

Parametric resonance in molecules with electrooptical anharmonism

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The possibility is shown of generating parametric resonance during the excitation of molecular vibrations by IR laser radiation. The phenomenon is caused by the nonlinear dependence of the dipole moment of the molecule on intranuclear separation (electrooptical anharmonism). Estimates are given of the necessary intensity of laser radiation and the effect of mechanical anharmonism is discussed.

Among the problems of quantum electronics, the excitation of molecular vibrations by laser radiation occupies an important place. The interest in this problem is a consequence of its close connection with laser chemistry,^{1,2} laser separation of isotopes,^{2,3} etc. One of the mechanisms for exciting vibrations is connected with the modulation parameters of the vibrating system (parametric excitation). The parametric excitation of the vibrational modes of molecules as a consequence of nonlinear intramode bonds (mechanical anharmonism) is investigated in Refs. 4 and 5.

In Ref. 6, the threshold of parametric excitation for certain molecules is computed. In Ref. 7, the possibility of applying the adiabatic approximation for molecules in the field of a light wave with a frequency close to molecular vibration frequencies is considered. The quasienergies of a parametrically excited anharmonic oscillator were investigated in Ref. 8. The possibility is pointed out in Ref. 9 of the effective excitation of molecules in two steps: In the first step the molecule is excited through an intense fundamental oscillation, and in the second step the molecule is excited with the help of radiation at a resonant harmonic or a combination frequency. The possibility is shown in the present work of the effective parametric excitation of a discrete molecular mode on the basis of utilizing electrooptic anharmonism. The nonlinear dependence of the dipole moment of the molecule on the intranuclear distance leads to a modulation of the molecular vibration frequencies in the field of laser radiation which establishes the conditions for generating parametric resonance in such a system and, as a consequence, a sharp growth in vibrational energy.

Estimates were obtained of the threshold of the radiation intensity taking into account the restriction from the disordering mechanism,¹⁰ which is stipulated by the dependence of the frequency of vibration on its energy.

We consider the effect of a laser IR field $E_0 \cos \omega t$ on a molecular vibrational mode with frequency ω_0 . We shall investigate the dynamics of the mode starting from the Hamiltonian

$$\hat{H} = \hat{p}^2/2 + \omega_0^2 q^2/2 - E_0 d \cos \omega t. \quad (1)$$

Here $\hat{p} = -i\hbar \partial / \partial q$ is the generalized momentum operator corresponding to the normal coordinate q ; d is the dipole moment of the molecule. The dipole moment d depends nonlinearly on the nuclear separation in the general case (electrooptical anharmonism¹¹). We treat this nonlinearity by ex-

panding d in a Taylor's series in terms of q up to the quadratic term

$$d = d(q) \approx d(0) + d_q q + \frac{1}{2} d_{qq} q^2, \quad (2)$$

$$d_q = \left. \frac{\partial d}{\partial q} \right|_{q=0}, \quad d_{qq} = \left. \frac{\partial^2 d}{\partial q^2} \right|_{q=0}.$$

Substituting Eq. (2) into Eq. (1) and dropping the term determining the energy shift of the equilibrium position of the nuclei as a consequence of the Stark effect ($E_0 \cos \omega t$) $d(0)$, we have

$$\hat{H} = \hat{p}^2/2 + \bar{\omega}^2 q^2/2 - E_0 \cos \omega t d_q q, \quad (3)$$

$$\bar{\omega}^2 = \omega_0^2 (1 + \lambda \cos \omega t), \quad \lambda = -E_0 d_{qq} / \omega_0^2. \quad (4)$$

The last term in Eq. (3) is responsible for the light-induced transitions between neighboring vibrational energy levels; and, in particular, for the generation of the usual optical resonance in the presence of molecular vibrations. We shall assume that the radiation frequency ω differs so much from the mode frequency ω_0 ($|\omega - \omega_0| \sim \omega_0$) that ordinary resonance is absent. This allows one to neglect the last term in Eq. (3). In this case the Hamiltonian of Eq. (3) corresponds to a quantum oscillator with a changing eigenfrequency.¹² The electrooptical anharmonism leads to a shaking-wall potential well, in which the nuclei are found, at a frequency ω ; and this also determines the modulation frequency of the mode. It is known that in the classical limit in such a system the generation of the phenomenon of parametric resonance is possible.

Using the Schrodinger equation for the quantum mechanical averages of the kinetic ($T = \langle \hat{p}^2/2 \rangle$) and potential ($U = \langle \bar{\omega}^2 q^2/2 \rangle$) energy of the mode, we obtain the following equations

$$\left. \begin{aligned} \frac{dT}{dt} &= \frac{i\hbar}{2} \bar{\omega}^2 - \bar{\omega}^2 \langle q\hat{p} \rangle, \\ \frac{dU}{dt} &= -\frac{i\hbar}{2} \bar{\omega}^2 + \bar{\omega}^2 \langle q\hat{p} \rangle + \frac{1}{\bar{\omega}^2} \frac{\partial \bar{\omega}^2}{\partial t} U, \\ \frac{d\langle q\hat{p} \rangle}{dt} &= 2(T - U). \end{aligned} \right\} \quad (5)$$

If until the radiation is turned on the system is represented by a linear oscillator in a stationary state, then the initial conditions for Eqs. (5) have the form

$$T(0) = U(0) = \frac{1}{2} W_0, \quad \langle q\hat{p} \rangle|_{t=0} = i\hbar, \quad (6)$$

Here W_0 is the total energy of the mode at $t = 0$.

