



Molecular dynamics in high electric fields



M. Apostol*, L.C. Cune

Department of Theoretical Physics, Institute of Atomic Physics, Magurele-Bucharest MG-6, POBox MG-35, Romania

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ABSTRACT

Molecular rotation spectra, generated by the coupling of the 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 of the azimuthal and zenithal motions. Second, rotation spectra are considered in the presence of a static electric field. Two particular cases are analyzed, corresponding to strong and weak fields. In both cases the classical motion of the dipoles consists of rotations and vibrations about equilibrium positions; this motion may exhibit parametric resonances. For strong fields a large macroscopic electric polarization may appear. This situation may be relevant for polar matter (like pyroelectrics, ferroelectrics), or for heavy impurities embedded in a polar solid. 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 related to parametric resonances. The extension of these considerations to magnetic dipoles is 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 weaker, effective, renormalized, static electric field.

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1. Introduction

Usually, the molecular dynamics in the presence of static electric fields is limited to weak fields, as those produced currently in the laboratory. A small, orientational polarization of the electric-dipole moments is well known in this case, governed by the Curie–Langevin–Debye law. Comparatively, more information is available for the dynamics of the magnetic moments in the presence of static magnetic fields available in the laboratory, although the magnetic moments are much smaller than the electric-dipole moments. Orientation, deflection, trapping of polar molecular beams in static electric fields are well known [1–7]. Various basic aspects of the dynamics of the polar molecules (rigid spatial rotators) in combined static and non-resonant electric fields has also been studied extensively in Refs. [8–14].

With the advent of high-power lasers, the interest for the molecular dynamics in high electric fields may be revived. Although the electric fields produced in the laser beams are oscillating in time, we show in this paper that their effect on the molecular dynamics is that of weaker, renormalized, static fields,

as a consequence of their much higher frequency in comparison with the molecular rotation or vibration frequencies.

First, we review briefly the spherical-pendulum molecular model with the aim of defining our working method, which consists in the separation of the azimuthal and zenithal motions. This approximate method is valid for heavy molecules. Second, we apply this method to high electric fields, where parametric resonances are highlighted in the molecular rotation spectra. Similar results are briefly discussed for weak electric fields. Further, the dipolar interaction is analyzed in polar matter, where it may produce a spontaneous polarization. A continuous model is introduced for the motion of this polarization, whose excitations are tentatively called “dipolons”; it is shown that their interaction with a time-dependent electric field may also exhibit parametric resonances. Such arguments are briefly extended to similar features exhibited by magnetic moments.

2. Free rotations

In many cases the free molecular rotations are described satisfactorily by a spherical-pendulum model (spatial, rigid rotator, spherical top) [15,16]. A spherical pendulum consists of a point of mass M which rotates freely in space at the end of a radius.

* Corresponding author.

E-mail address: apoma@theory.nipne.ro (M. Apostol).

$\mathbf{r} = r(\sin \theta \cos \varphi, \sin \theta \sin \varphi, \cos \theta)$, as described by the hamiltonian

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

if the point has a charge q , then there 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 hamiltonian given by Eq. (1) can be written as $H = \mathbf{L}^2/2I$, where \mathbf{L} is the angular momentum and $I = Mr^2$ is the moment of inertia. The eigenfunctions are the spherical harmonics, with the energy levels $E_l = \hbar^2 l(l+1)/2I$, $l = 0, 1, 2, \dots$

As it is well known, in the first-order of the perturbation theory for the interaction $H_{int}(t) = -dE \cos \theta \cos \omega t$ the rate of quantum transitions with frequency $\omega_0 = (E_{l+1} - E_l)/\hbar = (\hbar/I)(l+1)$ is

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

where the matrix elements denoted $(\cos \theta)_{lm}$ are given by

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

in Eq. (2) c_{lm} are the coefficients of the superposition of the wavefunctions, m being the quantum number of the component L_z of the angular momentum. The absorbed power (the spectrum) is

$$P = \hbar \omega_0 \sum_{m=-l}^l \frac{\partial |c_{lm}|^2}{\partial t} = \frac{\pi d^2 E^2}{2\hbar} \omega_0 \sum_{m=-l}^l |(\cos \theta)_{lm}|^2 \delta(\omega_0 - \omega) \\ = \frac{\pi d^2 E^2}{6\hbar} \omega_0 (l+1) \delta(\omega_0 - \omega) = \frac{\pi d^2 E^2}{6\hbar} (l+1)^2 \delta(\omega_0 - \omega) \quad (4)$$

and the net absorbed power at finite temperatures is given by

$$P_{th} = \frac{\pi d^2 E^2}{2\hbar} \omega_0 \times \sum_{m=-l}^l |(\cos \theta)_{lm}|^2 [e^{-\beta \hbar^2 l(l+1)/2I} - e^{-\beta \hbar^2 (l+1)(l+2)/2I}] \delta(\omega_0 - \omega)/Z, \quad (5)$$

