Theory of local mode excitation in polyatomics by frequency-modulated lasers

Xie Bo-Min and Ding Jian-Qiang
Institute of Mechanics, Chinese Academy of Sciences, Beijing, China

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We investigate in this paper the possibility of local model (LM) excitation in polyatomic molecules by frequency-modulated (FM) lasers. The interaction between the LM and all other background-forming vibrational modes is treated as a perturbation, whose characteristics can be drawn from the experimental LM overtone line shapes. An integral expression describing the LM energy absorption process is obtained by which one can devise the effective experimental way to excite the LM of polyatomics by FM lasers.

I. INTRODUCTION

The LM excitation or more generally bond-selective excitation in polyatomics by lasers is a subject of much concern and study recently.[1–3] In a previous paper[4] (hereafter referred to as I) we have shown that suitably adjusted FM laser can be used to excite anharmonic oscillators, much more effectively than the excitation by fixed frequency or by consecutive fixed frequencies. It has been long known that many polyatomic molecules have their own peculiar frequencies, characterizing the stretching or bending vibration of some specific bond.[5] In particular, the recent experiments of benzene and perdeuterobenzene[6] demonstrate clearly the LM property of its C–H (or C–D) bond, up to high vibrational quantum number. But the linewidth of the LM overtones is remarkably wide (FWHM = 50–100 cm^{-1}) which cannot be attributed to rotational effect.[7] Siebert, Reinhardt, and Hynes (SRH) have developed a delicate and convincing theory[8] to explain this phenomenon, and based their argument on the interaction between the LM and other vibrational modes. We suppose not only benzene, but also many other molecules with characteristic LM frequencies, possess these kinds of properties. Should bond-selective excitation and bond-selective reaction for an arbitrary molecule be a dream too ambitious, the same attempt for molecules with prominent LM characteristics may well be within our reach. It is the purpose of the present paper to show this possibility by making use of FM lasers.

By reasoning similar to that of Fano[9] in developing the quantum theory of spectral lines, the effect of the interaction between the LM and the background can be reduced to an equivalent decay rate of the excited LM overtones, and it can be further interrelated with the linewidth of the LM overtones. In this way the cumbersome problem of specifying the concrete form of the intramolecular interaction is avoided. Just as in the case of benzene, it is not difficult to use tunable lasers to diagnose the LM of other polyatomics and, meanwhile, if the latter really exists, to record its overtone line shapes, then from the expression deduced in this paper, we can make judgment whether the bond-selective excitation for this molecule is feasible or not, and if so, how to do it. In this respect, this paper is hoped to stimulate the interest of the experimentalists.

II. THEORY

For polyatomic molecules, its rotational frequency at room temperature is usually less than one-hundredth of its typical vibrational frequency (let alone the case of low temperature, e.g., in a supersonic stream), while the laser frequency is near the frequency of the LM in order to excite it. Therefore, viewed from the laser, the rotational motion of the molecule is very slow and its effect can be neglected in first approximation. We also assume only the LM under consideration has a dipole moment which is coupled directly with the laser, while all other vibrational modes are not coupled effectively with the EM field of the laser due to the frequency mismatch or simply due to the absence of dipole moment. The Hamiltonian of the molecule under the influence of the laser is, therefore,

$$H = H_0 - \hat{\mu}\mathscr{E}_0 f(t) q = H_L + H_B + V - \hat{\mu}\mathscr{E}_0 f(t) q \,, \quad (1)$$

with H_L the LM Hamiltonian, e.g., the Hamiltonian of the stretching vibration of a C–H or C–D bond, H_B the Hamiltonian of the background, comprising all other vibrational modes, V is the interaction between the LM and the background, which can be of a static character originated from the potential and/or of a dynamic character as elucidated by SRH in the study of C_6H_6.[8] Besides, q is the coordinate of the LM with dipole moment $\hat{\mu}$, $\mathscr{E}_0 f(t)$ is the laser electric field with amplitude $\mathscr{E}_0$. In Eq. (1) only one LM is introduced which does not imply any loss of generality. The density operator ρ of our system satisfies

