

Parametric resonance in molecular rotation spectra

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Abstract

It is shown that in the rotation spectra of dipolar molecules there exist parametric resonances (transitions). These resonances are computed explicitly for a spherical top in the presence of high electric fields, which may occur in polar molecular solids, or for polar inclusions (impurities) in polar environments. The approximation employed makes use of the separation of the precession motion from oscillations.

Consider a molecule endowed with an electric dipole moment \mathbf{d} , placed in a constant, uniform electric field \mathbf{E}_0 . The rotations of the molecule can be approximated by those of a spherical top (spherical pendulum, rigid, spatial rotator)[1, 2] with moment of inertia I , such that the hamiltonian can be written, in spherical coordinates, as

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

where the z -axis is chosen along the field \mathbf{E}_0 . The classical equation of motion $I \frac{d}{dt}(\dot{\varphi} \sin^2 \theta) = 0$ indicates the conservation of the component $L_z = I\dot{\varphi} \sin^2 \theta$ of the angular momentum, which leads to an effective potential $U_{eff} = \frac{L_z^2}{2I \sin^2 \theta} - dE_0 \cos \theta$. Usually, the electric field E_0 is as low as the inequality $dE_0 \ll L_z^2/I$ is fulfilled, even for the lowest values of L_z . Under these circumstances, the effective potential U_{eff} has a minimum value which is placed at $\theta_0 \simeq \pi/2$, and the field E_0 brings a contribution only in the second order of approximation. The effective potential can be expanded in powers of $\tilde{\theta} = \theta - \pi/2$, leading to a harmonic-oscillator hamiltonian

$$H \simeq \frac{1}{2}I\dot{\tilde{\theta}}^2 + \frac{1}{2}I\omega_0^2\tilde{\theta}^2 \quad (2)$$

(up to constant, irrelevant terms), where $\omega_0 = L_z/I$. The angle φ rotates freely with the precession frequency ω_0 ($\dot{\varphi} = \omega_0$). These classical rotations can be quantized, leading to $L_z = \hbar m$, m being any integer, the rotation energy $E_{rot} = L_z^2/2I = \hbar^2 m^2/2I$ and the vibration energy $E_{vibr} = \hbar\omega_0(n + 1/2) = \hbar^2 m(n + 1/2)/I$, $n = 0, 1, 2, \dots$. Obviously, this is only an approximate scheme for free rotations, valid at low temperature, where only the lowest energy levels m, n are excited, and for low values of the electric field which satisfy $dE_0 \ll \hbar/I$. As it is well known, the free rotations are described by the hamiltonian $L^2/2I$, where L is the angular momentum, with the energy levels $E_l = \hbar^2 l(l + 1)/2I$, $l = 0, 1, 2, \dots$ and spherical harmonics $Y_{lm}(\theta, \varphi)$, $m = -l, -l + 1, \dots, l$, as eigenfunctions. The effect of the electric field E_0 can be computed in the first order of the perturbation theory (second order in energy), finite-temperature mean values including (Stark

effect for rotations); as it is well known, in the classical limit we get $\overline{\cos\theta} = \beta dE_0/3$, where $\beta = 1/T$ is the inverse of the temperature T (which is the well-known Curie-Langevin law).[3]-[6]

A time-dependent electric field $\mathbf{E}(t) = E \cos\omega t(\sin\alpha, 0, \cos\alpha)$, which makes an angle α with the z -axis, generates an interaction hamiltonian $H_{int} = -dE(\sin\alpha \sin\theta \cos\varphi + \cos\alpha \cos\theta) \cos\omega t$. This interaction gives rise to transitions between rotational states l and $l+1$, $l = 0, 1, 2, \dots$, with frequency $\omega_l = \hbar(l+1)/I$, *i.e.* with frequency $\omega_0 = \hbar m/I$. Indeed, for θ in the vicinity of $\pi/2$, the interaction hamiltonian can be written as

$$\begin{aligned} H_{int} &= H_{int}^{(1)} + H_{int}^{(2)}, \\ H_{int}^{(1)} &\simeq dE\tilde{\theta} \cos\alpha \cos\omega t, \\ H_{int}^{(2)} &\simeq \frac{1}{4}dE\tilde{\theta}^2 \sin\alpha [\cos(\omega + \omega_0)t + \cos(\omega - \omega_0)t] \end{aligned} \quad (3)$$

(up to constant, irrelevant terms). The interaction hamiltonian $H_{int}^{(1)}$ generates transitions between states n and $n+1$ of the harmonic-oscillator hamiltonian given by equation (2), according to the matrix elements of $\tilde{\theta}$, with frequencies $\omega = \omega_0$. The interaction hamiltonian $H_{int}^{(2)}$ and the harmonic-oscillator hamiltonian given by equation (2) lead to the classical equation of motion of a parametric resonance. As it is well known, the resonance occurs, mainly, in the vicinity of $\omega \pm \omega_0 = 2\omega_0$ ($2\omega_0/n$, $n = 1, 2, 3, \dots$), *i.e.* $\omega = \omega_0, 3\omega_0$ (it is worth noting that $3\omega_0$ is, in fact, ω_0 for $m = 3$).[2] Indeed, the matrix elements of $\tilde{\theta}^2$ are non-vanishing between states n and $n+2$, which indicates transitions with frequency given by $\omega \pm \omega_0 = 2\omega_0$, as in the classical case. We conclude that in the spectrum of free molecular rotations there exist parametric resonances (transitions).