where

$$Z = \sum_{l=0}^{\infty} (2l+1) e^{-\beta \hbar^2 l(l+1)/2I} \quad (6)$$

is the partition function and $\beta = 1/T$ is the reciprocal of the temperature T (we set the Boltzmann's constant k_B equal to unity, $k_B = 1$); for $\beta \hbar^2/2I \ll 1$ the partition function is $Z \simeq 2I/\beta \hbar^2$ and

$$P_{th} = \frac{\pi d^2 E^2}{12I} (l+1)^3 \left(\frac{\beta \hbar^2}{I}\right)^2 e^{-\beta \hbar^2 l(l+1)/2I} \delta(\omega_0 - \omega) \\ = \frac{1}{2} P(l+1) \left(\frac{\beta \hbar^2}{I}\right)^2 e^{-\beta \hbar^2 l(l+1)/2I}. \quad (7)$$

For illustrative purposes we use $I = 10^{-38} \text{ g} \cdot \text{cm}^2$, which is a typical numerical value for the molecular moment of inertia (molecular mass $M = 10^5$ electronic mass $m_e = 10^{-27} \text{ g}$ (heavy molecules), the dipole length $r = 10^{-8} \text{ cm}$ (1 Å)), and get $\hbar/I = 10^{11} \text{ s}^{-1} \simeq 1 \text{ K}$ ($\omega_0 = \hbar(l+1)/I$); at room temperature there are many levels occupied, and we may use the inequality $\beta \hbar^2(l+1)/I \ll 1$ for a wide range of the quantum number l .

It is worth investigating to what extent the classical dynamics, properly quantized, may be used as an approximate representation for the quantum-mechanical spectrum of the spherical pendulum given above. An approximate scheme is useful for treating complicated situations, like the presence of high electric fields. The classical dynamics corresponding to the hamiltonian given by Eq. (1) is governed by the equations of motion

$$\ddot{\theta} = \dot{\varphi}^2 \sin \theta \cos \theta, \quad I \frac{d}{dt} (\dot{\varphi} \sin^2 \theta) = 0; \quad (8)$$

from the second Eq. (8) we get $\dot{\varphi} = L_z/I \sin^2 \theta$, which indicates the conservation of the component L_z of the angular momentum (as it is well known, the angular momentum is conserved in free rotations). The hamiltonian given by Eq. (1) can be written as

$$H = \frac{1}{2} I \dot{\theta}^2 + \frac{L_z^2}{2I \sin^2 \theta}; \quad (9)$$

we can see that an effective potential function $U_{eff} = L_z^2/2I \sin^2 \theta$ appears, which has a minimum for $\theta = \pi/2$. The relevant motion may be limited to small oscillations about the equatorial plane $\theta = \pi/2$. Introducing $\delta\theta = \theta - \pi/2$ we get

$$\frac{L_z^2}{2I \sin^2 \theta} = \frac{L_z^2}{2I} + \frac{L_z^2}{2I} \delta\theta^2 + \dots \quad (10)$$

and

$$H \simeq \frac{1}{2} I \delta\dot{\theta}^2 + \frac{L_z^2}{2I} \delta\theta^2 + \frac{L_z^2}{2I}. \quad (11)$$

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 governed by the hamiltonian given by Eq. (11); the frequency ω_0 is given by $\omega_0 = L_z/I$. We can check easily that the angular momentum 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 $\sin \alpha = IA\omega_0 / \sqrt{I^2 \omega_0^2 + I^2 A^2 \omega_0^2} \simeq A$, such that the motion will be an in-plane motion [17,18]. 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 $\delta\theta$ -motion governed by the harmonic-oscillator hamiltonian given by Eq. (11) can be quantized, the energy levels being $\hbar \omega_0(n+1/2)$, $n = 0, 1, 2, \dots$, where $\omega_0 = L_z/I = \hbar m/I$, $m = 0, 1, 2, \dots$; the harmonic-oscillator frequency $\omega_0 = \hbar m/I$ corresponds to the quantum-mechanical frequency $\omega_0 = (E_{l+1} - E_l)/\hbar = (\hbar/I)(l+1)$ (for large m values close to l values). The interaction $H_{int}(t) = -dE \cos \theta \cos \omega t$, where $\theta = \pi/2 + \delta\theta$ produces transitions of the type $n \rightarrow n+1$, with an absorbed power

$$P_n = \frac{\pi d^2 E^2}{4I} (n+1) \delta(\omega_0 - \omega) \quad (12)$$

(where the harmonic-oscillator matrix elements $(\delta\theta)_{n+1, n} = \sqrt{\hbar(n+1)/2I\omega_0}$ are used). The total power is obtained by summing P_n with respect to n up to some value N given by

$$(\delta\theta)_{N+1, N} = \sqrt{\frac{\hbar(N+1)}{2I\omega_0}} = \sqrt{\frac{N+1}{2m}} < 1, \quad (13)$$

which gives

$$P_{osc} = \sum_{n=0}^N P_n = \frac{\pi d^2 E^2}{2I} m(m+1/2) \delta(\omega_0 - \omega) \quad (14)$$

for $N = 2m - 1$; for large (and comparable) m and l this result can be compared with the exact absorbed power given by Eq. (4). We can see that there is a discrepancy of a numerical factor 1/3, which arises from the summation over m in Eq. (4); the main feature, which is the presence of the resonance at frequency $\omega = \omega_0$, is preserved in this approximation scheme.

