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Parametric resonance in rotation molecular spectra

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Abstract

The rotation molecular spectra, generated by the coupling of molecular electric-dipole moments to an external time-dependent electric field, are discussed in a few particular conditions which can be of some experimental interest. First, the spherical-pendulum molecular model is reviewed, with the aim of introducing an approximate method which consists in the separation between azimuthal and zenithal motions. Second, rotation spectra are considered in the presence of an external static electric field. Two particular cases are analyzed, corresponding to strong and weak fields. In both cases the dipoles perform rotations and vibrations around equilibrium positions, which may exhibit a parametric resonance. For strong fields a macroscopic electric polarization appears. This situation may be relevant for polar matter (like pyroelectrics, ferroelectrics), or for heavy impurities embedded in a polar solid, which may provide strong local static electric fields. The dipolar interaction is analyzed in polar condensed matter, where it is shown that new polarization modes appear for a spontaneous macroscopic electric polarization (these modes are tentatively called "dipolons"); one of the polarization modes is also related to a parametric resonance. The extension of these considerations to magnetic dipoles is also briefly discussed. The treatment is extended to strong electric fields which oscillate with a high frequency, as those provided by high-power lasers. It is shown that the effect of such fields on molecular dynamics is governed by a much smaller, effective, renormalized electric field.

Introduction. Many molecules possess a permanent electric-dipole moment in their ground state, which may couple to an external electric field; such a coupling may give rise to transitions in the molecular rotation. An external time-dependent electric field may also cause vibrations of the induced dipole moment. Typically, the molecular vibration-rotation spectra have frequencies in the range $\nu = 10^{13} - 10^{11}$(angular frequency $\omega = 10^{14} - 10^{12}$, infrared region).[1] We present here a new feature in the rotation molecular spectra, which is a parametric resonance caused by the presence of a external static electric field. We introduce also a dipolar interaction model in polar matter, which generate new polarization modes (tentatively called "dipolons"), including parametric resonances. The discussion is briefly extended to similar features exhibited by magnetic moments. The effect of strong, highly-oscillating electric fields, as those provided by high-power lasers, are also analyzed. It is shown that such fields are renormalized to effective, much smaller strengths, as a consequence of their much higher frequencies in comparison with the molecular rotation or vibration frequencies.

Free rotations. In many cases the free molecular rotations are described satisfactorily by using a spherical-pendulum model (spatial, rigid rotator, spherical top) for the molecule. A spherical pendulum consists of a point of mass M which rotates freely in space at the end of a radius $\mathbf{r} = r(\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$, as described by the hamiltonian

$$H = \frac{1}{2}M\dot{\mathbf{l}}^2 = \frac{1}{2}Ml^2(\dot{\theta}^2 + \dot{\varphi}^2\sin^2\theta) \ ; \tag{1}$$

if the point has a charge q, it is a dipole $\mathbf{d} = q\mathbf{r}$ which can couple to an external electric field $\mathbf{E}\cos\omega t$, with an interaction hamiltonian $H_{int}(t) = -dE\cos\theta\cos\omega t$. We take the electric field directed along the z-axis.

As it is well known, the angular momentum $\mathbf{L} = M\mathbf{r}\times\dot{\mathbf{r}}$ has the components $L_x = Mr^2(-\dot{\theta}\sin\varphi - \dot{\varphi}\sin\theta\cos\theta\cos\varphi)$, $L_y = Mr^2(\dot{\theta}\cos\varphi - \dot{\varphi}\sin\theta\cos\theta\sin\varphi)$, $L_z = Mr^2\dot{\varphi}\sin^2\theta$, so that the rotation hamiltonian can be written as

$$H = \frac{1}{2I}L^2 \ , \tag{2}$$

where $I = Mr^2$ is the moment of inertia. The quantum-mechanical expression for L^2 is

$$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \ , \tag{3}$$

with the eigenfunctions Y_{lm} (spherical harmonics) and the eigenvalues $\hbar^2 l(l+1)$, $l = 0, 1, ...$. The z-component of the angular momentum is $L_z = -i\hbar\frac{\partial}{\partial\varphi}$, with the same eigenfunctions Y_{lm}, $L_z Y_{lm} = \hbar m Y_{lm}$, $m = -l, -l+1, ...l$. Therefore, the energy levels of the spherical pendulum are $E_l = \frac{\hbar^2}{2I}l(l+1)/2I$; they are degenerate with respect to the quantum number m which takes $2l+1$ values.

The classical dynamics of the free motion is governed by the equations

$$\ddot{\theta} = \dot{\varphi}^2\sin\theta\cos\theta \ , \ I\frac{d}{dt}(\dot{\varphi}\sin^2\theta) = 0 \ ; \tag{4}$$

from the second equation (4) we get $\dot{\varphi} = L_z/I\sin^2\theta$, which indicates the conservation of the component L_z of the angular momentum. Moreover, making use of the equations of motion (4), we check easily the conservation of the other two components L_x and L_y of the angular momentum given above; indeed, the angular momentum $\mathbf{L}$ is conserved in the free motion of the spherical pendulum. The hamiltonian given by equation (1) can be written as

$$H = \frac{1}{2}I\dot{\theta}^2 + \frac{L_z^2}{2I\sin^2\theta} \ ; \tag{5}$$

the effective potential function $U_{eff} = L_z^2/2I\sin^2\theta$ has a minimum for $\theta = \pi/2$; the motion may be limited to small oscillations about the equatorial plane $\theta = \pi/2$. Indeed, introducing $\delta\vartheta = \theta - \pi/2$ we get

$$\frac{L_z^2}{2I\sin^2\theta} = \frac{L_z^2}{2I} + \frac{L_z^2}{2I}\delta\theta^2 + ... \tag{6}$$

and

$$H \simeq \frac{1}{2}I\delta\dot{\theta}^2 + \frac{L_z^2}{2I}\delta\theta^2 + \frac{L_z^2}{2I} \ , \tag{7}$$

$$L_x = I(-\delta\dot{\theta}\sin\varphi + \dot{\varphi}\delta\theta\cos\varphi) \ , \ L_y = I(\delta\dot{\theta}\cos\varphi + \dot{\varphi}\delta\theta\sin\varphi) \ , \ \dot{\varphi} = L_z/I = \omega_0 \ , \tag{8}$$

where we have introduced the frequency $\omega_0 = L_z/I$. We can see that there is a precession $\varphi = \omega_0 t$ about the z-axis and an oscillation $\delta\theta = A\cos(\omega_0 t + \delta)$, where A is an undetermined amplitude and δ is an undetermined phase, according to the small oscillations guverned by the hamiltonian given by equation (7). We can check easily that the angular momentum given by equations (8) is conserved ($\dot{\mathbf{L}} = 0$); the components of the angular momentum are $L_x = IA\omega_0 \cos\delta$, $L_y = IA\omega_0 \sin\delta$, and $L_z = I\omega_0$. We can rotate the equatorial plane $\theta = \pi/2$ by an angle given by $\sin\alpha = IA\omega_0/\sqrt{I^2\omega_0^2 + I^2A^2\omega_0^2} \simeq A$, such that the motion will be an in-plane motion. (For the classical dynamics of the spherical pendulum see Refs. [2, 3]).

