PHYSICAL REVIEW A VOLUME 60, NUMBER 2 AUGUST 1999

Classical dynamics of multiphoton excitation and dissociation of diatomic molecules by infrared laser pulses

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(Received 3 November 1998)

The dynamics of the vibrational excitation and dissociation of a diatomic molecule by infrared laser pulses is studied classically. The system is modeled by a Morse oscillator interacting with a classical electric field. A chirped infrared laser pulse with realistic pulse shape and time-dependent frequency is very efficient to pump the molecule to highly excited states. The addition of a second fixed-frequency laser pulse is found to drastically enhance the dissociation probabilities. [S1050-2947(99)04508-4]

PACS number(s): 33.80.Rv, 31.70.Hq

I. INTRODUCTION

The study of laser-induced excitation and dissociation of molecules has been a subject of interest in the past decades [1]. While experiments using a single monochromatic infrared laser have only been successfully performed for polyatomic molecules, diatomic molecules are the simplest systems to analyze theoretically. Recent developments in femtosecond pulse shaping [2–4] and optimal control theory [5] suggest that multiphoton dissociation of diatomic molecules is possible using either amplitude and frequency modulation or multiple overlapping laser pulses. On the experimental side, chirped pulses have been employed in the studies of quantum ladder climbing [6] and harmonic generation [7]. Chirped pulse amplification was invented over a decade ago [8], and is now used routinely in the compression and amplification of high intensity femtosecond lasers. Based on a quantum mechanical calculation of a one-dimensional (1D) model, Chelkowski *et al.* [9] first suggested that the dissociation threshold of a diatomic molecule can be lowered by two orders of magnitude by using a frequency-chirped laser, and hence dissociation without ionization of neutral diatomic molecules should be possible. The excitation of a 1D model diatomic molecule by a laser with linear frequency sweep was analyzed classically using a linear dipole moment [10], and the reduction of the dissociation threshold can be understood in term of bucket dynamics [11]. Good agreement between the quantum mechanical and classical calculation of the dissocation probabilities has been found, and the idea of bucket dynamics was shown to be equally applicable to the case of a realistic dipole moment function and a laser with nonlinear frequency chirp [12]. Further quantum mechanical studies of the dissociation of the diatomic molecule HF, both 1D [13–15] and 3D [16,17], and the triatomic molecule HCN [18] have demonstrated again that chirped lasers are effective.

Classical calculations are of course much easier than quantum calculations. Since classical and quantum results have been found to agree well [12], we employ the classical method in this paper to further study the excitation and dissociation dynamics of the NO molecule by chirped lasers. Ideally, a 3D study should be carried out. However, in the quantum mechanical comparison of the 1D and 3D models of HF [17], it was found that the 1D model still provides valuable information about the dissociation dynamics. Furthermore, the classical dynamics of the chirped pulse excitation can be readily described by the bucket dynamics for a 1D model, which provides valuable physical insight into the dynamical process. Thus we shall employ the 1D model in this study. In Sec. II we extend our previous derivation of the bucket dynamics to the general case of nonlinear chirping and realistic dipole moment function. In Sec. III, we first study the excitation and dissociation characteristics under a single chirped laser, and investigate the effects of varying the laser intensity, frequency, pulse length, and the chirping rate. We then consider the influence of a second fixed-frequency laser to the dissociation process. Finally, we present a summary and discussion in Sec. IV.

II. BUCKET DYNAMICS

The vibrations of a general diatomic molecule can be reasonably modeled by the Morse potential [19]

$$V(r)=D[e^{-2\alpha(r-r_e)}-2e^{-\alpha(r-r_e)}], \tag{1}$$

where r is the diatomic bond length and r_e its equilibrium value, D is the dissociation energy, and α characterizes the steepness of the potential. In order to treat all diatomic molecules in a unified fashion, it is convenient to use dimensionless units [10,12,21] so that the total time-dependent Hamiltonian for a diatomic molecule coupling with the classical radiation field of the laser by the electric dipole interaction is given by

TABLE I. Physical constants for NO and HF.

	NO	HF
α	2.77 Å^{-1}	2.22 Å^{-1}
D	6.614 eV	6.125 eV
q_e	0.43 a.u.[a]	0.31 a.u.
m_{red}	7.466 amu	0.959 amu
$\omega_0/2\pi c$	1921 cm^{-1}	4138 cm^{-1}
$1/\omega_0$	2.76 fs	1.28 fs
$\hbar_{\text{eff}}$	0.018	0.042
I_0	95.01×10^{15} W/cm^2	102.1×10^{15} W/cm^2

[a] Reference [20].

$$H(x,p,t)=\frac{1}{2}p^2+\frac{1}{2}(e^{-2x}-2e^{-x})-\mu(x)\mathcal{E}(t). \tag{2}$$

