One possible way to promote the bond-selective chemical reactions by frequency-modulated lasers

Xie Bo-Min and Ding Jia-Qiang
Institute of Mechanics, Chinese Academy of Sciences, Beijing, China
Wei Xie
Department of Physics, Tsin-Hua University, Beijing, China

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It is proposed in this paper that we can use frequency-modulated (FM) lasers to realize bond-selective chemical reactions or to raise the efficiency of molecular isotope separation. Examples are given for HF molecule and the C–H bond in some hydrocarbons.

I. INTRODUCTION

It is quite promising to make use of the remarkable frequency characteristics of lasers to realize bond-selective dissociation and reactions of the molecules.[1] This can provide not only low-temperature chemical reactions but also the possibility to synthesize some special molecules. But due to the anharmonicty of the molecular vibration and the interaction among the vibrational modes, much difficulty still exists if we use lasers with fixed frequencies for this purpose. For instance, if we use IR multiphoton absorption to excite polyatomics, the energy equilibration process caused by intermodal energy transfer is a serious obstacle for bond-selective excitation, whether ns or even ps pulse is used.[2,3] However, it is gratifying that a series of experimental studies[4] have shown that, in many hydrocarbons, the overtones of the C–H bond (or C–D bond) can be described quite accurately by the local-mode (LM) theory. If the potential of the C–H stretching motion is simulated by a Morse function or a simple polynomial and the change of the dipole moment with distance is properly considered, the energy levels, the oscillator strengths, the isotopic effect, and even the spectroscopic line profile all agree very well with the experimental data.[5–7] This is brought forth by the smallness of the mass of the H atom, so the fundamental stretching frequency of the C–H bond ($\cong 3000\ \mathrm{cm}^{-1}$) is much higher than the frequencies of other modes and its coupling with the latter is also weak.[8] We may effectively excite the stretching motion of the C–H bond without much stirring up the other modes. In the classical theory of the forced oscillations of anharmonic oscillators, it is well known that we can use FM excitation to pump up the anharmonic oscillator to quite high energy states, pumping through "nonlinear resonance."[9] In order to investigate the quantum mechanical case, a comparative analysis for both classical and quantum cases is made in Sec. II with the conclusion that some basic results of the classical case can be applied to the quantum case as well, at least when the amplitudes of vibration is not too large. Then in Sec. III we numerically computed the excitation of a quantum Morse oscillator pumped by FM lasers. The result shows that properly adjusted FM pulse can really excite the molecule to very high energy, much more effective than single frequency excitaton. Some problems relevant to the effect of the rotational band and to the technological feasibility are discussed in Sec. IV. The implications of the present study to the enhancement of isotopes separation are also discussed.

II. A COMPARATIVE STUDY OF CLASSICAL AND QUANTUM MECHANICAL DUFFING OSCILLATOR

First, we investigate the classical case. The equation of motion reads

$$m\frac{d^2q'}{dt'^2} + m\omega^2 q' - 4\epsilon' q'^3 = \mu E_0 f(t'), \tag{1}$$

where m is the reduced mass, ω the frequency at small amplitude, q' the displacement, t' the time, μ the dipole moment, $E_0 f(t')$ the external electric field intensity, and ϵ' is a small parameter. Put

$$\omega t' = t, \quad \sqrt{\frac{m\omega}{\hbar}}\, q' = q, \quad \frac{\hbar\epsilon'}{m^2\omega^3} = \epsilon, \quad \frac{\mu E_0}{\sqrt{\hbar m\omega^3}} = \epsilon K, \tag{2}$$

we rewrite Eq. (1) as

$$\frac{d^2q}{dt^2} + q - 4\epsilon q^3 = \epsilon K f(t). \tag{3}$$

The quantities introduced in Eq. (3) are nondimensionalized according to the quantum case discussed later. The method for solving Eq. (3) is well known, so we only cite the main results of the method of "multiple time scales." [9] Put

$$t_0 = t, \quad t_1 = \epsilon t, \tag{4}$$

$$q = q_0(t_0,t_1) + \epsilon q_1(t_0,t_1), \tag{5}$$

and let

$$f(t) = F(\epsilon t)\cos\omega_e t, \tag{6}$$

$$\omega_e = 1 + \epsilon\sigma, \tag{7}$$

where $F(\epsilon t)$ denotes the slowly varying amplitude, while Eq. (7) means that we are investigating the case of principal resonance when the excitation frequency is near the fundamental of the system. Substitute Eq. (5) into Eq. (3) and equate the terms of the same order in ϵ, we get

$$\frac{\partial^2 q_0}{\partial t_0^2} + q_0 = 0, \tag{8}$$

$$\frac{\partial^2 q_1}{\partial t_0^2} + q_1 = 4q_0^3 - 2\frac{\partial^2 q_0}{\partial t_0 \partial t_1} + \frac{KF(t_1)}{2} \times \{e^{i(t_0+\sigma t_1)} + e^{-i(t_0+\sigma t_1)}\}. \tag{9}$$