The nature of this approximation can also be seen from an expansion of the energy levels E_l in Taylor series with respect to l in the vicinity of a large value $l_0 \gg 1$; denoting $n = l - l_0$ we get

$$E_l \simeq E_{l_0} + \frac{\hbar^2}{I} (l_0 + 1/2)n \simeq E_{l_0} + \hbar \omega_0 n \quad (15)$$

for $m \simeq l_0$; on the right in Eq. (15) we can see the approximate harmonic-oscillator energy levels. We note (from Eqs. (7) and (14)) that the maximum of the transitions amplitudes is reached for $l \simeq \sqrt{I/\hbar^2}$ (which at room temperature acquires large values), and the harmonic-oscillator approximation overestimates the absorbed power at room temperature.

3. High 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 rotations in this field is given by

$$H = \frac{1}{2}I(\dot{\theta}^2 + \dot{\varphi}^2 \sin^2 \theta) - dE_0 \cos \theta \quad (16)$$

(for the Schroedinger equation with this hamiltonian see Refs. [19,20]). We apply to this hamiltonian the method of quantization of the classical motion described in the previous section. We show here that this method leads to special features in the spectrum, related to parametric resonance. The component L_z of the angular momentum is conserved, $\dot{\varphi} \sin^2 \theta = L_z/I$; consequently, an effective potential function

$$U_{\text{eff}} = \frac{L_z^2}{2I \sin^2 \theta} - dE_0 \cos \theta \quad (17)$$

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 · cm and temperature $T = 300 \text{ K} \simeq 4 \times 10^{-14}$ erg this condition requires an electric field $E_0 \gg T/d = 4 \times 10^4$ statvolt/cm $\simeq 1.2 \times 10^9$ V/m. This is a high electric field; for comparison, the electric field created by an electron charge at distance $1 \text{ \AA} = 10^{-8}$ cm is $4.8 \times 10^{-10}/10^{-16} = 4.8 \times 10^6$ statvolt/cm (atomic fields). Such a high 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 [21,22]. The electric field produced by the nearest neighbors, averaged over their small vibrations and rotations, gives 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 also that at lower temperatures (and high values of the electric dipoles) the field E_0 may be weaker. Similarly, high 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 Eq. (17) 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,

$$U_{\text{eff}} \simeq -dE_0 + 2dE_0\delta\theta^2; \quad (18)$$

the hamiltonian given by Eq. (16) becomes

$$H \simeq \frac{1}{2}I\delta\dot{\theta}^2 + \frac{1}{2}I\omega_0^2\delta\theta^2 - dE_0, \quad (19)$$

where $\omega_0 = 2\sqrt{dE_0/I}$ is sometimes known as Rabi's frequency [23,24]; according to our condition of high field, we have $\omega_0 > 10^{12} \text{ s}^{-1}$ (we consider electric fields that are not as high as to produce rotation frequencies 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 determined by the external field E_0 . An attempt to derive the harmonic-oscillator hamiltonian given by Eq. (19) has been made in Ref. [25].

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

$$H_{\text{int}} = -dE(t)(\sin \alpha \sin \theta \cos \varphi + \cos \alpha \cos \theta), \quad (20)$$

which provides two relevant interaction hamiltonians:

$$\begin{aligned} H_{1\text{int}} &= -\frac{1}{2}dE \sin \alpha [\cos(\omega + \frac{1}{2}\omega_0)t + \cos(\omega - \frac{1}{2}\omega_0)t] \delta\theta, \\ H_{2\text{int}} &= \frac{1}{2}dE \cos \alpha \cos \omega t \cdot \delta\theta^2. \end{aligned} \quad (21)$$

The interaction hamiltonian $H_{1\text{int}}$ 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 $H_{\text{int}} = h \cos \omega t$ (where h is a time-independent interaction hamiltonian), the transition rate between two states n and $n+s$, with energies E_n, E_{n+s} is

$$\frac{\partial |c_{n+s,n}|^2}{\partial t} = \frac{\pi}{2\hbar^2} |h_{n+s,n}|^2 \delta(\omega_{n,s} - \omega) \quad (22)$$