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H,\rho] \equiv -\frac{i}{\hbar}[H\rho,\rho H] \equiv -iH^{x}\rho \,, \quad (2)$$

where $H^{x} \equiv \hbar^{-1}[H]$ is the Liouville operator[10] corresponding to H, we also have $H^{x} = H_0^{x} - \hat{\mu}\mathscr{E}_0 f(t) q^{x}$. Since H_0 is independent of t, we can write Eq. (2) as

$$\frac{d}{dt}(e^{iH_0^{x}t}\rho) = i\hat{\mu}\mathscr{E}_0 f(t) e^{iH_0^{x}t}(q^{x}\rho) \,, \quad (3)$$

$$\rho(t) = e^{-iH_0^{x}t}\rho(0) + i\hat{\mu}\mathscr{E}_0 \int_0^t f(t') e^{-iH_0^{x}(t-t')}\{q^{x}\rho(t')\}\, dt' \,. \quad (4)$$

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Making use of the formula[11]

$$\theta(t)e^{-iH_0^x t}=\frac{i}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega t}\frac{1}{(\omega - H_0^x + i0)}\,d\omega\,, \quad (5)$$

where $\theta(t)=1(t>0)$, $\theta(t)=0\ (t<0)$, and assuming as usual $\rho(0)$ commutes with H_0, we get from Eq. (4),

$$\rho(t)=\rho(0)-\frac{\hat{\mu}\mathscr{E}_0}{2\pi}\int_0^t\int_{-\infty}^{\infty} f(t')e^{-i\omega(t-t')}$$
$$\times\frac{1}{(\omega - H_0^x + i0)}\{q^x\rho(t')\}d\omega\, dt'\,. \quad (6)$$

We use μ, ν, e_μ, e_ν to designate the orthonormal eigenstates and the eigenenergy of the LM H_L and use α, β for orthonormal eigenstates of the background H_B, then $(\mu\alpha, \nu\beta...)$ can be taken to be the basis functions of the molecule. Since the interaction V is presumably small (otherwise the molecule cannot show LM characteristics), for an initial ground state and when the external field is not on, we can take approximately $\rho(0)=\rho_L(0)\rho_B(0)$, the ground state energy is

$$\mathrm{Tr}\{H_L\rho(0)\}=\sum_{\mu\alpha,\nu\beta}(H_L)_{\mu\nu}\delta_{\alpha\beta}\delta_{\mu0}\delta_{0\nu}\delta_{\alpha0}\delta_{0\beta}$$
$$=(H_L)_{00}\equiv E_L(0)\,. \quad (7)$$

The LM energy from Eq. (6) is

$$E_l(t)\equiv\mathrm{Tr}\{H_L\rho(t)\}$$
$$=E_L(0)-\frac{\hat{\mu}\mathscr{E}_0}{2\pi}\int_0^t\int_{-\infty}^{\infty} f(t')e^{-i\omega(t-t')}$$
$$\times\mathrm{Tr}\left\{H_L\frac{1}{(\omega - H_0^x + i0)}(q^x\rho)\right\}d\omega\, dt'\,. \quad (8)$$

In case of $V=0$, it can be shown readily that Eq. (8) reduces to a self-evident expression

$$E_L(t)-E_L(0)$$
$$=i\hat{\mu}\mathscr{E}_0\int_0^t \theta(t-t')f(t')\mathrm{Tr}_L\{H_L q^x\rho_L(t')\}dt'$$
$$=\hat{\mu}\mathscr{E}_0\int_0^t f(t')\mathrm{Tr}_L\left\{\rho_L(t')\frac{dq}{dt'}\right\}dt'\,, \quad (9)$$

where Tr_L is the trace with respect to the LM only. Now consider the general case of $V\neq0$ but small, as the first approximation of the iteration solution, we can put $\rho=\rho_L(t)\rho_B(0)$ in the right-hand side of Eq. (8),

$$E_L(t)-E_L(0)$$
$$=\frac{\hat{\mu}\mathscr{E}_0}{2\pi}\int_0^t\int_{-\infty}^{\infty} f(t')e^{-i\omega(t-t')}$$
$$\times\mathrm{Tr}\left\{H_L\frac{1}{(\omega - H_L^x - H_B^x - V)}\right\}$$
$$\times[q^x\rho_L(t')\rho_B(0)]d\omega\, dt'\,, \quad (10)$$