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The solution of Eq. (8) can be written as

$$q_0=\frac{A(t_1)}{\sqrt{2}}e^{-it_0}+\frac{A^*(t_1)}{\sqrt{2}}e^{it_0}. \tag{10}$$

When Eq. (10) is substituted into Eq. (9), in order to avoid secular terms which would make the perturbation Eq. (5) void, we should put

$$\frac{dA}{dt_1}=i\left(3A^2A^*+\frac{KF(t_1)}{2\sqrt{2}}e^{-i\sigma t_1}\right). \tag{11}$$

So the approximate solution of Eq. (3) is

$$q=\frac{A(t_1)}{\sqrt{2}}e^{-it_0}+c.c.+O(\epsilon). \tag{12}$$

Now we turn to the quantum case. The Schrödinger equation is

$$i\hbar\frac{\partial\psi}{\partial t'}=-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial q'^2}+\frac{m\omega^2}{2}q'^2\psi$$
$$-\epsilon' q'^4\psi-\mu E_0 f(t')q'\psi, \tag{13a}$$

or after using the notations of Eqs. (2),

$$i\frac{\partial\psi}{\partial t}=-\frac{1}{2}\frac{\partial^2\psi}{\partial q^2}+\frac{q^2}{2}\psi-\epsilon q^4-\epsilon Kf(t)q\psi. \tag{13b}$$

Introducing the annihilation and creation operators a,a^+, $q\equiv(a+a^+)/\sqrt{2}$. We write the Hamiltonian as[10]

$$H=(a^+a+\tfrac{1}{2})-\epsilon\sum_{n,m}F_{nm}(a^+)^n a^m$$
$$-\frac{\epsilon Kf(t)}{\sqrt{2}}(a+a^+), \tag{14}$$

where

$$\sum_{n,m}F_{nm}(a^+)^n a^m=\tfrac{1}{4}(a^+)^4+(a^+)^3a+\tfrac{3}{2}(a^+)^2a^2$$
$$+a^+a^3+\tfrac{1}{4}a^4+\tfrac{3}{2}(a^+)^2+3a^+a+\tfrac{3}{2}a^2+\tfrac{3}{4} \tag{15}$$

by which F_{nm} are defined. Denote the evolution operator by U, i.e., $|\psi(t)\rangle=U|\psi(0)\rangle$. Then,

$$i\frac{\partial U}{\partial t}=HU. \tag{16}$$

We use the method of multiple time scales as before and put

$$U=u_0(t_0,t_1)+\epsilon u_1(t_0,t_1) \tag{17}$$

and assume $f(t)$ to have the form of Eqs. (6) and (7). Substituting U from Eq. (17) into Eq. (16) and comparing the terms of the same order in ϵ, we get

$$\frac{\partial u_0}{\partial t_0}=-i(a^+a+\tfrac{1}{2})u_0, \tag{18a}$$

$$\frac{\partial u_1}{\partial t_0}+i(a^+a+\tfrac{1}{2})u_1=-\frac{\partial u_0}{\partial t_1}$$
$$+i\left\{\sum_{n,m}F_{nm}(a^+)^n a^m+\frac{Kf(t)}{\sqrt{2}}(a^++a)\right\}u_0. \tag{18b}$$

Hence,

$$u_0=e^{-it_0[a^+a+(1/2)]}A(t_1), \tag{19}$$

where $A(t_1)$ is an undetermined operator. Putting u_0 from Eq. (19) into Eq. (18b) we get

$$\frac{\partial}{\partial t_0}\{e^{it_0[a^+a+(1/2)]}u_1\}=-\frac{dA}{dt_1}$$
$$+i\left\{\sum_{n,m}F_{nm}e^{i(n-m)t_0}(a^+)^n a^m+\frac{KF(t_1)}{2\sqrt{2}}\right.$$
$$\left.\times(e^{-i(t_0+\sigma a t_1)}+e^{i(t_0+\sigma a t_1)})(e^{-it_0}a+e^{it_0}a^+)\right\}A. \tag{20}$$

In writing Eq. (20), we have made use of the following formula for operators[11]:

$$e^{xA}Be^{-xA}=B+x[A,B]+\frac{x^2}{2!}[A,[A,B]]+\cdots. \tag{21}$$

In order to avoid secular terms in u_1, we should put

$$\frac{dA}{dt_1}-i\left\{\sum_n F_{nn}(a^+)^n a^n\right.$$
$$\left.+\frac{KF(t_1)}{2\sqrt{2}}(e^{i\sigma t_1}a+e^{-i\sigma t_1}a^+)\right\}A=0. \tag{22}$$