In the presence of the interaction the classical equations of motion are

$$\begin{gathered} \ddot{\theta} = \dot{\varphi}^2 \sin\theta\cos\theta - \tfrac{dE}{I}\sin\theta\cos\omega t \ , \\ I\tfrac{d}{dt}(\dot{\varphi}\sin^2\theta) = 0 \ ; \end{gathered} \tag{9}$$

we can see that the component $L_z = I\dot{\varphi}\sin^2\theta$ of the angular momentum is conserved, which leads again to the effective potential function $U_{eff} = \frac{L_z^2}{2I\sin^2\theta}$ in the hamiltonian given by equation (1); it follows that for low energies the angle θ oscillates around the minimum point $\theta = \pi/2$ of this potential function, and only for high energy values it may perform complete rotations. At usual temperatures and for usual electric fields the energies are low and l may acquire large values. In the classical limit, the spherical pendulum rotates as a quasi-planar rotator, with small oscillations around the equilibrium value $\theta = \pi/2$.[1] We limit ourselves to such small oscillations $\delta\theta$ around $\theta = \pi/2$, whose dynamics is governed by the harmonic-oscillator equation

$$\delta\ddot{\theta} + \omega_0^2\delta\theta = -\frac{dE}{I}\cos\omega t \ \ , \tag{10}$$

where $\omega_0 = L_z/I = \hbar m/I$; we include a damping term $2\gamma\delta\dot{\theta}$ and get the solution

$$\delta\theta = a\cos\omega t + b\sin\omega t \ \ , \tag{11}$$

where

$$a = \tfrac{dE}{2I\omega_0}\tfrac{\omega-\omega_0}{(\omega-\omega_0)^2+\gamma^2} \ , \ b = -\tfrac{dE}{2I\omega_0}\tfrac{\gamma}{(\omega-\omega_0)^2+\gamma^2} \tag{12}$$

for ω near ω_0; we can see that the classical dynamics yields a resonance for $\omega = \omega_0 = L_z/I$; the azimuthal angle $\varphi = \omega_0 t$ rotates freely. This approximation corresponds to $L_z \simeq L$ ($m \simeq l$, $L_x^2 + L_y^2 \ll L_z^2 \simeq L^2$). The mean absorbed power is

$$P = -dE\overline{\delta\dot{\theta}\cos\omega t} = -\frac{1}{2}dEb\omega_0 = \frac{d^2E^2}{4I}\frac{\gamma}{(\omega-\omega_0)^2+\gamma^2} \ \ , \tag{13}$$

which is a typical resonance function of ω.

For the interaction hamiltonian $H_{int}(t) = -dE\cos\theta\cos\omega t$ the transition rate of quantum jumps for $\omega_0 = (E_{l+1} - E_l)/\hbar = (\hbar/I)(l+1)$ is

$$\frac{\partial\left|c_{lm}\right|^2}{\partial t} = \frac{\pi d^2E^2}{2\hbar^2}\left|(\cos\theta)_{lm}\right|^2\delta(\omega_0 - \omega) \ \ , \tag{14}$$

where

$$(\cos\theta)_{lm} = (\cos\theta)_{l+1,m;l,m} = -i\sqrt{\frac{(l+1)^2 - m^2}{(2l+1)(2l+3)}} \tag{15}$$

(c_{lm} are the coefficients of the superposition of the wavefunctions); the absorbed power is

$$\begin{gathered} P_q = \hbar\omega_0\sum_{m=-l}^{l}\tfrac{\partial\left|c_{lm}\right|^2}{\partial t} = \tfrac{\pi d^2E^2}{2\hbar}\omega_0\sum_{m=-l}^{l}\left|(\cos\theta)_{lm}\right|^2\delta(\omega_0-\omega) = \\ = \tfrac{d^2E^2}{6\hbar}\omega_0(l+1)\tfrac{\gamma}{(\omega-\omega_0)^2+\gamma^2} = \tfrac{d^2E^2}{6I}(l+1)^2\tfrac{\gamma}{(\omega-\omega_0)^2+\gamma^2} \end{gathered} \tag{16}$$

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[1] For weak electric fields we may leave aside the coupling between vibrations and rotations.

(for $\gamma \rightarrow 0^+$) and the net absorbed power at finite temperatures is given by

$$\begin{gathered}P_{q,th}=\tfrac{\pi d^2E^2}{2\hbar}\omega_0\times\\ \times\sum_{m=-l}^{l}\left|(\cos\theta)_{lm}\right|^2\left[e^{-\beta\hbar^2l(l+1)/2I}-e^{-\beta\hbar^2(l+1)(l+2)/2I}\right]\delta(\omega_0-\omega)/Z\ ,\end{gathered}\tag{17}$$

where

$$Z=\sum_{l=0}(2l+1)e^{-\beta\hbar^2l(l+1)/2I}=\frac{2I}{\beta\hbar^2}\tag{18}$$

is the partition function ($\beta=1/T$ is the reciprocal of the temperature T); we get

$$\begin{gathered}P_{q,th}=\tfrac{\pi d^2E^2}{12I}(l+1)^3\left(\tfrac{\beta\hbar^2}{I}\right)^2e^{-\beta\hbar^2l(l+1)/2I}\delta(\omega_0-\omega)=\\ =\tfrac{1}{2}P_q(l+1)\left(\tfrac{\beta\hbar^2}{I}\right)^2e^{-\beta\hbar^2l(l+1)/2I}\end{gathered}\tag{19}$$

(the suffix q stands for "quantum-mechanical").

We use $I=10^{-38}g\cdot cm^2$, which is a typical numerical value for the molecular moment of inertia (molecular mass $M=10^5$ electronic mass $m_e=10^{-27}g$ (heavy molecules), the dipole length $r=10^{-8}cm$ (1Å)), and get $\hbar/I=10^{11}s^{-1}\simeq 1K$ ($\omega_0=\hbar m/I$, or $\omega_0=\hbar(l+1)/I$); at room temperature there are many levels occupied, and we may use $\beta\hbar^2(l+1)/I\ll 1$). It is worth noting that $\delta P_q=(\partial P_q/\partial l)$ ($\delta l=1$), as given by equation (16) resembles very much the power absorbed in the classical motion (after multiplying with the degeneracy factor $2l+1$), given by equation (13) (up to an irrelevant numerical factor); this is the expression of the quasi-classical approximation. Indeed, the quantum-mechanical transitions for the harmonic-oscillator given by equation (7) give an absorbed power $P=(\pi d^2E^2/4I)(n+1)\delta(\omega_0-\omega)$ (where we have used the matrix elements $(\delta\theta)_{n+1,n}=\sqrt{\hbar(n+1)/2I\omega_0}$), which is very close to $\delta P_q=(\pi d^2E^2/3I)(l+1)\delta(\omega_0-\omega)$ given by equation (16), providing $n\simeq l\simeq m$; the additional factor $l+1$ in equation (16) originates in the removal of the rotational degeneracy of the spherical pendulum in the harmonic-oscillator approximation. As a matter of fact, the harmonic-oscillator approximation used here is valid for $(\delta\theta)_{n+1,n}\ll 1$, which, using $\omega_0=L_z/I=m\hbar/I$, yields $n+1\ll 2m$; summing up the absorbed power $P=(\pi d^2E^2/4I)(n+1)\delta(\omega_0-\omega)$ with respect to n, we get a total power very similar with the exact result given by equation (16). We conclude that the separation of the azimuthal and zenithal motions for heavy molecules is a satisfactory approximation for the molecular rotations.