where as before $\rho_B(0)_{\alpha\beta}=\delta_{\alpha0}\delta_{0\beta}$. For the total molecular Hamiltonian $H_0=H_L+H_B+V$, we designate its orthonormal set of eigenfunctions by $(e_m, e_n...)$. In this basis, the trace in Eq. (10) is

$$\mathrm{Tr}(10)=\sum_{m,n}(H_L)_{nm}$$
$$\times\left\{\sum_{m'n'}\frac{\delta_{mm'}\delta_{nn'}}{\omega-\omega_{mn}}[q^x\rho_L(t')\rho_B(0)]_{m'n'}\right\}, \quad (11)$$

where $\omega_{mn}=\hbar^{-1}(e_m-e_n)$. For the two different bases $(m, n...)$ and $(\mu\alpha, \nu\beta...)$, we have, in the notations of bra and ket vectors

$$|m\rangle=\sum_{\mu\alpha}(\mu\alpha|m)|\mu\alpha\rangle,$$

$$\langle n|=\sum_{\nu\beta}\langle\nu\beta|(n|\nu\beta),$$

and

$$(H_L)_{n,m}=(n|H_L|m)=\sum_{\mu\alpha}(n|\mu\alpha)(\mu\alpha|m)e_\mu\,, \quad (12)$$

$$[q^x\rho_L(t')\rho_B(0)]_{mn}$$
$$=\sum_{\mu\nu}(m|\nu0)(\mu0|n)[q^x\rho_L(t')]_{\nu\mu}\,, \quad (13)$$

so we get from Eqs. (10), (11), and (5),

$$E_L(t)-E_L(0)$$
$$=i\hat{\mu}\mathscr{E}_0\int_0^t f(t')\theta(t-t')\sum_{mn}e^{-i\omega_{mn}(t-t')}$$
$$\times\left\{\sum_{\mu\alpha}(n|\mu\alpha)(\mu\alpha|m)e_\mu\right\}$$
$$\times\left\{\sum_{\mu'\nu'}(m|\nu'0)(\mu'0)|n)(q^x\rho_L)_{\nu'\mu'}\right\}dt'\,. \quad (14)$$

We can also write

$$|\nu'0\rangle=\sum_m(m|\nu'0)|m\rangle,$$

and since $e^{-i\omega_m t}|m\rangle$ is an eigenvector of the molecule, we have

$$|\nu'0(t-t')\rangle=\sum_m(m|\nu'0)e^{-i\omega_m(t-t')}|m\rangle\,, \quad (15)$$

which shows how an initial LM stata $|\nu'0\rangle$, due to the interaction V, will evolve. Equation (14) can be written as

$$E_L(t)-E_L(0)$$
$$=i\hat{\mu}\mathscr{E}_0\int_0^t f(t')\sum_{\mu\alpha}e_\mu\sum_{\nu'\mu'}(\mu\alpha|\nu'0(t-t'))$$
$$\times(\mu'0(t-t')|\mu\alpha)[q^x\rho_L(t')]_{\nu'\mu'}dt'\,. \quad (16)$$

Now we neglect all the cross product terms $[\mu\alpha|\nu'0(t-t')][\mu'0(t-t')|\mu\alpha]$ with $\nu'\neq\mu'$ because generally they have fast varying phase factor in time, we get

$$E_L(t)-E_L(0)$$
$$=i\hat{\mu}\mathscr{E}_0\int_0^t f(t')\sum_{\mu\alpha}e_\mu\sum_\nu|[\nu0(t-t')|\mu\alpha]|^2$$
$$\times[q^x\rho_L(t')]_{\nu\nu}\,dt'\,. \quad (17)$$