For solving Eq. (22), we put

$$A=e^{\gamma+\xi a^+}e^{-\xi^* a}B(t_1), \tag{23}$$

where $\gamma(t_1),\xi(t_1)$ are undetermined functions, ξ^* is the c.c. of ξ. $B(t_1)$ is an undetermined operator. For a harmonic oscillator, it can be shown readily that the exact solution of Eq. (22) can be written in the form of Eq. (23), while B has a simple expression. Putting Eq. (23) into Eq. (22) and making use of Eq. (21), we have

$$\left[\frac{d\gamma}{dt_1}+\frac{d\xi}{dt_1}(a^++\xi^*)\right]B-\frac{d\xi^*}{dt_1}aB+\frac{dB}{dt_1}$$
$$=i\left\{\sum_n F_{nn}(a^++\xi^*)^n(a+\xi)^n+\frac{KF}{2\sqrt{2}}\right.$$
$$\left.\times\left[e^{i\sigma t_1}(a+\xi)+e^{-i\sigma t_1}(a^++\xi^*)\right]\right\}B. \tag{24}$$

We equate to zero separately in Eq. (24) the terms which do not contain the operators a and a^+ and which contain a or a^+ only and obtain

$$\frac{d\gamma}{dt_1}=-\xi^*\frac{d\xi}{dt_1}+i\left\{\tfrac{3}{4}+3\xi\xi^*+\tfrac{3}{2}(\xi\xi^*)^2\right.$$
$$\left.+\frac{KF}{2\sqrt{2}}(e^{i\sigma t_1}\xi+e^{-i\sigma t_1}\xi^*)\right\}, \tag{25}$$

$$\frac{d\xi}{dt_1}=i\left\{3\xi+3\xi^2\xi^*+\frac{KF}{2\sqrt{2}}e^{-i\sigma t_1}\right\}, \tag{26}$$

$$\frac{dB}{dt_1}=i\{\tfrac{3}{2}(N^2+N)+3(\xi a^+N+\xi^*Na)$$
$$+6\xi\xi^*N+\tfrac{3}{2}\xi^2(a^+)^2+\tfrac{3}{2}(\xi^*)^2a\}B, \tag{27}$$

where $N=a^+a$. Another equation for ξ^* is the c.c. to Eq. (26). Equation (25) determines the normalization factor γ. Equation (26) is the quantum counterpart of Eq. (11). ξ represents the complex displacement of the wave packet [see Eq. (32)]. The additional term of Eq. (26) in comparison with Eq. (11) is brought forth by the noncommutating property of a and a^+. Equation (27) represents the quantum

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corrections, i.e., the dispersion effect of the wave packet. The approximate solution of Eq. (27) can be obtained by expanding B in terms of the powers of ξ when the amplitude $|\xi|$ is not too large. Put

$$B = B^{(0)} + \epsilon_1 B^{(1)} + \epsilon_1^2 B^{(2)} + \cdots, \tag{28}$$

and write ξ in Eq. (27) as $\epsilon_1\xi$, ξ^* as $\epsilon_1\xi^*$ (we shall put $\epsilon_1 = 1$ later on). Substituting Eq. (28) into Eq. (27) and equating the terms of the same order in ϵ_1, we get

$$\frac{dB^{(0)}}{dt_1} = i\tfrac{3}{2}(N^2+N)B^{(0)}, \tag{29a}$$

$$\frac{dB^{(1)}}{dt_1} = i\{\tfrac{3}{2}(N^2+N)B^{(1)} + 3(\xi a^+ N + \xi^* Na)B^{(0)}\}. \tag{29b}$$

Utilizing Eq. (21) we can solve Eqs. (29) successively. For $B^{(0)}$ and $B^{(1)}$ we get

$$B^{(0)} = e^{i(3/2)t_1(N^2+N)}, \tag{30a}$$

$$B^{(1)} = 3e^{i(3/2)t_1(N^2+N)} \int_0^{t_1} \{\xi e^{-i3t_1N} a^+ N + \xi^* e^{i3t_1(N+1)} N a\} dt_1. \tag{30b}$$

In Eqs. (30a) and (30b) use was already made of the conditions $B^{(0)}(0) = I$ (identity operator) and $B^{(1)}(0) = 0$. Summarizing the above results, we have

$$U = e^{-it_0[N+1/2]} e^{\gamma + \xi a^+} e^{-\xi^* a}\{B^{(0)} + B^{(1)} + \cdots\} + O(\epsilon). \tag{31}$$

Since $a|0\rangle = N|0\rangle = 0$ and assuming further $\psi(0) = |0\rangle$, we have [with errors of $O(\epsilon)$ and the square terms of the "amplitude"]

$$\begin{aligned}|\psi(t)\rangle &= U|\psi(0)\rangle = e^{-it_0[N+1/2]} e^{\gamma+\xi a^+}|0\rangle \\ &= e^{-i(t_0/2)+\gamma} e^{-it_0N} \sum_{n=0} \frac{\xi^n}{\sqrt{n!}}|n\rangle \\ &= e^{-i(t/2)+\gamma} \sum_{n=v} \frac{(\xi e^{-it})^n}{\sqrt{n!}}|n\rangle \\ &= \pi^{-1/4}\exp\left\{-i\frac{t}{2} + \gamma + \left(\frac{\xi e^{-it}}{\sqrt{2}}\right)^2 - \frac{1}{2}(q - \sqrt{2}\xi e^{-it})^2\right\}.\end{aligned} \tag{32}$$