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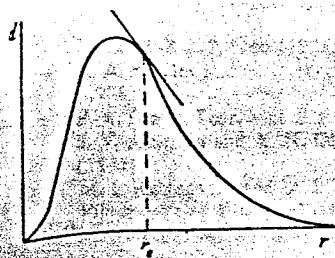


FIG. 1. Qualitative dependence of the dipole moment on the distance between nuclei.

As long as the parametric resonance manifests itself most strongly when the frequency of modulation of the parameters is close to double the unexcited eigenfrequency of the oscillator, we may assume that

$$\omega = 2\omega_0 + \delta, \quad (6a)$$

where δ is a small quantity.

Using the method of averaging¹³ one can find an approximate solution of the system of Eqs. (5), with the initial conditions of Eq. (6) for T and U . The expression for the total energy of oscillation $W = T + U$ has the form

$$W = W_0 \frac{\lambda^2 \omega_0^2}{16s^2} \left\{ \cosh 2st - \frac{4\delta^2}{\lambda^2 \omega_0^2} \right\}, \quad (7)$$

$$s = \frac{1}{2} \left[\left(\frac{\lambda \omega_0}{2} \right)^2 - \delta^2 \right]^{1/2}. \quad (8)$$

According to Eqs. (7) and (8), parametric resonance, involving a growth of vibrational energy with time, arises if the intensity of radiation exceeds the threshold value

$$I_{th} = \frac{c}{2\pi} \frac{\omega_0^2 \delta^2}{|d_{qq}|^2}. \quad (9)$$

The instability region is determined by the expression

$$-\frac{1}{2} |\lambda| \omega_0 < \delta < \frac{1}{2} |\lambda| \omega_0. \quad (10)$$

The quantity λ is the basic factor determining the possibility of parametric resonance in the system considered. Let us estimate the value of λ . One can find the order of magnitude of the second derivative d_{qq} in the example of a molecule with a homopolar bond (a CH bond, for example). The qualitative behavior of the dependence of the dipole moment of the molecule on nuclear separation r , characteristic for this case, is shown in Fig. 1.¹⁴

The maximum value of the dipole moment is attained at a distance between nuclei different from equilibrium. The equilibrium value is designated in Fig. 1 by r_e . It is easy to see that for sufficiently large amplitudes of oscillation the function $d(r)$ is nonlinear. One can also see from Fig. 1 that the value of the first derivative of the dipole moment ($d_r \sim e$) changes significantly at distances the order of r_e . This enables one to estimate the quantity d_{qq}

$$d_{qq} \sim \frac{1}{M} d_{rr} \sim \frac{1}{M} \frac{d_r}{r_e} \sim \frac{e}{Mr_e}, \quad (11)$$

where M is a characteristic nuclear mass. We note that the estimate shown agrees with the value of d_{rr} , which one can find on the basis of the experimentally detected dependence

of $d(r)$ for the ground electronic state $X^1\Sigma^+$ of the HF molecule.¹⁵ Using Eq. (11) and the determination of Eq. (4), we obtain the following

$$|\lambda| \sim \frac{E_0 e}{kr_e} \sim 10^{-11} I^{1/2}, \quad (12)$$

where the characteristic value $k \sim 10^5$ dyne/cm for $r_e \sim 10^{-8}$ cm is used for the elastic constant of the bond, $k \sim \omega_0^2 M$. For example, for $I \sim 10$ MW/cm², according to Eq. (2), the quantity $|\lambda| \sim 10^{-4}$.

Consideration of mechanical anharmonism leads to the fact that with a growth of vibrational excitation the frequency ω_0 changes, and the threshold condition of parametric resonance can be violated.¹⁰

We note that in Ref. 6 in estimating the threshold value of the radiation intensity this circumstance was not considered, which led, in our view, to lowered estimates. The anharmonism constants x for different molecules change within sufficiently broad limits, $x \sim 0.1-10$ cm⁻¹.¹⁶ For effective excitation of molecular vibrations it is necessary to overcome the effect of mechanical anharmonism during the crossing of lower energy levels (prior regions of the quasi-continuum of polyatomic molecules). Taking account of this circumstance, we substitute the value $\delta = 10$ cm⁻¹ in the threshold condition, Eq. (9). Then, using Eq. (11) for the threshold of the radiation intensity, we obtain the estimate: $I \sim 10^{12}$ W/cm². Frequently, however, one is able to compensate anharmonism by changes of rotational energy and anharmonic splitting of the vibrational levels.² In this case one may take for δ in Eq. (9) a typical value for the width of the radiation spectrum Δ : $\Delta = \delta \sim 0.01$ cm⁻¹. This leads to the following estimate for the intensity of radiation $I \sim 10^6$ W/cm². Depending on the choices of a specific molecule, the radiation intensity at which parametric resonance might be observed varies within the limits, $I \sim 10^6-10^{12}$ W/cm².

At moderate gas pressures the constants of vibrational relaxation, as a rule, are less than the values of δ considered; and therefore, taking into account relaxation, which leads only to a change in the limits of instability, Eq. (10), is immaterial.

In conclusion we note that the case of ordinary optical resonance, when $\omega \approx \omega_0$, in the case of parametric resonance considered, $\omega \sim 2\omega_0$. The possibility of the effective excitation of a new class of molecules with eigenfrequencies of vibration $\omega_0 \sim \omega/2$ appears. Vibrational excitation possesses a high frequency selectivity, which is important for laser separation of isotopes.

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