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 $H_{1\text{int}}$ we get

$$\frac{\partial |c_{n+1,n}|^2}{\partial t} = \frac{\pi}{16\hbar l \omega_0} d^2 E^2 (n+1) \sin^2 \alpha \delta(\omega - \Omega) \quad (23)$$

and the absorbed power

$$\begin{aligned} P &= \hbar \Omega \frac{\partial |c_{n+1,n}|^2}{\partial t} = \frac{\pi}{16l\omega_0} d^2 E^2 \Omega (n+1) \sin^2 \alpha \delta(\omega - \Omega) \\ &= \frac{\pi}{16l\omega_0} d^2 E^2 \Omega (n+1) \sin^2 \alpha \delta(\omega - \Omega). \end{aligned} \quad (24)$$

In order to compute the mean power the thermal weights $e^{-\beta\hbar\omega_0 n} / \sum e^{-\beta\hbar\omega_0 n}$ 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

$$\begin{aligned} P_{\text{th}} &= \frac{\pi}{16l\omega_0} d^2 E^2 \Omega \sum_{n=0} (n+1) [e^{-\beta\hbar\omega_0 n} - e^{-\beta\hbar\omega_0 (n+1)}] \\ &\quad \times \sin^2 \alpha \delta(\omega - \Omega) \Big/ \sum_{n=0} e^{-\beta\hbar\omega_0 n}, \end{aligned} \quad (25)$$

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

We should limit ourselves 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 $(\delta\theta)_{n+1,n} = \sqrt{\hbar(n+1)/2l\omega_0}$ 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 $I = 10^{-38} \text{ g} \cdot \text{cm}^2$ we get $n \ll 80$ for $T = 300 \text{ K}$ (and $n \ll 8$ for $T = 3 \text{ K}$). Consequently, for $\beta\hbar\omega_0 \gg 1$ we may extend the summation in Eq. (25) to large values of n ; we get P_{th} independent of temperature. Making use of the expressions for the transverse components L_{xy} of the angular momentum we get $L_x \simeq -(1/2)l\omega_0\theta_0 \cos \omega_0 t/2$ and $L_y \simeq -(1/2)l\omega_0\theta_0 \sin \omega_0 t/2$, which show that the high-field approximation corresponds to $L_x^2 + L_y^2 \simeq L_z^2 \gg L_z^2$ (small values of the component L_z).

Under the same conditions, the harmonic-oscillator hamiltonian given by Eq. (19) and the interaction hamiltonian $H_{2\text{int}}$ given by Eq. (21),

$$H' = H + H_{2int} = \frac{1}{2}I\dot{\theta}^2 + \frac{1}{2}I\omega_0^2(1 + h \cos \omega t)\delta\theta^2, \quad (26)$$

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

$$\delta\ddot{\theta} + \omega_0^2(1 + h \cos \omega t)\delta\theta = 0, \quad (27)$$

which is the well-known equation of parametric resonance (Mathieu's equation) [26]. As it is well known, beside periodic solutions, the classical Eq. (27) has also aperiodic solutions, which may grow indefinitely with increasing time; these are (parametrically) resonant solutions, which occur for ω in the neighborhood of $2\omega_0/n$, $n = 1, 2, 3, \dots$. As we can see immediately, the solutions of Eq. (27) are determined by the initial conditions $\delta\theta(t=0)$ and $\delta\dot{\theta}(t=0)$ (as for any second-order differential equation). The initial conditions are vanishing due to thermal fluctuations, so the classical solutions of Eq. (27) 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 [27]). These transitions have frequency $2\omega_0$, in accordance with the classical dynamics. The transition rate is

$$\frac{\partial |c_{n+2,n}|^2}{\partial t} = \frac{\pi h^2}{128} \omega_0^2(n+1)(n+2)\delta(2\omega_0 - \omega) \quad (28)$$

and the absorbed power

$$P = 2h\omega_0 \frac{\partial |c_{n+2,n}|^2}{\partial t} = \frac{\pi h^2}{64} h\omega_0^3(n+1)(n+2)\delta(2\omega_0 - \omega) \quad (29)$$

where we may restrict, in principle, to the lowest states. The intensity given by Eq. (29) is small, because, especially, of the factor $(E/E_0)^2$ ($h = \frac{E}{2E_0} \cos \alpha$). The temperature dependence is given by

$$P_{th} = \frac{\pi h^2}{64} h\omega_0^3 \sum_{n=0}^{\infty} (n+1)(n+2) \times [e^{-\beta h\omega_0(2n+1)} - e^{-\beta h\omega_0(2n+3)}] \delta(2\omega_0 - \omega) \left/ \left[\sum_{n=0}^{\infty} e^{-\beta h\omega_0 n} \right]^2 \right., \quad (30)$$

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

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) sample; in amorphous samples the average over angles α should be taken ($\overline{\cos^2 \alpha} = \frac{1}{3}$). In solids, the width of the absorption line (the damping parameter) 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 (internal) quenching field is weak, and the parametric resonance is not likely to occur.