This represents the motion of a Schrödinger wave packet[12] with the amplitude $\sqrt{2}|\xi|$ for which no dispersion effect exists. The equation satisfied by ξ is essentially the same as the classical one. Putting $\xi = \rho e^{i\theta}$, we get from Eq. (26),

$$\frac{d\rho}{dt_1} = \frac{KF(t_1)}{2\sqrt{2}} \sin\theta', \tag{33a}$$

$$\frac{d\theta'}{dt_1} = (3+\sigma)\rho + 3\rho^3 + \frac{KF}{2\sqrt{2}}\cos\theta', \tag{33b}$$

where $\theta' = \theta + \sigma t_1$. In case $F =$ constant, Eqs. (33) possess stationary solution $d\rho/dt_1 = d\theta'/dt' = 0$ and the "response curve"[9] interrelating the "amplitude" $|\rho|$ and the excitation frequency $\sigma (= (\omega_e - 1)/\epsilon)$ is

$$(3+\sigma)\rho + 3\rho^3 + \frac{KF}{2\sqrt{2}} = 0. \tag{34}$$

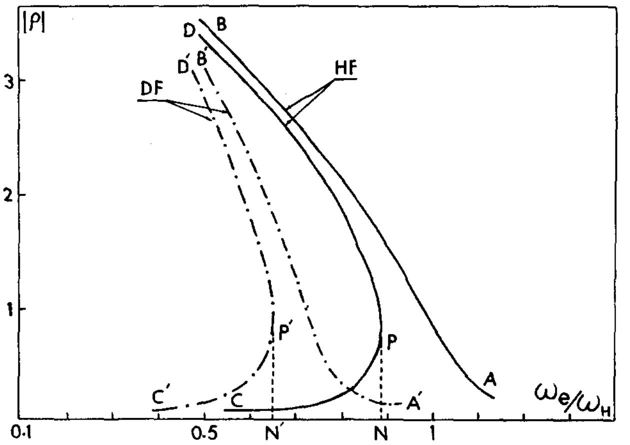

FIG. 1. Classical response curve of Duffing oscillator. Electric field coupling strength $\mu E_0 = 0.3$ eV/a_0 (a_0 Bohr radius), $K = 7.82$; AB–CPD is for HF; A′B′–C′P′D′ is for DF. ω_e = laser frequency, ω_H = mechanical frequency of HF.

Figure 1 depicts the response curves of HF and DF with the necessary data obtained in the following way. When the potential of the oscillator is $(\omega^2 q^2/2 - \epsilon q^4)$, the energy levels of the bound states can be obtained by ordinary perturbation method[8]: $E_n = \hbar\omega[(n+\frac{1}{2}) - \frac{3}{2}\epsilon(n+\frac{1}{2})^2]$ $(n = 0,1,2,\ldots)$. For HF we have[13] $\hbar\omega = 0.5137$ eV, $(\omega = 4143\ \mathrm{cm}^{-1})$, $\epsilon = 0.014$, the coupling strength of the electric field with the dipole of HF is taken to be $\mu E_0 = 0.3$ eV/a_0 (a_0 Bohr radius), so we get K = 7.82. For DF we may use the rule[5] $\omega \propto 1/\sqrt{m}$, and from Eq. (2) $K \propto m^{3/4}$ (m = the reduced mass) to get the necessary data. It is well known from classical theory that if we use an excitation force with gradually decreasing frequency, the amplitude of the oscillator may grow up continuously, zig-zagging up either of the lines AB or A′B′. For two isotopic oscillators, the response curves of them will be somewhat different due to the differences in m and ω, such as the curves AB–CPD and A′B′–C′P′D′. Since DP and D′P′ are unstable states, if we start the excitation with a frequency somewhere between N and N′, it is imaginable that the energy of one oscillator will increase along A′B′, while the energy of the other one cannot grow much along PC. This situation is surely helpful for isotope separation and is confirmed by numerical computation in the next section.

III. EXCITATION OF A QUANTUM MECHANICAL MORSE OSCILLATOR BY FM LASER

Previously, Walker and Preston[13] (WP) made a detailed numerical computation of the excitaiton of an anharmonic oscillator with a Morse potential by a laser of fixed frequency (the concrete example is a HF molecule). They found both the quantum and classical solutions were close to each other in regard to the energy absorption and the averaged motion of the oscillator as well. This is understandable from our previous analysis. We have mentioned before that the stretching motion of the C–H bonds of quite a few hydrocarbons can be adequately described by the LM theory with a Morse potential. Their relevant data are close to those of HF molecules. The vibrational energy levels can also be expressed as $E_n = n(A + nB)$. Table I shows the mechanical

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TABLE I. Mechanical frequency X_1, anharmonicity X_2, dipole moment[a] $M(x)$ of HF and the C–H, C–D bonds of some hydrocarbons.