Strong static electric field. Consider a constant, uniform electric field $\mathbf{E}_0=E_0(0,0,1)$ oriented along the z-axis; the potential energy of an electric dipole $\mathbf{d}=d(\sin\theta\cos\varphi,\sin\theta\sin\varphi,\cos\theta)$ of arbitrary orientation θ, φ is $U=-dE_0\cos\theta$. The hamiltonian of rotation in this field is given by

$$H=\frac{1}{2}I(\dot{\theta}^2+\dot{\varphi}^2\sin^2\theta)-dE_0\cos\theta\ ,\tag{20}$$

where I is the moment of inertia of the dipole, considered as a sherical pendulum (spherical top). The equation of motion

$$I\frac{d}{dt}(\dot{\varphi}\sin^2\theta)=0\tag{21}$$

indicates that the component L_z of the angular momentum is conserved, $\dot{\varphi}\sin^2\theta=L_z/I$; consequently, an effective potential function

$$U_{eff}=\frac{L_z^2}{2I\sin^2\theta}-dE_0\cos\theta\tag{22}$$

appears in the hamiltonian. We assume that the dipole energy dE_0 is much greater than the rotation energy L_z^2/I, which is of the order of the temperature T. For typical value $d = 10^{-18} statcoulomb \cdot cm$ and temperature $T = 300K \simeq 4\times10^{-14} erg$ this condition requires an electric field $E_0 \gg T/d = 4\times10^4 statvolt/cm \simeq 1.2\times10^9 V/m$. This is a strong electric field; for comparison, the electric field created by an electron charge at distance $1\text{Å} = 10^{-8}cm$ is $4.8\times10^{-10}/10^{-16} = 4.8\times10^6 statvolt/cm$ (atomic fields). A strong static electric field may appear as an internal field in polar condensed matter (*e.g.*, pyroelectrics, ferroelectrics). At low temperatures the free molecular rotations may be hindered, and the dipoles get quenched in parallel, equilibrium positions; they may only perform small rotations and vibrations around these equilibrium positions. The transitions from free rotations to small vibrations around quenched positions in polar matter is seen in the curve of the heat capacity *vs* temperature.[4, 5] The electric field produced by the nearest neighbours, averaged over their small vibrations and rotations, give rise to a local, static (mean) electric field, which can be as high as the atomic fields. The condition $E_0 \gg T/d$ shows that at lower temperatures (and high values of the electric dipoles) the field E_0 may be lower. Similarly, strong static electric fields may appear locally near polar impurities with large moments of inertia, embedded in polar matter. Under such conditions the effective potential given by equation (22) has a minimum value for $\theta_0 \simeq (L_z^2/IdE_0)^{1/4} \simeq (T/dE_0)^{1/4} \ll 1$; it can be expanded in powers of $\delta\theta = \theta - \theta_0$ around this minimum value as

$$U_{eff} \simeq -dE_0 + 2dE_0\delta\theta^2 \ ; \tag{23}$$

the hamiltonian given by equation (20) becomes

$$H \simeq \frac{1}{2}I\delta\dot{\theta}^2 + \frac{1}{2}I\omega_0^2\delta\theta^2 - dE_0 \ , \tag{24}$$

where $\omega_0 = 2\sqrt{dE_0/I}$ is sometimes known as Rabi's frequency;[6, 7] according to our condition of strong field, we have $\omega_0 \gg 10^{12}s^{-1}$ (we consider electric fields that are not as high as to produce rotation frquencies comparable with the molecular vibration frequencies). Therefore, the dipoles exhibit quenched equilibrium positions in the static electric field E_0, where they perform small oscillations and rotations. The angle φ rotates freely with the frequency $\dot{\varphi} \simeq L_z/I\sin^2\theta_0 = \frac{1}{2}\omega_0$ ($\varphi = \frac{1}{2}\omega_0 t$). It is worth noting that the frequency ω_0 is given by the static field E_0.

Consider an external time-dependent field $\mathbf{E}(t) = E(t)(\sin\alpha, 0, \cos\alpha)$, $E(t) = E\cos\omega t$, which makes an angle α with the z-axis; its interaction with the dipole is

$$H_{int} = -dE(t)(\sin\alpha\sin\theta\cos\varphi + \cos\alpha\cos\theta) \ , \tag{25}$$

which provides two relevant interaction hamiltonians:

$$\begin{gathered} H_{1int} = -\tfrac{1}{2}dE\sin\alpha\left[\cos(\omega + \tfrac{1}{2}\omega_0)t + \cos(\omega - \tfrac{1}{2}\omega_0)t\right]\delta\theta \ , \\ H_{2int} = \tfrac{1}{2}dE\cos\alpha\cos\omega t \cdot \delta\theta^2 \ . \end{gathered} \tag{26}$$

The interaction hamiltonian H_{1int} produces transitions between the harmonic-oscillator states n and $n+1$ with the resonance frequency $\Omega = \frac{1}{2}\omega_0$, $\frac{3}{2}\omega_0$. In general, for an interaction $H_{int} = h\cos\omega t$, the rate of transition between two states n and $n+s$, with energies E_n, E_{n+s} is

$$\frac{\partial\left|c_{n+s,n}\right|^2}{\partial t} = \frac{\pi}{2\hbar^2}\left|h_{n+s,n}\right|^2\delta(\omega_{n;s} - \omega) \tag{27}$$

in the first order of the perturbation theory, where $\omega_{n;s} = (E_{n+s} - E_n)/\hbar$ and $c_{n+s,n}$ are the coefficients of the superposition of the wavefunctions. For H_{1int} we get

$$\frac{\partial\left|c_{n+1,n}\right|^2}{\partial t} = \frac{\pi}{16\hbar I\omega_0}d^2E^2(n+1)\sin^2\alpha\delta(\omega - \Omega) \tag{28}$$

and the absorbed power

$$P_q = \hbar\Omega \tfrac{\partial |c_{n+1,n}|^2}{\partial t} = \tfrac{\pi}{16 I\omega_0} d^2 E^2 \Omega (n+1) \sin^2\alpha\delta(\omega-\Omega) = \\ = \tfrac{1}{16 I\omega_0} d^2 E^2 \Omega (n+1) \sin^2\alpha \tfrac{\gamma}{(\omega-\Omega)^2+\gamma^2} \ , \ \gamma \rightarrow 0^+ \ , \tag{29}$$

which is a typical resonance curve. In order to compute the mean power the thermal weigths $e^{-\beta\hbar\omega_0 n}/\sum e^{-\beta\hbar\omega_0 n}$ should be inserted, where $\beta = 1/T$ is the inverse of the temperature T; in addition, the reverse transitions must be taken into account. Since $\beta\hbar\omega_0 \gg 1$, only the lowest states n are excited by interaction. The temperature dependence is given by

$$P_{q,th} = \tfrac{\pi}{16 I\omega_0} d^2 E^2 \Omega \sum_{n=0} (n+1) \left[e^{-\beta\hbar\omega_0 n} - e^{-\beta\hbar\omega_0 (n+1)} \right] \times \\ \times \sin^2\alpha\delta(\omega-\Omega)/\sum_{n=0} e^{-\beta\hbar\omega_0 n} \ , \tag{30}$$

where the summation over n is, in principle, limited.