4. Weak 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 Eq. (17) has a minimum value for $\theta_0 \approx \frac{\pi}{2}$ and the hamiltonian reduces to the free hamiltonian given by Eq. (11); 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 $\dot{\varphi} = \omega_0 = L_z/I$. In contrast with the high-field case, where the frequency $\dot{\varphi}$ is fixed by the high 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 $\hbar/I \approx 10^{11} \text{ s}^{-1}$ for typical values $I = 10^{-38} \text{ g} \cdot \text{cm}^2$. 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 $\frac{\hbar^2}{I} = 1 \text{ K}$ (for our numerical values). The approximation described above is valid for $\delta\theta_{n+1,n} = \sqrt{\hbar(n+1)/2I\omega_0} \ll 1$, which leads to $\hbar(n+1) \ll 2L_z$, or $n+1 \ll m$. Similarly, the transverse components of the angular momentum are very small, $L_x^2 + L_y^2 \ll L_z^2 \approx L_z^2$ ($m \approx l$); at room temperature m may acquire as high values as $m = 300$. All this is practically the same as for the free rotations.

The interaction hamiltonian given by Eq. (20) leads to two relevant interactions

$$\begin{aligned} H_{1int} &= dE \cos \alpha \cos \omega t \cdot \delta\theta, \\ H_{2int} &= \frac{1}{4} dE \sin \alpha [\cos(\omega + \omega_0)t + \cos(\omega - \omega_0)t] \cdot \delta\theta^2. \end{aligned} \quad (31)$$

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

$$P_n = \frac{\pi}{4I} d^2 E^2 (n+1) \cos^2 \alpha \delta(\omega_0 - \omega). \quad (32)$$

For $n \ll m$ we restrict ourselves to small values of n in Eq. (32) and sum over a few values of m in $\delta(\omega_0 - \omega) = \delta(\hbar m/I - \omega)$ with the statistical weight $e^{-\beta \hbar^2 m^2/2I}$ (low temperatures). 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

$$P_{th} = \frac{\pi}{4I} d^2 E^2 \cos^2 \alpha \cdot C \sum_{m>0} e^{-\beta \hbar^2 m^2/2I} \times \left\{ \sum_{n=0}^{\infty} (n+1) [e^{-\beta \hbar \omega_0 n} - e^{-\beta \hbar \omega_0 (n+1)}] \right/ \left[\sum_{n=0}^{\infty} e^{-\beta \hbar \omega_0 n} \right] \delta(\omega_0 - \omega) \right\}, \quad (33)$$

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

$$P_{th} = \frac{\pi}{4} d^2 E^2 \cos^2 \alpha \sqrt{\frac{2\pi\beta}{I}} e^{-\beta \hbar \omega^2/2}. \quad (34)$$

The interaction hamiltonian H_{2int} given by Eq. (31) 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

$$P_n = \frac{\pi \hbar \Omega}{128 I^2 \omega_0^2} d^2 E^2 (n+1)(n+2) \sin^2 \alpha \delta(\Omega - \omega). \quad (35)$$

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

$$P_{th} = \frac{\pi \hbar}{128 I^2} d^2 E^2 \sin^2 \alpha \cdot C \sum_{m>0} \frac{\Omega}{\omega_0^2} e^{-\beta \hbar^2 m^2/2I} \times \left\{ \sum_{n=0}^{\infty} (n+1)(n+2) [e^{-\beta \hbar \omega_0 (2n+1)} - e^{-\beta \hbar \omega_0 (2n+3)}] \right/ \left[\sum_{n=0}^{\infty} e^{-\beta \hbar \omega_0 n} \right]^2 \right\} \times \delta(\Omega - \omega); \quad (36)$$

summation over n gives

$$P_{th} = \frac{\pi\hbar}{64I^2} d^2 E^2 \sin^2 \alpha \cdot C \sum_{m>0} \frac{\Omega}{\omega_0^2} e^{-\beta\hbar^2 m^2/2I} \frac{e^{-\beta\hbar\omega_0}}{(1 + e^{-\beta\hbar\omega_0})^2} \delta(\Omega - \omega) \quad (37)$$

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

It is worth noting that the weak 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). It is also worth noting that the expansion of the effective potential function U_{eff} in powers of $\delta\theta$ is an approximation to free rotations with constant L_z , instead of constant \mathbf{L} .