Compound	$X_1(\mathrm{cm}^{-1})$	$X_2(\mathrm{cm}^{-1})$	$M(x)$ (D)
Benzene C–H bond[c,d]	3154	-57	$-0.81x+0.2x^2$
Benzene C–D bond[d]			$-0.95x+0.42x^2$
Cyclopentane C–H bond[c]	3017	-60	
Cyclohexane[c]	3006	-57.7	
Naphthalene C–H bond[e]	3104	-57.7	
HF[b]	4143	-86.8	$1.5x$

[a] x is the difference of the atomic distance minus the equilibrium value (Å).

[b] Calculated from the data of Ref. 13.

[c] Reference 4.

[d] Reference 5.

[e] Reference 6.

frequency (i.e., the classical frequency at small amplitude) $X_1 = \mathrm{A–B}$ and the anharmonicity $X_2 = \mathrm{B}$ of some such molecules. Similar to WP, we take HF as a typical example for our numerical study. The Morse potential is $V = D(1-e^{-\alpha x})^2$, the energy levels of the bound states are

$$E_n = 4Dx_e g(n) \quad (n = 0,1,2,\ldots), \tag{35}$$

$$g(n) = (n+\tfrac{1}{2}) - x_e(n+\tfrac{1}{2})^2, \tag{36}$$

where $x_e = \hbar\alpha/(2\sqrt{2mD})$. The relevant data of HF are[13]: $D = 6.125$ eV, $\alpha = 1.1741\ a_0^{-1}$, $m_H = 1.007\,97$ amu, $m_F = 18.9984$ amu. Now the total Hamiltonian is $\{H_0 + \mu E(t')x\}$,

$$H_0 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x).$$

We expand the wave function in terms of the eigenfunctions of H_0 but only retain the lowest 12 terms (all bound states) for numerical computation. Taking more terms does not increase the practical precision.[13] Denoting the coefficients of the expansion by a_i $(i = 0,1,\ldots 11)$. We have

$$\frac{d\mathbf{a}}{d\tau} = i\,\overline{\mathbf{W}}\mathbf{a}, \tag{37}$$

where $\tau = \Omega_0 t'/2\pi$. Ω_0 is a characteristic frequency defined in Eq. (45). $\mathbf{a}$ is a single column matrix with element a_i, $\overline{\mathbf{W}}$ is a (12×12) square matrix with the element

$$\overline{W}_{nn'} = -\frac{2\pi}{\Omega_0\hbar}\left[E_n\delta_{nn'} + \frac{\mu E(t)}{\alpha}(\alpha x_{nn'})\right], \tag{38}$$

where $\delta_{mn'} = 1$ $(n = n')$ or $O(n\neq n')$. When $n > n'$, we have[14]

$$\alpha x_{nn'} = \frac{(-1)^{n+n'}}{[g(n)-g(n')]}\left\{\frac{[1-(2n'+1)x_e][1-(2n+1)x_e]x_e^{n-n'}(n!)}{[1-(n'+1)x_e][1-(n'+2)x_e]\cdots[1-nx_e](n'!)}\right\}^{1/2}, \tag{39}$$

while when $n = n'$, we can calculate from the eigenfunctions of the Morse potential[15] to get

$$\alpha x_{nn} = -N_n^2\sum_{i,j=0}^{n} a_i^{(n)}a_j^{(n)} \times\{\psi(k-2n+i+j-1)-\ln k\} \times\Gamma(k-2n+i+j-1), \tag{40}$$

$$N_n^2 = \frac{(k-n-1)(k-n-2)\cdots(k-2n)}{n!\,\Gamma(k-2n-1)}, \tag{41}$$

$$a_i^{(n)} = \frac{(-1)^i}{(k-2n)(k-2n-1)\cdots(k-2n+i-1)} \times\frac{(n!)}{(i!)(n-i)!}, \tag{42}$$

where $\Gamma(z)$ is the Eulerian Γ function, $\psi(z) = (d/dz)\ln\Gamma(z)$, $k = 1/x_e$. For HF $x_e = 0.021$, we take $x_e = 0.02$, so $k = 50$. In calculating αx_{nn} according to Eq. (40), we encounter the products and divisions of large numbers which bring forth inaccuracies. In circumventing this we may use the normalization condition

$$1 = N_n^2\sum_{i,j=0}^{n} a_i^{(n)}a_j^{(n)}(k-2n+i+j-2)!, \tag{43}$$

and transform Eq. (40) to

$$\alpha x_{nn} = (\gamma + \ln k) - L_n/M_n,$$

$$L_n = \sum_{i,j=0}^{n} a_i^{(n)}a_j^{(n)} \times\left(\sum_{m=1}^{k-2n+i+j-2}\frac{1}{m}\right)\frac{(k-2n+i+j-2)!}{(k-2n+2)!}, \tag{44}$$

$$M_n = \sum_{i,j=0}^{n} a_i^{(n)}a_j^{(n)}\frac{(k-2n+i+j-2)!}{(k-2n-2)!}.$$

In Eq. (44), $\gamma = 0.5772$ is the Euler constant. The initial condition for the matrix Eq. (37) is taken to be $a_i(0) = \delta_{i0}$, i.e., the molecule is in the ground state initially. The field strength of the laser is taken to be $E(t') = E_0\cos\Omega t'$, while