We should limit ourselevs to the lowest states of the harmonic oscillator, since the oscillation amplitude $\delta\theta$ must be much smaller than the angle θ_0. The matrix element $(\delta\theta)_{n+1,n} = \sqrt{\hbar/2I\omega_0}\sqrt{n+1}$ for the harmonic oscillator should be much smaller than $\theta_0 \simeq (L_z^2/IdE_0)^{1/4}$, which implies $\hbar(n+1) \ll 4L_z \simeq 4\sqrt{IT}$; for typical values $I = 10^{-38} g\cdot cm^2$ (10^5 electronic mass for the molecular mass, $10^{-8} cm$ for the dipole length) we get $n \ll 80$ for $T = 300K$ (and $n \ll 8$ for $T = 3K$). Consequently, for $\beta\hbar\omega_0 \gg 1$ we may extend the summation in equation (30) to $n = \infty$; we get $P_{q,th}$ independent of temperature. Making use of the expressions $L_x = I(-\dot\theta\sin\varphi - \dot\varphi\sin\theta\cos\theta\cos\varphi)$, $L_y = I(\dot\theta\cos\varphi - \dot\varphi\sin\theta\cos\theta\sin\varphi)$, we get $L_x \simeq -(1/2)I\omega_0\theta_0\cos\omega_o t/2$ and $L_y \simeq -(1/2)I\omega_0\theta_0\sin\omega_o t/2$ for the transverse components of the angular momentum, which show that the strong-field approximation corresponds to $L_x^2 + L_y^2 \simeq L^2 \gg L_z^2$.

Under the same conditions, the harmonic-oscillator hamiltonian given by equation (24) and the interaction hamiltonian H_{2int} given by equation (26),

$$H^{'} = H + H_{2int} = \frac{1}{2} I \delta\dot\theta^2 + \frac{1}{2} I\omega_0^2 (1 + h\cos\omega t)\delta\theta^2 \ , \tag{31}$$

where $h = \frac{E}{2E_0}\cos\alpha$, lead to the classical equation of motion

$$\delta\ddot\theta + \omega_0^2 (1 + h\cos\omega t)\delta\theta = 0 \ , \tag{32}$$

which is the well-known equation of parametric resonance (Mathieu's equation).[8] As it is well known, beside periodic solutions, the classical equation (32) has also aperiodic solutions, which may grow indefinitely with increasing the time; these are (parametrically) resonant solutions, which occur for ω in the neighbourhood of $2\omega_0/n$, $n = 1, 2, 3...$. As we can see immediately, the solutions of equation (32) are determined by the initial conditions $\delta\theta(t=0)$ and $\delta\dot\theta(t=0)$ (as for any homogeneous equation). The initial conditions are vanishing due to thermal fluctuations, so the classical solutions of equation (32) are ineffective.

The quantum-mechanical dynamics is different. The interaction hamiltonian H_{2int} produces transitions between the harmonic-oscillator states n and $n+2$ (due to the matrix elements of $\delta\theta^2$; this is an example of a double-quanta process[9]). These transitions have frequency $2\omega_0$, in accordance with the classical dynamics. The transition rate is

$$\frac{\partial \left|c_{n+2,n}\right|^2}{\partial t} = \frac{\pi h^2}{128}\omega_0^2 (n+1)(n+2)\delta(2\omega_0 - \omega) \tag{33}$$

and the absorbed power

$$P_q = 2\hbar\omega_0 \tfrac{\partial |c_{n+2,n}|^2}{\partial t} = \tfrac{\pi h^2}{64}\hbar\omega_0^3(n+1)(n+2)\delta(2\omega_0-\omega) = \\ = \tfrac{h^2}{64}\hbar\omega_0^3(n+1)(n+2)\tfrac{\gamma}{(2\omega_0-\omega)^2+\gamma^2}\ ,\ \gamma \to 0^+\ , \tag{34}$$

where we may restrict, in principle, to the lowest states. The intensity given by equation (34) is small, because, especially, of the factor $(E/E_0)^2$. The temperature dependence is given by

$$P_{q,th} = \tfrac{\pi h^2}{64}\hbar\omega_0^3 \sum_{n=0}(n+1)(n+2)\times \\ \times \left[e^{-\beta\hbar\omega_0(2n+1)} - e^{-\beta\hbar\omega_0(2n+3)}\right]\delta(2\omega_0-\omega)/\left[\sum_{n=0} e^{-\beta\hbar\omega_0 n}\right]^2\ , \tag{35}$$

in accordance with the direct transitions $n \to n+1 \to n+2$ and the corresponding reverse transitions; $P_{q,th}$ is also diminished by the thermal factor $e^{-\beta\hbar\omega_0}$ for $\beta\hbar\omega_0 \gg 1$.

The parametric resonance disappears for $\alpha = \frac{\pi}{2}$, *i.e.* for the applied field $\mathbf{E}$ at right angle with the quenching field $\mathbf{E}_0$. The effect of the parametric resonance depends on the orientation of the solid; in amorphous samples the average over angles α should be taken ($\overline{\cos^2\alpha} = \frac{1}{3}$). The parameter γ in equation (34), which gives the width of the absorption line, is a damping parameter; in solids it originates, very likely, in the dipolar interaction. Since the dipolar interaction is taken mainly in the quenching effect, we may expect a small damping, and, consequently, rather sharp resonance lines. In liquids, beside the random distribution of the dipoles (and the average over angle α), we may expect the usual motional narrowing of the line. In gases the quenching field is weak, and the parametric resonance is not likely to occur.

Weak static electric field. Consider now the opposite case, when the field E_0 is weak, such that $dE_0 \ll L_z^2/I$. The effective potential U_{eff} given by equation (22) has a minimum value for $\theta \simeq \frac{\pi}{2}$ and the hamiltonian given by equation (20) reduces to

$$H \simeq \frac{1}{2}I\dot{\widetilde{\theta}}^2 + \frac{1}{2}I\omega_0^2\dot{\widetilde{\theta}}^2\ , \tag{36}$$

where $\widetilde{\theta} = \theta - \frac{\pi}{2}$ and $\omega_0 = L_z/I$; the field E_0 brings only a small correction to the $\pi/2$-shift in θ, while its contribution to the hamiltonian is a second-order effect. The angle φ moves freely with angular velocity $\dot{\varphi} = \omega_0$. In contrast with the high-field case, where the frequency $\dot{\varphi}$ is fixed by the static field E_0, in the low-field case we may quantize the φ-motion, according to $L_z = \hbar m$, m integer, such that $\omega_0 = \frac{\hbar}{I}m$; the lowest value of this frequency is $\hbar/I \simeq 10^{11}s^{-1}$ for typical values $I = 10^{-38}g\cdot cm^2$ (10^5 electronic mass for the molecular mass, $10^{-8}cm$ for the dipole length). We can see that the molecular rotations are described by a set of harmonic oscillators with frequencies $\omega_0 = \frac{\hbar}{I}m$, beside the φ-precession (which has the same frequencies ω_0). The energy quanta are $\hbar\omega_0 = \frac{\hbar^2}{I}m$, with the lowest value $\frac{\hbar^2}{I} = 1K$ (for our numerical values). The approximation described above is valid for $\widetilde{\theta}_{n+1,n} = \sqrt{\hbar(n+1)/2I\omega_0} \ll 1$, which leads to $\hbar(n+1) \ll 2L_z$, or $n \ll m$. Similarly, the transverse components of the angular momentum are very small, $L_x^2 + L_y^2 \ll L^2 \simeq L_z^2$ ($m \simeq l$); at room temperature m may acquire as high values as $m = 300$.