In Eq. (17) the term $|(\nu0(t-t')|\mu\alpha)|^2$ obviously means the probability that an initial LM $|\nu0\rangle$ while decaying via the interaction V, will stay on the state $|\mu\alpha\rangle$ after time $(t-t')$. In studying such process for benzene, SRH[8] introduced the idea of successive "tiers" to describe the gradual lowering of the LM quantum number and the gradual excitation of the background vibrations. We suppose similar intramolecular mechanism also prevails in other polyatomics. In order to delineate such process in a general and convenient way, it is natural to borrow some notions from the theory of stochastic process.[12] Consider that the LM is initially at the vibrational state of quantum number $\mu = k$, due to the interaction V, the LM quantum number will decay through successive tiers to $(k-1)$, $(k-2)$,...,etc. As SHR showed clearly in their calculation for benzene,[8] if only a finite number of tiers and finite number of Fermi resonances are taken into account, the decaying process of LM will have a certain recurrent time—an artifact that can hardly occur because more and more resonances are involved with the progress of the LM energy dissipation. Since the LM decaying process in the later stage does not affect our calculation very much (see below), we do not need go into the details but simply assume (1) if at time t the LM is at the state of quantum number k, due to the interaction V the probability that the transition $k \rightarrow (k-1)$ taking place in $(t, t+\Delta t)$ is $\nu_k \Delta t + o(\Delta t)$, (2) in $(t, t+\Delta t)$, the probability of transition to a state causing the LM to shift more than one energy level is $o(\Delta t)$, and (3) the probability of no change is $1 - \nu_k \Delta t + o(\Delta t)$, then from the theory of "birth and death process,"[12] we get the following set of equations for the probability $P_i(t)$ of the LM having quantum number i at time t:

$$\begin{aligned}
\frac{dP_k}{dt} &= -\gamma_k P_k \quad (k \geqslant 1), \\
\frac{dP_{k-1}}{dt} &= \gamma_k P_k - \gamma_{k-1} P_{k-1}, \\
&\cdots \\
\frac{dP_1}{dt} &= \gamma_2 P_2 - \gamma_1 P_1, \\
\frac{dP_0}{dt} &= \gamma_1 P_1,
\end{aligned} \tag{18}$$

with the initial condition $P_i(0) = \delta_{ik}$. It can be shown readily that Eq. (18) is a "true" stochastic process, i.e., $d(\Sigma_{i=0}^{k} P_i)/dt = 0$ and $\Sigma_{i=0}^{k} P_i = 1$. The constants γ_k can be interrelated directly to the overtone line width (see below). From the experimental results of benzene,[6] these width (FWHM) vary in the range (30–100) cm^{-1} for different overtones of C–H or C–D bonds. For the sake of simplicity in the following calculation, we take all γ_k equal to some average value $\bar{\gamma}$. In this case, the solution of Eq. (18) is especially simple (in the general case of different γ_k, the solution can also be found without difficulty):

$$\begin{aligned}
P_k &= e^{-\bar{\gamma}t} \; (k \geqslant 1). \\
P_{k-1} &= \frac{\bar{\gamma}t}{1!} e^{-\bar{\gamma}t}, \\
&\cdots \\
P_1 &= \frac{(\bar{\gamma}t)^{k-1}}{(k-1)!} e^{-\bar{\gamma}t}, \\
P_0 &= 1 - \sum_{i=1}^{k} P_i,
\end{aligned} \tag{19}$$

and if $k = 0$, we have naturally $P_0 = 1$ always. Now putting

$$S_\nu = \sum_{\mu<\nu} \sum_{\alpha} e_\mu |(\nu 0(t-t')|\mu\alpha)|^2, \tag{20}$$

and obviously we should identify

$$\sum_{\alpha} |(\nu 0(t-t')|\mu\alpha)|^2 = P_\mu (\mu < \nu)$$

so we get

$$\begin{aligned}
S_\nu = e^{-\bar{\nu}(t-t')} \Big\{ &(e_\nu - e_0) + \frac{\bar{\nu}(t-t')}{1!}(e_{\nu-1} - e_0) \\
&+ \cdots + \frac{\bar{\nu}^{\nu-1}(t-t')^{\nu-1}}{(\nu-1)!}(e_1 - e_0) + e_0 \Big\}.
\end{aligned} \tag{21}$$