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

$$H = \frac{1}{2} I (\dot{\theta}^2 + \dot{\varphi}^2 \sin^2 \theta) \quad (38)$$

can also be written as

$$H = \frac{1}{2I} P_\theta^2 + \frac{1}{2I \sin^2 \theta} P_\varphi^2 \quad (39)$$

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

$$const \cdot dP_\theta dP_\varphi d\theta e^{-\beta P_\theta^2/2I} e^{-\beta P_\varphi^2/2I \sin^2 \theta}, \quad (40)$$

or, integrating over momenta, $\frac{1}{2} \sin \theta d\theta$. In the presence of the field we have the distribution $\simeq \frac{1}{2} \sin \theta d\theta \cdot e^{\beta dE_0}$ (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 [28–31]. 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 $E_l = \hbar^2 l(l+1)/2I$ and renormalize the wavefunction in the first-order of the theory of perturbation; using these renormalized wavefunctions, there appear diagonal matrix elements of $\cos \theta$, which we denote by $(\widetilde{\cos \theta})_{lm,lm}$; the mean value of this quantity is given by $\overline{\cos \theta} = \sum (\widetilde{\cos \theta})_{lm,lm} \Delta(\beta E_l) e^{-\beta E_l} / \sum e^{-\beta E_l}$, which leads to the classical result $= \beta dE_0/3$, as expected.

5. 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 $\bar{d} = \beta d^2 E_0/3$, as noted above.

For typical values of the dipole moments $d = 10^{-18}$ statcoulomb · cm separated by distance of the order $a = 10^{-8}$ cm (1 Å) the interaction energy is $\simeq d^2/a^3 = 10^{-12}$ erg $\simeq 10^3$ K (1 eV = 1.6×10^{-12} erg, 1 K = 1.38×10^{-16} erg, 1 eV = 1.1×10^4 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. (The estimation given here should take into account the time average of the dipole interaction energy with respect to molecular motion). The corresponding dipolar field is of the order $d/a^3 = 10^6$ statvolt/cm (i.e., of the order of the atomic fields).

The interaction energy of two dipoles \mathbf{d}_1 and \mathbf{d}_2 separated by distance \mathbf{a} is given by

$$U = -\frac{3(\mathbf{d}_1 \mathbf{d}_2) a^2 - (\mathbf{d}_1 \mathbf{a})(\mathbf{d}_2 \mathbf{a})}{a^5}. \quad (41)$$

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

$$U = -\frac{d_1 d_2}{a^3} [2 \cos \theta_1 \cos \theta_2 + 3 \sin \theta_1 \sin \theta_2 \cos(\varphi_1 - \varphi_2)]; \quad (42)$$

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 neighborhood of this minimum value the interaction energy behaves like

$$U = \frac{d_1 d_2}{a^3} [-3 + \frac{3}{2}(\delta\theta_1^2 + \delta\theta_2^2) - 2\delta\theta_1 \delta\theta_2 + \frac{3}{2}(\delta\varphi_1 - \delta\varphi_2)^2] \\ = \frac{d_1 d_2}{a^3} [-3 + \frac{1}{4}(\delta\theta_1 + \delta\theta_2)^2 + \frac{5}{4}(\delta\theta_1 - \delta\theta_2)^2 + \frac{3}{2}(\delta\varphi_1 - \delta\varphi_2)^2], \quad (43)$$

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, for not too high temperatures, 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.

These considerations are based on the dipolar interaction given by Eq. (41), which, in principle, is valid for distances a much longer than the dimension of the dipoles. However, since the dipolar interaction decreases rapidly with increasing distance, we may also use it for distances equal to a few dipole lengths. In addition, for heavy molecules the charge imbalance implies a large charge and, consequently, a small displacement, which amounts to a more localized dipole; so, the condition for validity of the dipolar interaction may be fulfilled much more satisfactorily than we use to think. It is relevant in this respect the analysis made in Ref. [32].

As it is well known, pyroelectrics (or electrets) have a permanent electric polarization [33]; 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); it seems that all these substances are piezoelectric. There are also structural modifications associated with finite discontinuities in polarization, 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 (4 Å); the dipole of a cell is $d \simeq 5 \times 10^{-18}$ statcoulomb · cm (the saturation polarization – the dipole moment per unit volume – at room temperature is 8×10^4 statcoulomb · 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 $\delta = 0.1 \text{ \AA}$; 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 polarization [34].

In a continuum model of polarized substance the dipolar interaction given by Eq. (43) (with identical dipoles d) gives the interaction hamiltonian

$$H_{int} = \frac{1}{a^3} \int d\mathbf{r} \left[\frac{d^2}{a^3} \delta\theta^2 + \frac{5d^2}{4a} (\text{grad}\delta\theta)^2 + \frac{3d^2}{2a} (\text{grad}\delta\varphi)^2 \right], \quad (44)$$