The interaction hamiltonian given by equation (25) leads to two relevant interactions

$$H_{1int} = dE\cos\alpha\cos\omega t\cdot\widetilde{\theta}\ , \\ H_{2int} = \tfrac{1}{4}dE\sin\alpha\left[\cos(\omega+\omega_0)t + \cos(\omega-\omega_0)t\right]\cdot\widetilde{\theta}^2\ . \tag{37}$$

The interaction H_{1int} produces transitions between the harmonic-oscillator states n and $n+1$, with an absorbed power

$$P_q = \frac{\pi}{4I} d^2 E^2 (n+1) \cos^2 \alpha \delta(\omega_0 - \omega) \ . \tag{38}$$

For n, m ($n \ll m$) we restrict ourselves to small values of n in equation (38) and sum over a few values of m in $\delta(\omega_0 - \omega) = \delta(\hbar m/I - \omega)$ with the statistical weight $e^{-\beta\hbar^2 m^2/2I}$. As long as $\hbar/I \gg \gamma$, where γ is the resonance width, the spectrum exhibits a few, distinct absorption lines at frequencies $\omega_0 = \hbar m/I$ (a band of absorption). In general, the temperature dependence is given by

$$\begin{array}{c} P_{q,th} = \frac{\pi}{4I} d^2 E^2 \cos^2 \alpha \cdot C \sum_{m>0} e^{-\beta\hbar^2 m^2/2I} \times \\ \times \left\{ \sum_{n=0} (n+1) \left[e^{-\beta\hbar\omega_0 n} - e^{-\beta\hbar\omega_0 (n+1)} \right] / \sum_{n=0} e^{-\beta\hbar\omega_0 n} \right\} \delta(\omega_0 - \omega) \ , \end{array} \tag{39}$$

where $\omega_0 = \hbar m/I$ and $C \sum_{m>0} e^{-\beta\hbar^2 m^2/2I} = 1$. At room temperature we may extend the summation over n, m and get the envelope of this function

$$P_{q,th} = \frac{\pi}{4} d^2 E^2 \cos^2 \alpha \sqrt{\frac{2\pi\beta}{I}} e^{-\beta I \omega^2/2} \ . \tag{40}$$

The interaction hamiltonian H_{2int} given by equation (37) produces transitions between states n and $n+2$ (separated by frequency $2\omega_0$) for external frequencies $\Omega = \omega_0$, $3\omega_0$. The absorbed power is

$$P_q = \frac{\pi\hbar\Omega}{128 I^2 \omega_0^2} d^2 E^2 (n+1)(n+2) \sin^2 \alpha \delta(\Omega - \omega) \ . \tag{41}$$

These parametric resonances occurring at frequencies $\Omega = \omega_0$, $3\omega_0$ are superposed over the transitions produced by H_{1int}. The temperature dependence is given by

$$\begin{array}{c} P_{q,th} = \frac{\pi\hbar}{128 I^2} d^2 E^2 \sin^2 \alpha \cdot C \sum_{m>0} \frac{\Omega}{\omega_0^2} e^{-\beta\hbar^2 m^2/2I} \times \\ \times \left\{ \sum_{n=0} (n+1)(n+2) \left[e^{-\beta\hbar\omega_0 (2n+1)} - e^{-\beta\hbar\omega_0 (2n+3)} \right] / \left[\sum_{n=0} e^{-\beta\hbar\omega_0 n} \right]^2 \right\} \delta(\Omega - \omega) \ ; \end{array} \tag{42}$$

summation over n gives

$$P_{q,th} = \frac{\pi\hbar}{64 I^2} d^2 E^2 \sin^2 \alpha \cdot C \sum_{m>0} \frac{\Omega}{\omega_0^2} e^{-\beta\hbar^2 m^2/2I} \frac{e^{-\beta\hbar\omega_0}}{(1 + e^{-\beta\hbar\omega_0})^2} \delta(\Omega - \omega) \tag{43}$$

whence we can get either the band of absorption or the envelope.

It is worth noting that the low field E_0 does not appear explicitly in the above formulae; its role is that of setting the z-axis, to highlight the directional effect of the interaction field E through the angle α, and to reduce the conservation of the angular momentum $\mathbf{L}$ to the conservation of only one component L_z. In addition, the parametric resonances are a new feature in the presence of the electric field. It is also worth noting that the expansion of the effective potential function U_{eff} in powers of $\widetilde{\theta}$ is an approximation to free rotations with $L_z = const$, instead of $\mathbf{L} = const$.

It is also worth noting that a weak static electric field has an influence on the statistical behaviour, as it is well known. Indeed, the hamiltonian of rotations

$$H = \frac{1}{2} I (\dot{\theta}^2 + \dot{\varphi}^2 \sin^2 \theta) \tag{44}$$

can also be written as

$$H = \frac{1}{2I}P_\theta^2 + \frac{1}{2I\sin^2\theta}P_\varphi^2 \tag{45}$$

with the momenta (angular momenta) $P_\theta = I\dot{\theta}$ and $P_\varphi = I\dot{\varphi}\sin^2\theta$. The classical statistical distribution is

$$const \cdot dP_\theta dP_\varphi d\theta e^{-\beta P_\theta^2/2I} e^{-\beta P_\varphi^2/2I\sin^2\theta} \ , \tag{46}$$

or, integrating over momenta, $\frac{1}{2}\sin\theta d\theta$. In the presence of the field we have the distribution $\simeq \frac{1}{2}\sin\theta d\theta \cdot e^{\beta \mathbf{d}\mathbf{E}_0}$ (since $\beta dE_0 \ll 1$), which leads, for example, to $\overline{\cos\theta} = \beta dE_0/3$. This is the well-known Curie-Langevin-Debye law.[10]-[13] In the quantum-mechanical regime, for $dE_0 \ll \hbar^2/I$, the interaction $-dE_0\cos\theta$ brings a second-order contribution to the energy levels $E_l = \hbar^2 l(l+1)/2I$, there appear diagonal matrix elements of $\widetilde{(\cos\theta)}_{lm,lm}$ in the first-order of the perturbation theory, and the mean value is given by $\overline{\cos\theta} = \sum \widetilde{(\cos\theta)}_{lm,lm}\Delta(\beta E_l)e^{-\beta E_l}/\sum e^{-\beta E_l} = \beta dE_0/3$.

Dipolar interaction. Although many molecules possess an electric dipole moment d, even in their ground state, usually the dipole-dipole interaction is neglected in rarefied condensed matter, on the ground that the distance between the dipoles is large. In these conditions, at finite temperatures, the electric dipoles are randomly distributed; they get slightly aligned in the presence of a static external electric field $\mathbf{E}_0$, which provides a small interaction energy, leading to an induced orientational polarization $\overline{d} = \beta d^2 E_0/3$, known as the Curie-Langevin-Debye law, as noted above ($\beta = 1/T$ is the inverse of the temperature T).

For typical values of the dipole moments $d = 10^{-18} statcoulomb \cdot cm$ separated by distance $a = 10^{-8}cm$ (1Å) the interaction energy is $\simeq d^2/a^3 = 10^{-12}erg \simeq 10^3 K$ ($1eV = 1.6\times10^{-12}erg$, $1K = 1.38\times10^{-16}erg$, $1eV = 1.1\times10^4 K$). This is not a small energy (it corresponds approximately to a frequency $10^{13}Hz$), and, apart from special circumstances, the electric dipole-dipole interaction cannot be neglected in condensed matter. (The estimation given here should take into account the temporal average of the dipole interaction energy with respect to possible molecular motions).