A simple physical picture can be envisioned by comparing Eq. (17) with Eq. (9). Due to the interaction V, the LM experiences a dissipation process in addition to the excitation by the external field. The terms in Eq. (17) with $\mu > \nu$ should have negligible population and can be discarded, and due to the exponential factor in Eq. (21), the memory effect of this dissipation in the integral of Eq. (17) decays fast with time, therefore, as we said before, the details of the later state of this dissipation process cannot have much effect upon the LM energy. We get finally from Eqs. (17) and (20),

$$\begin{aligned}
E_L(t) - E_L(0) &= i\hat{\mu}\mathscr{E}_0 \int_0^t f(t') \sum_\nu S_\nu \{q^x \rho_L(t')\}_{\nu\nu} \, dt' \\
&= 2\hat{\mu}\mathscr{E}_0 \hbar^{-1} \int_\sigma^t f(t') \sum_\nu S_\nu \\
&\quad \times \Big\{ \operatorname{Im} \sum_k \rho_L(t')_{\nu k} q_{k\nu} \Big\} dt',
\end{aligned} \tag{22}$$

where Im means imaginary part.

The decay constant $\bar{\gamma}$ can be obtained from the experimental overtone linewidth in the following way. The broad overtone line shapes actually consist of numerous transitions.[8] If we denote as before $|\nu 0\rangle$ the LM eigenstate and $|m\rangle$ the eigenstate of the molecule (including the interaction V), then we have from Eq. (15),

$$(\nu 0|\nu 0(t)) = \sum_m |(\nu 0|m)|^2 e^{-i\omega_m t}. \tag{23}$$

Due to numerous Fermi resonances via potential energy and/or kinetic energy coupling in polyatomics, many eigenstates $|m\rangle$ have near energies and also carry oscillator strength from the ground state. Leaving aside the dipole transition matrix, the overtone spectrum is

$$\begin{aligned}
\Sigma(\omega) &= \sum_m |(\nu 0|m)|^2 S[\omega - (\omega_m - \omega_0)] \\
&= (2\pi)^{-1} \sum_m |(\nu 0|m)|^2 \int_{-\infty}^{\infty} e^{i[\omega - (\omega_m - \omega_0)]t} \, dt \\
&= (2\pi)^{-1} \int_{-\infty}^{\infty} [\nu 0|\nu 0(t)] e^{i(\omega + \omega_0)t} \, dt.
\end{aligned} \tag{24}$$

$\Sigma(\omega)$ might be an aggregate of sticks, but due to the rotational and Coriolis effect, it is unlikely that they can be resolved to such details.[8] On the other hand, from the first expression of Eq. (19), we have $P_\nu(t) = |(\nu_0|\nu_0(t)]|^2 = e^{-\bar{\gamma}t}$, so we can take approximately

$$|\nu 0(t)\rangle = |\nu 0\rangle e^{-i\omega_\nu t - \bar{\gamma} t/2} \quad (t \geqslant 0)\,, \tag{25a}$$

$$|\nu 0(t)\rangle = |\nu 0\rangle e^{-i\omega_\nu t + \bar{\gamma} t/2} \quad (t \leqslant 0)\,. \tag{25b}$$

Equation (25b) simply means the fictitious decay process in reverse time, then from Eq. (24),

$$\Sigma(\omega) = \frac{1}{\pi} \frac{(\bar{\gamma}/2)}{[\omega - (\omega_\nu - \omega_0)]^2 + (\bar{\gamma}/2)^2}\,, \tag{26}$$

i.e., a Lorentzian shape of FWHM $\bar{\gamma}$ centered at $(\omega_\nu - \omega_0)$. Of course the actual line shape is not always so simple due to the intricacies of the interaction, nevertheless for our present purpose it suffices to extract the value of $\bar{\gamma}$ by comparing Eq. (26) with the experimental data. Besides the effect of the interaction V, the experimental linewidth also consists of the contributions from the rotation and the Coriolis effect, which make the profile even broader. We do not need to distinguish these different sources of linewidth in determining $\bar{\gamma}$, since all of them cause decaying of the LM overtones. Equations (21) and (22) are the main results of the present paper for the calculation of the LM excitation by FM lasers.