Consider now a very high electric field E_0 , such that the minimum value of the effective potential U_{eff} is placed at $\theta_0 \simeq (L_z^2/IdE_0)^{1/4} \ll 1$. The molecular rotations are quenched in this case about the direction of the field. For a molecular mass $10^4 - 10^5$ electron mass ($10^{-27}g$) and molecular dimension $1\text{\AA} = 10^{-8}cm$ we get the typical value for the molecular moment of inertia $I = 10^{-39} - 10^{-38}g \cdot cm^2$; the frequency $\omega_0 = \hbar/I$ given above (for $m = 1$) is $\omega_0 = 10^{11} - 10^{12}s^{-1}$ (terahertz-far infrared region); it corresponds to quanta of rotation energy $\hbar^2/I = 1 - 10K$ ($1K = 1.3 \times 10^{-16}erg$).[7] For a typical dipole moment $d = 10^{-18}esu$ we get $E_0 \gg 10^2 - 10^3 statvolt/cm$ ($1 statvolt/cm = 3 \times 10^4 V/m$) in order to fulfil the condition $dE_0 \gg \hbar^2/I$. This is a very high electric field, which may occur in polar molecular solids, or near polar impurities embedded in polar environments (the electric field generated by a molecular dipole $d = 10^{-18}esu$ at distance 1\AA is $10^6 statvolt/cm$). The occurrence of such an electric field is very similar with the potential $U_0(1 - \cos 2\theta)$ which may act upon rotating molecules in crystals, driving the transition from rotations to vibrations (quenched rotations) which is seen in the curve of the heat capacity *vs* temperature.[8, 9] Under these circumstances, an expansion in powers of $\tilde{\theta} = \theta - \theta_0$ leads to the hamiltonian

$$H = \frac{1}{2}I\dot{\tilde{\theta}}^2 + \frac{1}{2}I\omega_0^2\tilde{\theta}^2 \quad (4)$$

(up to constant, irrelevant terms), where $\omega_0 = 2\sqrt{dE_0/I}$; the angle φ rotates freely with the angular velocity $\omega_0/2$ ($\dot{\varphi} = \omega_0/2$). Since $dE_0 \gg \hbar^2/I$, the frequency ω_0 is at least of the order of \hbar/I ; such frequencies ($\hbar/I, \sqrt{dE_0/I}$) are known as Rabi frequencies.[10, 11]

The hamiltonian of interaction with the time-dependent electric field $E(t)$ given above becomes

in this case

$$\begin{aligned}
 H_{int} &= H_{int}^{(1)} + H_{int}^{(2)} , \\
 H_{int}^{(1)} &= -\frac{1}{2}dE\tilde{\theta} \sin \alpha [\cos(\omega + \omega_0/2)t + \cos(\omega - \omega_0/2)t] + \\
 &\quad + dE\theta_0\tilde{\theta} \cos \alpha \cos \omega t , \\
 H_{int}^{(2)} &= \frac{1}{2}dE\tilde{\theta}^2 \cos \alpha \cos \omega t .
 \end{aligned} \tag{5}$$

The interaction hamiltonian $H_{int}^{(1)}$ produces transitions between harmonic-oscillator states n and $n + 1$ (matrix elements of $\tilde{\theta}$) with frequencies $\omega \pm \omega_0/2 = \omega_0$, *i.e.* $\omega = \omega_0/2, 3\omega_0/2$, as well as transitions of a much lower intensity (corresponding to the $\theta_0\tilde{\theta}$ -term) with frequency $\omega = \omega_0$. The interaction hamiltonian $H_{int}^{(2)}$, which, classically, generates parametric resonances for ω in the vicinity of $2\omega_0/n$, $n = 1, 2, 3, \dots$, produces quantum transitions, of low intensity, between harmonic-oscillator states n and $n + 2$, with frequency $\omega = 2\omega_0$.

It is worth estimating the transition rate of the interaction hamiltonian $H_{int}^{(2)}$. For an interaction hamiltonian of the form $H_{int} = h \cos \omega t$ the transition rate between two states n and m is $\partial |c_{nm}|^2 / \partial t = (\pi/2\hbar^2) |h_{nm}|^2 \delta(\omega - \omega_{nm})$ (with standard notations); the absorbed power is $P = \hbar\omega_{nm} \partial |c_{nm}|^2 / \partial t$. For the hamiltonian $H_{int}^{(2)}$ given by equation (5) we get

$$P = \frac{\pi}{16I^2\omega_0} d^2 E^2 (n+1)(n+2) \delta(\omega - 2\omega_0) \cos^2 \alpha , \tag{6}$$

where we have used the matrix elements $(\tilde{\theta})_{n+1,n} = \sqrt{\hbar(n+1)/2I\omega_0}$ of the harmonic-oscillator. The mean absorbed power is given by

$$\bar{P} = \frac{\pi}{16I^2\omega_0} d^2 E^2 \delta(\omega - 2\omega_0) \cos^2 \alpha \cdot C \sum_{n=0}^{\infty} (n+1)(n+2) e^{-\beta\hbar\omega_0 n} , \tag{7}$$

where C is a normalization constant (and $\beta = 1/T$ is the inverse of the temperature T). For low temperatures only a few terms contribute to the summation in equation (7).

In conclusion, we may say that we have identified parametric-resonance contributions to the rotational spectra of electric dipolar molecules in electric fields. These resonances are computed explicitly for spherical-top molecules in high electric fields, which may occur in polar molecular solids or for polar impurities in polar environments, by separating approximately molecular precession from zenithal oscillations.

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