$$\Omega = \Omega_0(1-\beta\tau), \tag{45}$$

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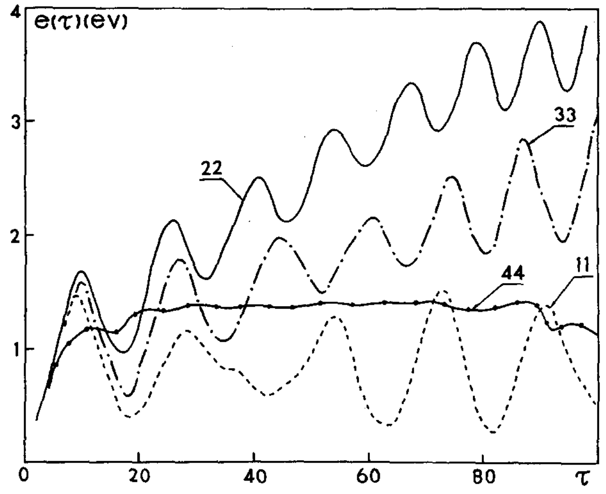

FIG. 2. HF excited by FM lasers, influence of different modulation speed β. Laser electric field $E(t') = E_0 \cos \Omega t' = E_0 \cos 2\pi(1-\beta\tau)\tau$. Electric field coupling strength fixed at $\mu E_0 = 0.3$ eV/a_0. The FM is $\Omega = \Omega_0(1-\beta\tau)$, $\tau = \Omega_0 t'/2\pi$. Mechanical frequency ω_H of HF: $\hbar\omega_H = 0.5137$ eV, $e(\tau)$ the energy absorbed by HF. 11: $\Omega_0 = 0.9467\ \omega_H$ $\beta = 0$ [WP's result (Ref. 13) recalculated], 22: $\Omega_0 = 0.9467\ \omega_H$ $\beta = 1.8\times10^{-3}$, 33: $\Omega_0 = 0.9467\ \omega_H$ $\beta = 0.9\times10^{-3}$, 44: $\Omega_0 = 0.9467\ \omega_H$ $\beta = 9\times10^{-3}$.

where β is a small parameter, Ω_0 the initial frequency of the laser, and we write

$$E(t') = E_0 \cos 2\pi(1-\beta\tau)\tau. \tag{46}$$

We take in accordance with WP $E_0 = 0.96$ V, $\mu E_0 = 0.3$ eV/a_0 and use Magnus method[16–18] to solve Eq. (37). When $\Delta\tau = \tau_i - \tau_{i-1}$ is sufficiently small, we get, from Eq. (37),

$$\mathbf{a}(\tau_i) = e^{i\Delta\tau \overline{\mathbf{W}}(\bar{\tau})}\,\mathbf{a}(\tau_{i-1}), \tag{47}$$

where $\bar{\tau} = 05(\tau_i + \tau_{i-1})$. Let $\mathbf{S}$ be the matrix which diagonalize $\overline{\mathbf{W}}(\bar{\tau})$, i.e., $\mathbf{S}^{-1}\overline{\mathbf{W}}\mathbf{S} =$ diagonal $\mathbf{D}(\bar{\tau})$. Since $\overline{\mathbf{W}}$ is real, $\mathbf{S}$ and $\mathbf{S}^{-1}$ are also real. It can be shown readily,

$$e^{i\Delta\tau\overline{\mathbf{W}}(\bar{\tau})} = \mathbf{S}(\mathbf{S}^{-1}\,e^{i\Delta\tau\overline{\mathbf{W}}}\,\mathbf{S})\mathbf{S}^{-1} = \mathbf{S}(\bar{\tau})e^{i\tau\Delta\mathbf{D}(\bar{\tau})}\,\mathbf{S}^{-1}(\bar{\tau}),$$

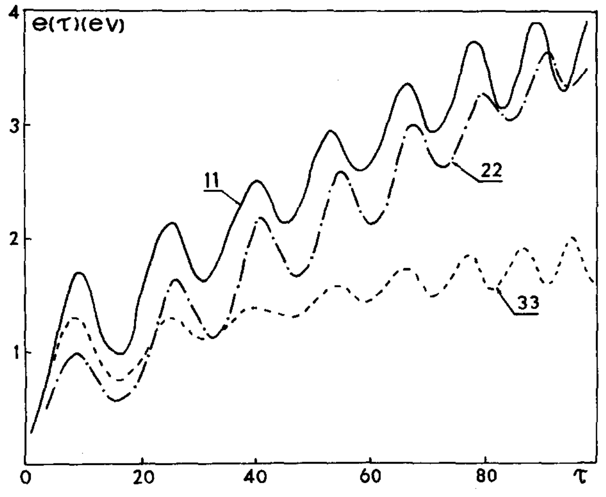

FIG. 3. FM excitation of HF, influence of different initial frequency Ω_0. 11: $\Omega_0 = 0.9467\ \omega_H$ $\beta = 1.8\times10^{-3}$, 22: $\Omega_0 = 1.0064\ \omega_H$ $\beta = 1.8\times10^{-3}$, 33: $\Omega_0 = 0.90\ \omega_H$ $\beta = 1.8\times10^{-3}$.