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

$$H = \frac{1}{a^3} \int d\mathbf{r} \left[\frac{1}{2} I \dot{\delta}\theta^2 + \frac{1}{2} I \dot{\delta}\varphi^2 + \frac{1}{2} I \omega_0^2 \delta\theta^2 + \frac{1}{2} I v_\theta^2 (\text{grad}\delta\theta)^2 + \frac{1}{2} I v_\varphi^2 (\text{grad}\delta\varphi)^2 \right], \quad (45)$$

where I is the moment of inertia of the dipoles and $\omega_0^2 = 2d^2/la^3$, $v_\theta^2 = 5d^2/2la = 5\omega_0^2 a^2/4$, $v_\varphi^2 = 3d^2/la = 3\omega_0^2 a^2/2$. The dipole density $1/a^3$ should include the number of nearest neighbors; if we restrict ourselves to the highly anisotropic (layered) model, then the hamiltonian density in Eq. (45) is two-dimensional. We can see that the dipolar interaction may generate dipolar waves (waves of orientational polarizability), governed by the wave equations

$$\frac{d^2}{dt^2} \delta\theta + \omega_0^2 \delta\theta - v_\theta^2 \Delta \delta\theta = 0, \quad \frac{d^2}{dt^2} \delta\varphi - v_\varphi^2 \Delta \delta\varphi = 0; \quad (46)$$

the spectrum of these dipolar waves is $\omega_\theta^2 = \omega_0^2 + v_\theta^2 k^2$ 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 · cm, $a = 10^{-8}$ cm and $I = 10^{-38}$ g · cm² 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 $\mathbf{E}(\mathbf{r}, t) = \mathbf{E} \cos(\omega t - \mathbf{k}\mathbf{r})$ be a radiation electric field (plane wave) which makes an angle α with the polarization direction; the interaction hamiltonian is

$$H' = -\frac{1}{a^3} \int d\mathbf{r} (d\mathbf{E}) \cos(\omega t - \mathbf{k}\mathbf{r}), \quad (47)$$

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

$$H' = -\frac{1}{a^3} \int d\mathbf{r} (dE) (\delta\theta \sin \alpha - \frac{1}{2} \delta\theta^2 \cos \alpha) \cos(\omega t - \mathbf{k}\mathbf{r}) \quad (48)$$

(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 Eq. (46) 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,

$$\frac{d^2}{dt^2} \delta\theta + \omega_0^2 \delta\theta = \frac{dE}{I} \sin \alpha \cos \omega t - \frac{dE}{I} \delta\theta \cos \alpha \cos \omega t. \quad (49)$$

The first interaction term gives

$$\frac{d^2}{dt^2} \delta\theta + \omega_0^2 \delta\theta + 2\gamma \frac{d}{dt} \delta\theta = \frac{dE}{I} \sin \alpha \cos \omega t, \quad (50)$$

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

$$\delta\theta_1 = a \cos \omega t + b \sin \omega t, \quad (51)$$

where

$$a = -\frac{dE}{2I\omega_0} \sin \alpha \frac{\omega - \omega_0}{(\omega - \omega_0)^2 + \gamma^2}, \quad b = \frac{dE}{2I\omega_0} \sin \alpha \frac{\gamma}{(\omega - \omega_0)^2 + \gamma^2} \quad (52)$$

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

$$P = dE \sin \alpha \cos \omega t \dot{\delta}\theta_1 = \frac{1}{2} dE \sin \alpha \cdot b \omega_0 = \frac{\pi}{4I} d^2 E^2 \sin^2 \alpha \delta(\omega_0 - \omega). \quad (53)$$

The second interaction term in Eq. (49) gives the Mathieu's equation

$$\ddot{\delta}\theta_2 + \omega_0^2 (1 + h \cos \omega t) \delta\theta_2 = 0, \quad (54)$$

where $h = (dE/I\omega_0^2) \cos \alpha$ (a damping term can be included). As it was discussed before the thermal fluctuations wipe out the parametric resonances associated with this equation. All the above considerations are valid for a classical dynamics. The quantization of the hamiltonians H and H' given by Eqs. (45) and (48) (which is performed according to the well-known standard rules), leads to standard absorption and emission processes, and to quantum transitions similar with Eqs. (28)–(30). It is worth noting that the static electric field E_0 in equations (28)–(30) is replaced here by $E_0 = d/2a^3$ (by comparing the frequencies ω_0 given in Eqs. (19) and, respectively, (45)), as expected for a (high) 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 [35–41]. 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 $a = 1 \mu\text{m}$ (10^4 \AA) we get a frequency $\omega_0 \simeq 10$ MHz.

6. 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 as high as $E_0 = 10^9$ statvolt/cm for laser intensities 10^{20} W/cm². Under the action of such strong fields the molecules are usually ionized, but the molecular ions may retain their electric dipoles 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 the particle with mass 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 measured with respect to the z -axis; the angle θ may perform slow oscillations; we assume $\alpha \ll \theta$. The equation of motion can be written as

$$I\ddot{\alpha} = -dE_0 \sin(\theta + \alpha) \cos \omega_h t \simeq -dE_0 \sin \theta \cos \omega_h t; \quad (55)$$

