)$$

and to solve the equation for z in the regions $\theta_0 \ll 1$ and $\pi - \theta_0 \ll 1$ where z is expressed in terms of Laguerre polynomials. We then have

$$\begin{aligned} z_{m,n}^{\pm} &\approx \left[\frac{2\mu^{1+|m|} n!}{(|m|+n)!} \right]^{1/2} \{ e^{-1/2\mu\theta_0^2} L_n^{|m|}(\mu\theta_0^2) \pm e^{-1/2\mu(\pi-\theta_0)^2} L_n^{|m|}[\mu(\pi-\theta_0)^2] \}, \\ n &= 0, 1, 2, \dots, \quad m = 0, \pm 1, \pm 2, \dots \end{aligned} \quad (31)$$

These two solutions have a definite symmetry with re-

spect to the point $\pi/2$. The energy eigenvalues are in the same approximation

$$\varepsilon_{m,n} \approx \frac{\hbar^2}{J} \frac{dE_0}{\sqrt{2}\hbar\omega_0} (2n + |m| + 1) + \frac{\hbar^2}{2J} |m| (|m| + 1). \quad (32)$$

Making use of these solutions, we calculate the probability of the emission of a quantum (in first-order perturbation theory in the radiation field); this leads to the following expressions for the scattering cross sections:

$$\sigma^{(1)} = \frac{2\pi}{3c^4} \frac{d^4}{J^2} \left| \int d\theta_0 \sin^2 \theta_0 w_{m'n'}^* w_{mn} \right|^2, \quad (33)$$

$$\hbar\omega = \hbar\omega_0 + \varepsilon_{m'n'} - \varepsilon_{mn},$$

$$\sigma^{(2)} = \frac{\pi}{3c^4} \frac{d^4}{J^2} \left| \int d\theta_0 \sin \theta_0 \cos \theta_0 w_{m\pm 1, n'}^* w_{m,n} \right|^2, \quad (34)$$

$$\hbar\omega = \hbar\omega_0 + \varepsilon_{m'n'} - \varepsilon_{m\pm 1, n'}.$$

In particular, the elastic cross section for scattering by the ground state ($m = m' = n = n' = 0$) is

$$\sigma_{\text{el}}^{(1)} \approx \frac{16\pi}{3c^4} \frac{d^4}{J^2} \left(\frac{\hbar\omega_0}{dE_0} \right)^2, \quad (35)$$

which coincides with the classical result (20') if the quantum value of the energy (32) is substituted in it.

For inelastic scattering ($m = m' = 0$, $n = 0 \rightarrow n' = 1$) we obtain the same expression, and for the transition ($n = n' = 0$, $m = 0 \rightarrow m' = \pm 1$) the cross section is large

$$\sigma_{\text{inel}}^{(2)} \approx \frac{2\sqrt{2}\pi}{3c^4} \frac{d^4}{J^2} \frac{\hbar\omega_0}{dE_0}. \quad (36)$$

The corresponding frequency is $\omega \approx \omega_0 - dE_0\sqrt{2}J\omega_0$. An analogous expression is obtained for the transition which corresponds to the emitted frequency $\omega \approx \omega_0 + dE_0\sqrt{2}J\omega_0$.

The results obtained are applicable to the scattering of a sufficiently intense electromagnetic wave with a frequency of the order of $10^{-2} - 10^{-1}$ eV by a rarefied gas whose molecules have a dipole moment. Such molecules are, for example (the dipole moment in atomic units is indicated in parentheses): HF (1.91), HCl (1.08), KF (7.3), KCl (10.6), and KI (6.8). In spite of the fact that the cross sections for scattering by a rigid rotator are small ($\sim d^4/J^2$), in the indicated frequency region they do nevertheless exceed by one or two orders of magnitude the cross sections for scattering due to the polarizability of the molecules. As has been shown in this paper, the shifting of lines in the Raman scattering depends essentially on the intensity of the incident wave if the interaction of the dipole with the wave is not small compared with the energy of the free rotation of the molecule ($\alpha \gtrsim \varepsilon_0$).

We have considered the spectrum of Eq. (28) when condition (29) is satisfied. In the opposite limiting case ($\mu \ll 1$) one can calculate the corrections to the energy levels of a free rotator in the usual way. These corrections will give rise to a Stark effect in a rapidly varying field.^[3] For example,

$$\Delta\varepsilon(l=0, m=0) = \frac{1}{6} \frac{d^2 E_0^2}{J\omega_0^2}, \quad \Delta\varepsilon(1, 0) = \frac{1}{10} \frac{d^2 E_0^2}{J\omega_0^2},$$

and in general

$$\Delta\varepsilon(l, m) = \frac{d^2 E_0^2}{J\omega_0^2} \frac{l(l+1) + m^2 - 1}{2(2l+3)(2l-1)}$$

We note that the obtained results concerning the rotational spectrum of a molecule in the field of a wave allow one in principle to consider the problem of the frequencies and intensities of absorption lines.

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