III. NUMERICAL EXAMPLE OF THE EXCITATION OF C–H BOND

We take the data relevant to the C–H bond of benzene[4,8] as an example. The reduced mass of the C–H bond $m = m_C m_H/(m_C + m_H)$ with m_C, m_H the mass of the carbon and hydrogen atoms, respectively. The potential energy $V(q)$ of the bond stretching motion is simulated by a Morse function $V(q) = D(1 - e^{-\alpha q})^2$, with bound state energy levels

$$E_n = 4D\chi_e g(n) \quad (n = 0,1,2,...)\,, \tag{27a}$$

$$g(n) = (n + \tfrac{1}{2}) - \chi_e (n + \tfrac{1}{2})^2\,, \tag{27b}$$

where $\chi_e = \hbar\alpha/(2\sqrt{2mD})$. Comparing Eq. (27) with the empirical formula of benzene $E_n(\mathrm{cm}^{-1}) = 3157(n + \frac{1}{2}) - 57(n + \frac{1}{2})^2$, we get $\chi_e = \frac{1}{55}$, $D = 5.3828$ eV, $\alpha = 1.78$ Å^{-1}, and the mechanical frequency (i.e., the frequency of a classical Morse oscillator at small amplitude) $\hbar\omega_{\mathrm{CH}} = \hbar\alpha\sqrt{2D/m} = 3156\ \mathrm{cm}^{-1}$. We take the dipole moment of C–H bond to be $\hat{\mu} q = 0.8q$ D (q in Å) and the laser field strength $\hat{\mu}\mathscr{E}_0/\alpha = 0.26$ eV which corresponds approximately to an intensity of 10^{14} W/cm^2, a value achievable with modern focusing ps technique. Let the FM laser be

$$f(\tau) = \cos 2\pi(1 - \beta\tau)\tau\,, \tag{28}$$

where β is an adjustable parameter and $\tau = \Omega_0 t/(2\pi)$, Ω_0 the initial frequency of the laser field. As in paper I, we take $\Omega_0 = 0.9467\,\omega_{\mathrm{CH}} = 2988\ \mathrm{cm}^{-1}$. According to Eq. (22), we should first calculate the density matrix $\rho_L(t)_{\nu k}$ of the excitation of a pure LM. This can be done following the procedure in paper I, but this time we take 24 bound states (the total number of bound states is 27) to ensure that the populations of the few highest states are small in the course of excitation. Using the notations in paper I, let the coefficient of expansion of the wave function be a_i $(i = 0,1,...,23)$, then by definition $(\rho_L)_{nk} = a_n a_k^*$. We get from Eqs. (21) and (22),

$$\begin{aligned} e_L(\tau) &\equiv [E_L(\tau) - E_L(0)]/(4D\chi_e) \\ &= 4\pi\hat{\mu}\mathscr{E}_0(\alpha\hbar\Omega_0)^{-1} \\ &\quad \times \int_0^\tau f(\tau') \sum_{n=0}^{23} S_n(\tau - \tau') Q_n(\tau') d\tau'\,, \end{aligned} \tag{29}$$

$$\begin{aligned} S_n(\tau - \tau') = e^{-\gamma(\tau - \tau')} \Big\{ &(g_n - g_0) \\ &+ \frac{\gamma(\tau - \tau')}{1!}(g_{n-1} - g_0) + \cdots \\ &+ \frac{\gamma^{n-1}(\tau - \tau')^{n-1}}{(n-1)}(g_1 - g_0) + g_0 \Big\}\,, \end{aligned} \tag{30}$$

$$Q_n(\tau) = \sum_{k=0}^{23} \mathrm{Im}\, a_n(\tau) a_k^*(\tau) (\alpha q)_{kn}\,, \tag{31}$$

where the matrix element $(\alpha q)_{kn}$ has an explicit expression as shown in paper I, and $\gamma = 2\pi\bar{\gamma}/\Omega_0$ (FWHM = 50 cm^{-1} corresponds to $\gamma = 0.1051$). Figures 1 and 2 depict the results of calculation. The value of the FM parameter β is fixed after several test runs to select a better one. But it can be seen from Fig. 2 that its value is not very sensitive for the result, and this is favorable for designing the experiment. The linewidth of the overtones has a crucial effect on the effective excitation of the LM, but if the laser field strength is sufficiently high, average FWHM linewidth of 50 cm^{-1} or even more does not constitute an obstacle (Fig. 1, curves 1–3). When the field strength is not high enough, even the pure LM cannot build up very soon, the intramolecular interac-