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

$$\bar{E}_{kin} = \frac{d^2 E_0^2}{4I\omega_h^2} \sin^2 \theta \quad (56)$$

replaces the interaction energy $-dE_0 \cos \theta$ of the static field in the effective potential energy U_{eff} given by Eq. (17); the effective potential becomes

$$U_{eff} = \frac{L_z^2}{2I \sin^2 \theta} + \frac{d^2 E_0^2}{4I\omega_h^2} \sin^2 \theta. \quad (57)$$

This function has a minimum value for $\tilde{\theta}_0 = \arcsin \theta_0 / R^{1/4}$ and $\tilde{\theta}'_0 = \pi - \tilde{\theta}_0$, where $R = dE_0 / 2I\omega_h^2$ is a renormalization factor and $\theta_0 = (L_z^2 / IdE_0)^{1/4} < R^{1/4}$, i.e. the θ_0 value corresponding to high fields, as expected; it is worth noting that there are two values of the equilibrium angle: $\tilde{\theta}_0$ and $\pi - \tilde{\theta}_0$. The molecules are practically aligned along the field [42,43]. The dipole may perform small vibrations about these equilibrium angles with the frequency $\tilde{\omega}_0 = \omega_0 \sqrt{3R/4}$, where $\omega_0 = 2\sqrt{dE_0/I}$ is the characteristic frequency for high static fields given in Eq. (19) (for $\tilde{\theta}_0 \ll 1$). We can see that for highly-oscillating electric fields we get the results for static fields renormalized according to $E_0 \rightarrow \tilde{E}_0 = E_0 R$.

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

$$\frac{L_z^2}{IdE_0} < \frac{dE_0}{2I\omega_h^2} \ll 1 \quad (58)$$

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

$$\frac{\sqrt{2}L_z\omega_h}{d} < E_0 \ll \frac{2I\omega_h^2}{d}. \quad (59)$$

For $L_z^2/I = T$ and our numerical parameters $I = 10^{-38} \text{ g} \cdot \text{cm}^2$, $T = 300 \text{ K} = 4 \times 10^{-14} \text{ erg}$, $d = 10^{-18} \text{ statcoulomb} \cdot \text{cm}$ and $\omega_h = 2\pi \cdot 10^{15} \text{ s}^{-1}$ we get approximately $10^8 \text{ statvolt/cm} < E_0 \ll 10^{10} \text{ statvolt/cm}$, 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 molecular rotation spectra are affected in the same manner as in static electric field, providing the time-dependent field strength is renormalized by the factor $R \ll 1$ introduced here. It is worth noting that the interaction $-dE_0 \cos \theta \cos \omega_h t$ linear in the field is replaced by an effective interaction which is quadratic in the field, as shown in Eq. (57); while this effective interaction affects the slow rotations, it does not couple to the (slow) translation motion.

7. Discussion and conclusions

We have shown here that the approximate method of separating the azimuthal rotations from zenithal oscillations may be used to get insight into the rotation spectrum of heavy molecules (viewed as a spherical pendulum) in electric fields. Using this method, a particular feature has been pointed out in these spectra, related to parametric resonance. 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 about their equilibrium positions give rise to special features in the spectrum, in particular to parametric resonances. Similar parametric resonances appear in the presence of weak static electric fields, although they are small contributions, superposed over regular transitions. It was shown that the dipole–dipole interaction can lead to an equilibrium state of quenched dipoles, which possesses a macroscopic polarization; the motion of this macroscopic polarization proceeds by particular modes which have been tentatively called “dipolons” (polarization waves). The excitation of these modes may also lead to parametric resonances. It was also shown that a strong, highly-oscillating electric field, like the fields provided by the high-power lasers, behaves in the same manner as static electric fields, 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 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 ($\mu \simeq 10^{-23} \text{ erg/Gs}$); if the magnetic moments are in thermal equilibrium, their interaction energy $\mu^2/a^3 \simeq 10^{-6} \text{ K}$ is effective at much lower temperatures; the characteristic frequency of “electric dipolons” $\omega_0 = \sqrt{2d^2/la^3} \simeq 10^{13} \text{ s}^{-1}$ becomes $\omega_0 = \sqrt{2\mu^2/la^3} \simeq 10^8 \text{ s}^{-1}$ for “magnetic dipolons”. For electronic magnetic moments $\mu \simeq 10^{-20} \text{ erg/Gs}$ the interaction energy is $\simeq 1 \text{ K}$ and the characteristic frequency is $\omega_0 \simeq 10^{11} \text{ s}^{-1}$. If the magnetic moment is higher by a factor of, say, 5 and the number of nearest neighbors is 4, then the effective magnetic dipolar energy (for electronic moments) increases to $\simeq 100 \text{ K}$, which is of the order of magnitude of usual ferromagnetic transition temperatures; then, the “magnetic dipolons” become magnons (ferromagnetic resonances) [34]. The dipole interaction as source of ferromagnetism is different from the Weiss mean field approach; it resembles more the Bloch theory of magnons [44].

Author contribution statement

Both authors contributed equally to this paper.

Conflict of interest

No conflict of interest.

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