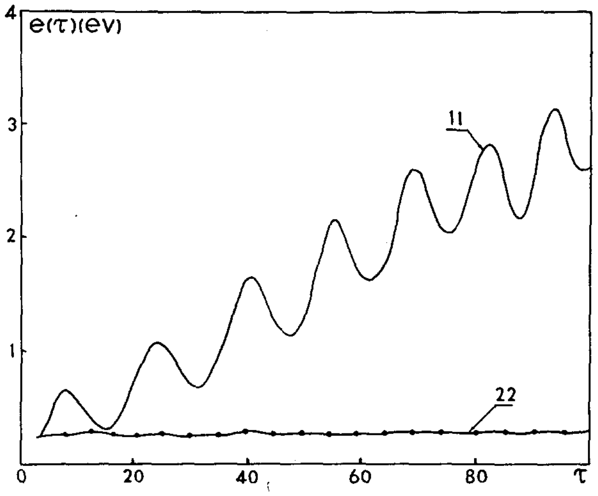

FIG. 4. Selection action of FM excitation for HF and DF. $E(t') = E_0 \cos \Omega t' = E_0 \cos 2\pi(1-\beta\tau)\tau$ $\mu E_0 = 0.3$ eV/a_0, $\Omega(t') = \Omega_0(1-\beta\tau)$, $\tau = \Omega_0 t'/2\pi$. Mechanical frequencies of HF (ω_H) and of DF (ω_D): $\hbar\omega_H = 0.5137$ eV, $\hbar\omega_D = 0.3727$ eV, $\Omega_0 = 0.7533\ \omega_H = 1.037\ \omega_D$, $\beta = 1.5\times10^{-3}$. 11: energy absorption of DF, 22: energy absorption of HF.

while $e^{i\Delta\tau\mathbf{D}(\bar{\tau})}$ is diagonal. Eq. (47) can be written as

$$\mathbf{a}(\tau_i) = \mathbf{S}(\bar{\tau})e^{i\Delta\tau\mathbf{D}(\bar{\tau})}\mathbf{S}^{-1}(\bar{\tau})\mathbf{a}(\tau_{i-1}); \tag{48}$$

the numerical work can be simplified a lot in this way. The step $\Delta\tau = 0.1$ yields satisfactory precision.

The results are depicted in Figs. 2–4. Just as we have conjectured, the FM laser has much superiority in exciting the anharmonic molecule. The curve 22 in Fig. 2 shows the molecule is actually pumped to increasingly higher states. At $\tau = 100$ ($t' \cong 0.8$ ps), the molecule already absorbs eight photons, much more efficiently than in the case of fixed-frequency excitation (curve 11 in Fig. 2). It can also be seen that just as in classical case, the modulation speed β is quite influential. Figure 3 demonstrates that the selection of initial frequency Ω_0 is also important. We can get some idea of the appropriate value of Ω_0 from the response curve in Fig. 1. Figure 4 is a typical result which shows that with the same FM laser DF is effectively excited while HF is practically not excited at all.

IV. DISCUSSIONS AND CONCLUSIONS

We must consider the following problems before applying the idea advanced in this paper to practice. Firstly, although the C–H bonds in many hydrocarbons show spectacular LM characteristics, but the recent experiments and theoretical analyses[19–21] indicate that those observed overtones are not purely local modes. Their linewidths are rather broad (FWHM ≅ 100 cm^{-1}), and the lifetime of the excited LM is short (about 0.1 ps by calculation). Therefore, it is natural to ask: can we really excite the C–H or C–D bonds locally by FM signals? Taking benzene as an example—although some details of the intramolecular energy transfer process need refinement—the analysis of Sibert *et al.*[21] already provided a clear physical picture. There exist interactions between the LM of the C–H bond and other molecular

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vibrational modes, though weak enough so that the characteristics of LM demonstrate distinctly; but since the vibrational modes are numerous, Fermi resonances of different tiers exist among them. The profile of the LM absorption line actually consists of many transitions of near frequencies, and the lifetime of a pure LM overtone is also short due to these interactions. Now if we use the aforementioned FM signal to excite the molecule, the response of the various transitions composing the profile will be different. All those transitions not belonging to LM cannot always keep pace with the signal and will be gradually eliminated due to detuning or dephasing. The more modes involved in the transition, the more difficult for them to keep pace with the signal, and only those transitions involving basically LM can be excited consecutively to high energy states. In other words, the FM excitation has better selectivity than single-frequency excitation or consecutive single-frequency excitations (i.e., each single frequency acts for some time consecutively). In regard to the short life of LM overtones, since the process is something like going through the nonlinear resonance continuously in classical case, the stay on these overtone states is instantaneous so that the overtone life does not constitute an obstacle (of course the laser intensity should be strong enough so that the LM can be pumped up quite fast, e.g., the HF molecule discussed in the last section can absorb 8 photons in 0.8 ps). We conclude from these considerations that FM excitation has great superiority and potential.