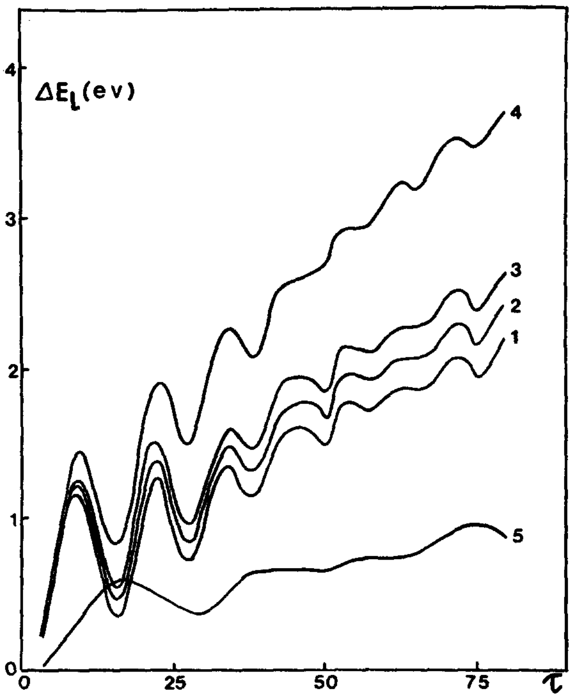

FIG. 1. Effect of overtone linewidth on the LM excitation of C–H bond in benzene. LM energy absorption $\Delta E_L = E_L(\tau) - E_L(0)$ in eV. $\tau = \Omega_0 t/(2\pi)$, $\Omega_0 = 2988\ \mathrm{cm}^{-1}$; field strength $\hat{\mu}\mathscr{E}_0/\alpha = 0.26$ eV (laser intensity $\cong 10^{14}$ W/cm^2), FM parameter $\beta = 3.2 \times 10^{-3}$. For curves 1–4, $\gamma = 0.1051$, 0.08, 0.06, and 0 (i.e., FWHM of overtone lines = 50, 38, 29, and 0 cm^{-1}), respectively. The effect of field strength is shown in curve 5: $\hat{\mu}\mathscr{E}_0/\alpha = 0.1$, $\beta = 1 \times 10^{-3}$, and $\gamma = 0$.

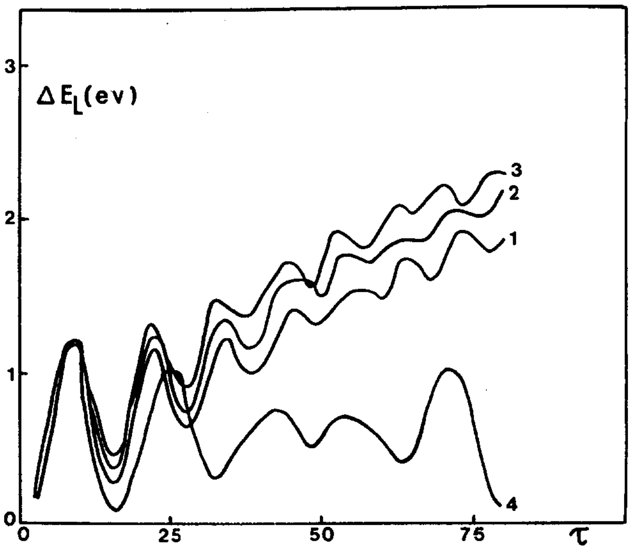

FIG. 2. Effect of FM parameter β on the LM excitation of C–H bond in benzene. Field strength $\hat{\mu}\mathscr{E}_0/\alpha = 0.26$ eV, $\bar{\gamma} = 0.1051$. For curves 1–3: $\beta = 2.8\times10^{-3}, 3.2\times10^{-3}, 3.6\times10^{-3}$, respectively. 4: $\beta = 0$, $\bar{\gamma} = 0$.

tion naturally hinders us from achieving the goal of LM excitation (Fig. 1, curve 5).

It can be seen from the above that FM laser is a quite promising agent to enhance the LM excitation in polyatomic molecules, so long as the latter possess distinct LM overtones with not excessive linebreadth. The technological difficulty is perhaps not so tremendous as it first looks, e.g., we can use piezoelectric or electro-optic devices to change the optical cavity length during the pulse in a controllable way to get the desired center-frequency shift.

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