The interaction energy of two dipoles $\mathbf{d}_1$ and $\mathbf{d}_2$ separated by distance $\mathbf{a}$ (much longer than the dimension of the dipoles) is given by

$$U = -\frac{3(\mathbf{d}_1\mathbf{d}_2)a^2 - (\mathbf{d}_1\mathbf{a})(\mathbf{d}_2\mathbf{a})}{a^5} \ . \tag{47}$$

We introduce the angles (θ_1, φ_1) and (θ_2, φ_2) for the directions of the two dipoles with respect to the axis $\mathbf{a}$ and the interaction energy becomes

$$U = -\frac{d_1 d_2}{a^3}[2\cos\theta_1\cos\theta_2 + 3\sin\theta_1\sin\theta_2\cos(\varphi_1-\varphi_2)] \ ; \tag{48}$$

this energy has four extrema for $\theta_1 = \theta_2 = 0,\ \pi/2$ and $\varphi_1 - \varphi_2 = 0,\ \pi$; only for $\theta_1 = \theta_2 = \pi/2$, $\varphi_1 - \varphi_2 = 0$ the interaction energy has a local minimum; in the neighbourhood of this minimum value the interaction energy behaves like

$$\begin{gathered} U = \tfrac{d_1 d_2}{a^3}[-3 + \tfrac{3}{2}(\delta\theta_1^2 + \delta\theta_2^2) - 2\delta\theta_1\delta\theta_2 + \tfrac{3}{2}(\delta\varphi_1 - \delta\varphi_2)^2] = \\ = \tfrac{d_1 d_2}{a^3}[-3 + \tfrac{1}{4}(\delta\theta_1 + \delta\theta_2)^2 + \tfrac{5}{4}(\delta\theta_1 - \delta\theta_2)^2 + \tfrac{3}{2}(\delta\varphi_1 - \delta\varphi_2)^2] \ , \end{gathered} \tag{49}$$

where $\delta\theta_{1,2} = \theta_{1,2} - \pi/2$ are small deviations of the angles $\theta_{1,2}$ from the polarization axis $\pi/2$; similarly, $\delta\varphi_{1,2}$ are small deviations of the angles $\varphi_{1,2}$ from their equilibrium values $\varphi_{1,2}$, subjected to the condition $\varphi_1 - \varphi_2 = 0$. It follows that the electric dipoles exhibit quenched equilibrium positions $\theta_1 = \theta_2 = \pi/2$, $\varphi_1 - \varphi_2 = 0$, such that they are parallel to each other and perpendicular to the distance between them; they may perform small rotations and vibrations around these equilibrium positions. For the other three extrema the interaction energy has either a saddle point ($\theta_1 = \theta_2 = 0$, $\varphi_1 - \varphi_2 = 0, \pi$) or a maximum ($\theta_1 = \theta_2 = \pi/2$, $\varphi_1 - \varphi_2 = \pi$). It is very likely that the structural environment is distorted such as the dipoles take advantage of the energy minimum. For instance, a structural elongation along the direction $\theta_1 = \theta_2 = 0$ decreases appreciably the dipolar interaction along this direction (which goes like $1/a^3$!), such that the corresponding contribution to the energy may be neglected. Under such circumstances, we may expect the dipoles to be (spontaneously) aligned along an arbitrary axis (in isotropic matter), giving rise to an electric (macroscopic) polarization along such an axis. The neglect of the interaction along the direction $\theta_1 = \theta_2 = 0$ makes this model highly anisotropic, with a layered structure of the aligned dipoles.

As it is well known, substances that have a permanent electric polarization are called pyroelectrics (or electrets);[14] if the polarization is singular just below a critical temperature and vanishes above, those substances are called ferroelectrics (in the state above the critical temperature they are also called paraelectrics); they exhibit a second-order phase transition; it seems that all these substances are piezoelectric. There are also structural modifications associated with finite discontinuities in polarization (first-order phase transitions), a typical example being barium titanate ($BaTiO_3$); the dimension of the elementary cell in the crystal of $BaTiO_3$ is $a \simeq 4 \times 10^{-8} cm$ (4Å); the dipole of a cell is $d \simeq 5 \times 10^{-18} statcoulomb \cdot cm$ (the saturation polarization - the dipole moment per unit volume - at room temperature is $8 \times 10^4 statcoulomb \cdot cm$); if Ba^{2+} and Ti^{4+} are displaced by δ with respect to O^{2-}, then the dipole moment d is achieved for a slight displacement $\delta = 0.1$Å; we can see that the distance a between the dipoles is much longer than the dimension δ of the dipoles. In addition, $BaTiO_3$ exhibits several structural modifications (from cubic to tetragonal to monoclinic to rhombohedral with decreasing temperature), in all polarized phases the structure being elongated along the direction of the polarization.[15]

In a continuum model of polarized substance the dipolar interaction given by equation (49) (with identical dipoles d) gives the interaction hamiltonian

$$H_{int} = \frac{1}{a^3} \int d\mathbf{r} \left[\frac{d^2}{a^3} \delta\theta^2 + \frac{5d^2}{4a} (grad\delta\theta)^2 + \frac{3d^2}{2a} (grad\delta\varphi)^2 \right] \ , \tag{50}$$

which, together with the kinetic part, leads to the full hamiltonian

$$\begin{gathered} H = \tfrac{1}{a^3} \int d\mathbf{r} [\tfrac{1}{2} I \dot{\delta\theta}^2 + \tfrac{1}{2} I \dot{\delta\varphi}^2 + \tfrac{1}{2} I \omega_0^2 \delta\theta^2 + \\ + \tfrac{1}{2} I v_\theta^2 (grad\delta\theta)^2 + \tfrac{1}{2} I v_\varphi^2 (grad\delta\varphi)^2 \ , \end{gathered} \tag{51}$$

where I is the moment of inertia of the dipoles and $\omega_0^2 = 2d^2/Ia^3$, $v_\theta^2 = 5d^2/2Ia = 5\omega_0^2 a^2/4$, $v_\varphi^2 = 3d^2/Ia = 3\omega_0^2 a^2/2$. The dipole density $1/a^3$ should include the number of nearest neighbours; if we restrict ourselves to the highly anisotropic (layered) model, then the hamiltonian density in equation (51) is two-dimensional. We can see that the dipolar interaction may generate dipolar waves (waves of orientational polarizability), governed by the wave equations

$$\ddot{\delta\theta} + \omega_0^2 \delta\theta - v_\theta^2 \Delta\delta\theta = 0 \ , \ \ddot{\delta\varphi} - v_\varphi^2 \Delta\delta\varphi = 0 \ ; \tag{52}$$

the spectrum of these dipolar waves is given by $\omega_\theta^2 = \omega_0^2 + v_\theta^2 k^2$ and, respectively, $\omega_\varphi^2 = v_\varphi^2 k^2$ (in the layered model the wavevector $\mathbf{k}$ is two-dimensional); for typical values $d = 10^{-18} statcoulomb \cdot cm$, $a = 10^{-8} cm$ and $I = 10^{-38} g \cdot cm^2$ (10^5 electronic mass for the molecular mass, $10^{-8} cm$ for the dipole length) we get the frequency $\omega_0 \simeq 10^{13} s^{-1}$ (infrared region) and the wave velocities $v_{\theta,\varphi} \simeq 10^5 cm/s$ (the wavelengths are $\lambda_{\theta,\varphi} \simeq \pi\sqrt{5}a$, $\pi\sqrt{6}a$). It is worth noting that the coordinates $\delta\theta$, $\delta\varphi$ are the tilting angles of the polarization with respect to its equilibrium direction. Tentatively, we may call these polar-matter modes "dipolons". They contribute to the anomalous heat-capacity curve *vs* temperature.