Secondly, how does the rotational band of the molecule affect the LM excitation? The reasoning underlying this question is similar to the first one and the answer is also optimistic. The selection action of the frequency-modulated signal only chooses those vib-rotational transitions which can always match the signal and in this way excites the LM to high energy state. A numerical computation for this problem is now underway and will be published elsewhere.

The third question is about the technological feasibility to realize this sort of FM. In order to attain necessary high power density, we should use short pulse. If the duration of the pulse is T, then its frequency bandwidth is $\Delta\nu \approx T^{-1}$. Taking the calculation in Sec. III as an example in the duration of $\tau = 100$, the change of the signal frequency is $\Delta\Omega \cong 0.18\ \Omega_0$; the modulation cannot be fruitful unless $\Delta\nu < \Delta\Omega$, i.e., $T > (0.18\,\Omega_0)^{-1} \cong 7$ fs. Obviously, ns or even ps pulses suffice for this requirement. As far as the authors are aware, there seems to be no ready method to achieve the FM for such short pulse, nevertheless it is not an impossibility in principle. With the rapid progress of pulse and modulation techniques, it is worthwhile to do such experiments in the future.

Finally, we would like to point out that if the idea put forward in this paper is applied to a specific normal mode of some molecule, such as ν_5 mode of CHF_3 (or CDF_3), a molecule used for the separation of light isotopes,[22] or the ν_3 mode of SF_6, it turns out that due to the smallness of the anharmonicity of these modes [if the energy of the pertaining modes is expressed by Eq. (35), then[23,24] for CDF_3 $x_e \cong 7.2 \times 10^{-3}$, for SF_6 $x_e = 1.3 \times 10^{-3}$], the selective action of FM is not so remarkable as in the case of HF. This is also understandable from the classical perception. Therefore among the various bonds with characteristic frequencies[8] in molecules, it is advisable to choose those with large anharmonicity to experiment on with FM excitation.

[1] See, for instance, Physics Today **33** (No. 11) (1980).

[2] P. A. Schultz, Aa. S. Sudbø, E. R. Grant, Y. R. Shen, and Y. T. Lee, J. Chem. Phys. **72**, 4985 (1980).

[3] Xie Bo-Min and Wei Xie, J. Chem. Phys. **84**, 114 (1986).

[4] H. L. Fang and R. L. Swofford, in *Advances in Laser Spectroscopy*, edited by B. A. Garetz and J. R. Lombardi (Heyden, London, 1982), Vol. 1 and the references therein.

[5] M. S. Burberry and A. C. Albrecht, J. Chem. Phys. **70**, 147 (1979).

[6] I. Schek, J. Jortner, and M. L. Sage, Chem. Phys. Lett. **64**, 209 (1979).

[7] D. F. Heller and S. Mukamel, J. Chem. Phys. **70**, 463 (1979).

[8] G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand, New York, 1954), Vol. II, pp. 194–196; Vol. I, p. 92.

[9] A. H. Nayfeh and D. T. Mook, *Nonlinear Oscillations* (Wiley, New York, 1979), Chap. 4.

[10] Z. Z. Gan, G. Z. Yang, K. A. Feng, and X. Y. Huang, Chinese J. Phys. **27**, 664 (1978).

[11] A. Messiah, *Quantum Mechanics* (North-Holland, Amsterdam, 1961), Vol. 1, p. 339.

[12] L. I. Schiff, *Quantum Mechanics*, 3rd ed. (McGraw–Hill, New York, 1968), pp. 74–76.

[13] R. B. Walker and R. K. Preston, J. Chem. Phys. **67**, 2017 (1977).

[14] H. S.Heaps and G. Herzberg, Z. F. Phys. **133**, 48 (1952).

[15] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon, New York, 1971), p. 72.

[16] W. Magnus, Commun. Pure Appl. Math. **7**, 649 (1954).

[17] P. Pechukas and J. Light, J. Chem. Phys. **44**, 3897 (1966).

[18] J. C. Light, in *Methods of Computational Physics*, edited by M. Rotenberg (Academic, New York, 1971), Vol. 10.

[19] R. G. Bray and M. J. Berry, J. Chem. Phys. **71**, 4909 (1979).

[20] K. V. Reddy, D. F. Heller, and M. J. Berry, J. Chem. Phys. **76**, 2814 (1982).

[21] E. L. Sibert III, W. P. Reinhart, and J. T. Hynes, J. Chem. Phys. **81**, 1115 (1984).

[22] D. K. Evans, R. D. McAlpine, and H. M. Adams, J. Chem. Phys. **77**, 3551 (1982).

[23] B. W. Kirk and P. M. Wilt, J. Mol. Spectrosc. **58**, 102 (1975).

[24] A. V. Nowak, J. Quant. Spectrosc. Radiat. Transfer **15**, 945 (1975).

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