The dipolar waves can couple to an external time-dependent electric field. Let $\mathbf{E}(\mathbf{r},t)=\mathbf{E}\cos(\omega t-\mathbf{kr})$ be a radiation electric field (plane wave) which makes an angle α with the polarization direction; the interaction hamiltonian is

$$H^{'}=-\frac{1}{a^3}\int d\mathbf{r}\mathbf{d}\mathbf{E}\cos(\omega t-\mathbf{kr})\ , \tag{53}$$

where $\mathbf{E}=E(\sin\alpha\cos\varphi^{'},\ \sin\alpha\sin\varphi^{'},\ \cos\alpha)$ and $\mathbf{d}=d(\sin\delta\theta\cos\varphi,\ \sin\delta\theta\sin\varphi,\ \cos\delta\theta)$; we may limit ourselves to $\varphi=\varphi^{'}$, and get

$$H^{'}=-\frac{1}{a^3}\int d\mathbf{r}dE(\delta\theta\sin\alpha-\frac{1}{2}\delta\theta^2\cos\alpha)\cos(\omega t-\mathbf{kr}) \tag{54}$$

(up to irrelevant terms); we can see that the φ-waves do not couple to the external electric field (within the present approximation). Moreover, since the wavelength of the radiation field is much longer than the wavelength of the dipolar interaction ($v_{\theta,\varphi}\ll c$, where c is the speed of light), we may drop out the spatial dependence (spatial dispersion) both in equation (52) and in the interaction hamiltonian $H^{'}$; we are left with the equation of motion of a harmonic oscillator under the action of an external force,

$$\ddot{\delta\theta}+\omega_0^2\delta\theta=\frac{dE}{I}\sin\alpha\cos\omega t-\frac{dE}{I}\delta\theta\cos\alpha\cos\omega t\ . \tag{55}$$

The first interaction term gives

$$\ddot{\delta\theta}_1+\omega_0^2\delta\theta_1+2\gamma\dot{\delta\theta}_1=\frac{dE}{I}\sin\alpha\cos\omega t\ \ , \tag{56}$$

where a damping term has been introduced; this is the equation of motion of a harmonic oscillator under the action of a harmonic force; the (particular) solution is

$$\delta\theta_1=a\cos\omega t+b\sin\omega t\ \ , \tag{57}$$

where

$$a=-\frac{dE}{2I\omega_0}\sin\alpha\frac{\omega-\omega_0}{(\omega-\omega_0)^2+\gamma^2}\ ,\ b=\frac{dE}{2I\omega_0}\sin\alpha\frac{\gamma}{(\omega-\omega_0)^2+\gamma^2} \tag{58}$$

for ω near ω_0; we get a resonance for $\omega=\omega_0$; the absorbed mean power is

$$P=dE\sin\alpha\overline{\cos\omega t\dot{\delta\theta}_1}=\frac{1}{2}dE\sin\alpha\cdot b\omega_0=\frac{\pi}{4I}d^2E^2\sin^2\alpha\delta(\omega_0-\omega)\ . \tag{59}$$

The second interaction term in equation (55) gives the Mathieu's equation

$$\ddot{\delta\theta}_2+\omega_0^2(1+h\cos\omega t)\delta\theta_2=0\ \ , \tag{60}$$

where $h=(dE/I\omega_0^2)\cos\alpha$ (a damping term can be included). As it is well known,[8] the Mathieu's equation has both periodic and aperiodic solutions; the latter, which may increase indefinitely, give the parametric resonances occurring at $\omega=2\omega_0/n$, $n=1,\ 2,\ 3,\ldots$. The parameter h acquires, usually, very small values (it dictates the rate of the increase in time of the resonant solutions). The thermal fluctuations wipe out these parametric resonances, as discussed before. All the above considerations are valid for a classical dynamics. The quantization of the hamiltonians H and

$H^{'}$ given by equations (51) and (54) (which is performed according to the well-known standard rules), leads to standard absorption and emission processes, and to quantum transitions (jumps) similar with equations (33)-(35). It is worth noting that the static electric field E_0 in equations (33)-(35) is replaced here by $E_0 = d/2a^3$ (by comparing the frequencies ω_0 given in equations (24) and, respectively, (51)), as expected for a (strong) electric field generated by a dipolar interaction.

The spontaneous polarization caused by the dipolar interaction as described above may appear in polarization domains, randomly distributed in polar matter (pyroelectrics, ferroelectrics), or in granular matter, where charges may accumulate at the interfaces.[16]-[22] This is known as the Maxwell-Wagner-Sillars effect (an average over the angle α should then be taken in the absorbed power). In the latter case the distance between the dipoles is much larger than the atomic distances and, consequently, the characteristic frequency ω_0 is much lower; for instance, for a distance $a = 1\mu m$ (10^4Å) we get a frequency $\omega_0 \simeq 10MHz$.

Highly-oscillating electric fields. High-power lasers may provide strong electric fields which oscillate in time with a frequency ω_h much higher than the frequencies of molecular rotations or vibrations. Usually, the frequency ω_h is in the optical range, $\omega_h = 2\pi \times 10^{15}s^{-1}$, and the strength of the electric field may attain values of the order $E_0 = 10^9 statvolt/cm$ for laser intensities $10^{20}w/cm^2$. Under the action of such strong fields the molecules are usually ionized, but the molecular ions retain their electric dipole which perform a non-relativistic motion. Indeed, the non-relativistic approximation is ensured by the inequality $\eta = qA_0/2Mc^2 \ll 1$, where q is the charge of a particle with masss M and A_0 is the amplitude of the vector potential. For a proton in a potential $A_0 = 5 \times 10^3 statvolt$, corresponding to the field amplitude $E_0 = 10^9 statvolt/cm$, we get $\eta = 10^{-3} \ll 1$.

Consider an electric field $E_0 \cos\omega_h t$ oriented along the z-axis. An electric dipole d acted by this field performs rapid oscillations of an angle α about, in general, a certain angle θ with respect to the z-axis, which may perform slow oscillations; we assume $\alpha \ll \theta$. The equation of motion can be written as

$$I\ddot{\alpha} = -dE_0 \sin(\theta + \alpha)\cos\omega_h t \simeq -dE_0 \sin\theta \cos\omega_h t \ ; \tag{61}$$

the corresponding kinetic energy is $E_{kin} = I\dot{\alpha}^2/2 = (d^2E_0^2/2I\omega_h^2)\sin^2\theta \sin^2\omega_h t$; its time average

$$\overline{E}_{kin} = \frac{d^2E_0^2}{4I\omega_h^2}\sin^2\theta \tag{62}$$

replaces the interaction energy $-dE_0\cos\theta$ of the static field in the effective potential energy U_{eff} given by equation (22); the effective potential becomes

$$U_{eff} = \frac{L_z^2}{2I\sin^2\theta} + \frac{d^2E_0^2}{4I\omega_h^2}\sin^2\theta \ . \tag{63}$$

This function has a minimum value for $\widetilde{\theta}_0 = \arcsin\theta_0/R^{1/4}$ and $\widetilde{\theta'}_0 = \pi - \widetilde{\theta}_0$, where $R = dE_0/2I\omega_h^2$ and $\theta_0 = (L_z^2/IdE_0)^{1/4} < R^{1/4}$, *i.e.* for strong fields; it is worth noting that there are two values of the equilibrium angle: $\widetilde{\theta}_0$ and $\pi - \widetilde{\theta}_0$. The dipole may perform small vibrations about these equilibrium angles with the frequency $\widetilde{\omega}_0 = \omega_0\sqrt{3R/4}$, where $\omega_0 = 2\sqrt{dE_0/I}$ is the frequency for static fields given in equation (24) (for$\widetilde{\theta}_0 \ll 1$). We can see that for highly-oscillating electric fields we get the results for static fields renormalized according to $E_0 \rightarrow \widetilde{E}_0 = E_0R$.

From $\theta_0/R^{1/4} < 1$ and $\alpha = (dE_0/I\omega_h^2)\widetilde{\theta}_0 \ll \widetilde{\theta}_0$ we get the inequalities

$$\frac{L_z^2}{IdE_0} < \frac{dE_0}{2I\omega_h^2} \ll 1 \tag{64}$$

(which are compatible because $L_z \ll I\omega_h$); these inequalities imply

$$\frac{\sqrt{2}L_z\omega_h}{d} < E_0 \ll \frac{2I\omega_h^2}{d} \ . \tag{65}$$

For $L_z^2/I = T$ and our numerical parameters $I = 10^{-38} g \cdot cm^2$, $T = 300K = 4 \times 10^{-14} erg$, $d = 10^{-18} esu$ and $\omega_h = 2\pi{\cdot}10^{15} s^{-1}$ we get approximately $10^8 statvolt/cm < E_0 \ll 10^{10} statvolt/cm$, which corresponds to a renormalization parameter $R = 10^{-10}E_0/8\pi^2 \ll 1$. We conclude that in strong highly-oscillating electric fields, like those provided by high-power lasers, the rotation molecular (spherical pendulum) spectra are affected in the same manner as in strong static electric field, providing the time-dependent field intensity is renormalized by the factor $R \ll 1$ introduced here. In addition, we note that the slow translation motion is not affected by highly-oscillating electric fields.

Discussion and conclusions. We have shown here that the rotations of a (heavy) molecule viewed as a spherical pendulum can be approximated by azimuthal rotations and zenithal oscillations. In the presence of a time-dependent external electric field the molecular electric dipole moment couples to the electric field giving rise to rotation (and vibration) molecular spectra. Arguments have been given that in polar matter there could appear local strong static electric fields, which can lead to quenched equilibrium positions for the dipoles and a macroscopic electric polarization. The small rotations and oscillations which these dipoles may perform around their equilibrium positions give rise to special features in the spectrum, in particular to parametric resonances. A similar situation appears in the presence of weak static electric fields. The dipole-dipole interaction has also been examined and it was found that, indeed, it can lead to an equilibrium state of quenched dipoles; this state possesses a macroscopic polarization, whose motion proceeds by particular modes which have been tentatively called "dipolons". The excitation of these modes may also lead to parametric resonances. A strong highly-oscillating electric field, like the fields provided by high-power lasers, behaves in the same manner as static electric fields, provided they are renormalized by factors much smaller than unity (factor R above).

All the discussion made in this paper for electric dipole moments can also be applied, in principle, to magnetic moments, magnetic fields, magnetization and magnetic matter (*e.g.,* ferromagnetics). The main difference is the magnitude; the nuclear magnetic moments are five orders of magnitude smaller than the electric dipole moments ($\mu \simeq 10^{-23} erg/Gs$); if the magnetic moments are in thermal equilibrium their interaction energy $\mu^2/a^3 \simeq 10^{-6}K$ is effective at much lower temperatures; the characteristic frequency of "electric dipolons" $\omega_0 = \sqrt{2d^2/Ia^3} \simeq 10^{13} s^{-1}$ becomes $\omega_0 = \sqrt{2\mu^2/Ia^3} \simeq 10^8 s^{-1}$ for "magnetic dipolons". For electronic magnetic moments $\mu \simeq 10^{-20} erg/Gs$ the interaction energy is $\simeq 1K$ and the characteristic frequency is $\omega_0 \simeq 10^{11} s^{-1}$. If the magnetic moment is higher by a factor of, say, 5 and the number of nearest neighbours is 4, then the effective magnetic dipolar energy increases to $\simeq 100K$, which is of the order of magnitude of usual ferromagnetic transitions temperatures; then, the "magnetic dipolons" become magnons (ferromagnetic resonances).[15] The dipole interaction as source of ferromagnetism is different from the Weiss mean field approach (which requires a great exchange magnetic field since it employs the comparison with the very small magnetization at finite temperature); it looks more similar to Bloch's theory of magnons.[23]

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Appendix. For convenience, we give here a few elements for the Mathieu's equation. Mathieu's equation (32) is solved by means of the perturbation theory for $h \ll 1$.[3] Beside periodic solutions, it has also aperiodic solutions, which may increase exponentially in time. For the unperturbed solutions $\cos\omega_0 t$, $\sin\omega_0 t$ the h-term in equation (32) gives rise to terms of the form $\cos(\omega_0\pm\omega)t$, $\sin(\omega_0\pm\omega)t$; and so on, in higher orders of the perturbation theory. It follows that a resonance may occur for $\omega=2\omega_0+\varepsilon$, $\varepsilon\ll\omega_0$; the solution is

$$\delta\theta\simeq a\cos(\omega_0+\frac{\varepsilon}{2})t+b\sin(\omega_0+\frac{\varepsilon}{2})t\ , \tag{66}$$

where a and b are slowly-varying functions of time. We get

$$2\dot{a}+(\varepsilon+h\omega_0/2)b=0\ ,\ 2\dot{b}-(\varepsilon-h\omega_0/2)a=0\ , \tag{67}$$

with a, $b\sim e^{st}$, where $s^2=\frac{1}{4}(h^2\omega_0^2/4-\varepsilon^2)$, for $-h\omega_0/2<\varepsilon<h\omega_0/2$. If the damping is included, the coefficients a and b go like $e^{(s-\gamma)t}$ and the resonance occurs for $-\sqrt{(h\omega_0)^2/4-4\gamma^2}<\varepsilon<\sqrt{(h\omega_0)^2/4-4\gamma^2}$; a threshold occurs now for the perturbation amplitude h.

For the sake of definiteness we may set $\varepsilon=0$; the initial conditions for $\delta\theta$ and $\delta\dot{\theta}$ are provided by fluctuations; we can see that their mean values are vanishing. The amplitude a can be written approximately as

$$\delta\theta\simeq\pi e^{st}\cos\omega_0 t\ ,\ s=\frac{1}{4}h\omega_0\ ; \tag{68}$$

its Fourier transform is

$$\delta\theta(\omega)\simeq-\frac{\pi(s+i\omega)}{(\omega_0^2-\omega^2)+2is\omega}\ , \tag{69}$$

or

$$\delta\theta(\omega)\simeq-\frac{\pi}{2}\delta(\omega-\omega_0) \tag{70}$$

for ω close to ω_0; the energy absorbed per unit time is obtained from equation (32) as

$$P=-hI\omega_0^2\overline{\delta\theta\delta\dot{\theta}\cos2\omega_0 t}\ , \tag{71}$$

where s is set equal to zero and the damping parameter γ is included; we get $P=\frac{1}{4}a^2hI\omega_0^2\gamma$. Parametric resonance occurs also for $\omega=2\omega_0/n$, $n=(1),2,3,...$, within a more narrow ε-range.

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