Here energy is measured in units of $2D$, $x=\alpha(r-r_e)$, and $\mu(x)$ is the reduced dipole moment function of the molecule normalized to $d\mu(0)/dx=1$ at the equilibrium bond distance. Time is measured in units of $1/\omega_0$, where $\omega_0=\alpha\sqrt{2D/m_{\text{red}}}$ is the harmonic frequency of the Morse oscillator, and m_{red} is the reduced mass of the molecule. $\mathcal{E}(t)$ is the reduced electric field of the laser pulse,

$$\mathcal{E}(t)=BU(t;T_p)\cos\Phi(t), \tag{3}$$

where $\Phi(t)$ is the phase of the electric field, and $U(t;T_p)$ is the envelope function. The dimensionless amplitude B is related to the actual electric field strength of the laser E by $B=q_eE/(2\alpha D)$ where q_e is the effective charge of the molecule, and hence the laser intensity I is given in terms of B by

$$I=I_0B^2, \quad \text{where} \quad I_0=(c/8\pi)(2\alpha D/q_e)^2, \tag{4}$$

in Gaussian units. We list in Table I the physical constants for the molecules NO and HF, which are commonly employed in the study of multiphoton excitation. Also listed in Table I is the effective Planck's constant $\hbar_{\text{eff}}$, which is described in Sec. III. Notice that at the laser intensities of interest in this study, $I\sim10^{13}$–10^{14} W/cm^2, the values of B are rather small, being $\sim$0.01–0.05 for both the NO and HF molecules.

In our study, we use the envelope function

$$U(t;T_p)=\begin{cases}\sin^2\dfrac{\pi t}{2t_r}, & 0<t<t_r,\\ 1, & t_r<t<T_p-t_r,\\ \cos^2\dfrac{\pi(t-T_p+t_r)}{2t_r}, & T_p-t_r<t<T_p,\\ 0, & \text{otherwise,}\end{cases} \tag{5}$$

and we assume the rise time of the pulse to be $t_r=62.8$, which corresponds to about ten cycles of the natural frequency of the oscillator. The instantaneous frequency of the chirped laser is given by the time derivative of its phase by [18,16] $\Omega_{\text{ins}}(t)=d\Phi(t)/dt$. We model the phase of the chirped laser by

$$\Phi(t)=\Omega_0t\left[1-\frac{\alpha_c}{n_p+1}\left(\frac{t}{T_p}\right)^{n_p}\right], \quad n_p=1,2, \tag{6}$$

so that the instantaneous frequency can be written as [15]

$$\Omega_{\text{ins}}(t)=\Omega_0\left[1-\alpha_c\left(\frac{t}{T_p}\right)^{n_p}\right]. \tag{7}$$

Note that $\Omega_{\text{ins}}(T_p)=\Omega_0(1-\alpha_c)$ and hence α_c represents the fractional decrease of the instantaneous frequency at the end of the pulse. $\Omega_{\text{ins}}(t)$ is assumed to be a slowly varying function of time compared to $\mathcal{E}(t)$. We will study mainly the linear chirping case with $n_p=1$, which can be produced experimentally by a pulse shaper consisting of two parallel gratings [6].

In previous studies [10,12,15], the laser phase is written as $\Phi(t)=\Omega(t)t$. $\Omega(t)$ is treated as the driving frequency about which we expanded the equations of motion [10,12], and the derivation was restricted only to the case of linear chirping $n_p=1$. As discussed by Chelkowski and Bandrauk [18,16], it is the instantaneous driving frequency $\Omega_{\text{ins}}(t)$ that is physically meaningful, and in the original derivation of the bucket dynamics [11], expansion was made using $\dot{\Phi}$. Here we provide a more direct derivation of the bucket dynamics.

For bound state motion, the total Hamiltonian can be expressed in term of the action-angle variables (i,θ) [12,21] and expanded in a Fourier series as

$$H(\theta,i,t)=H_0(i)+B\sum_{n=0}^{\infty}G_n(i)\times\{\cos[n\theta-\Phi(t)]+\cos[n\theta+\Phi(t)]\}, \tag{8}$$

where $H_0(i)=-\frac{1}{2}(1-i)^2$ is the unperturbed Hamiltonian of the Morse oscillator, and the $\{G_n(i)\}$ are the Fourier components of $\mu(x(i,\theta))$. Since Ω_{ins} is slowly varying, by adiabatic invariance, i will also be slowly varying. The dynamics will then be dominated by the mth resonance term satisfying $m\theta-\Phi(t)\simeq\text{const}$ or $m\dot{\theta}-\dot{\Phi}\simeq0$. Using the unperturbed equation of motion for θ, the resonant condition is given by

$$m\omega(i)-\dot{\Phi}=0, \quad m=1,2,\ldots, \tag{9}$$

where the unperturbed frequency of the oscillator is obtained from the derivative of H_0 with respect to the action: $\omega(i)=H_0'$. For the Morse oscillator, $\omega(i)=1-i$, and hence the instantaneous resonance action can be obtained explicitly from Eq. (9):

$$i_r^m(t)=1-\dot{\Phi}(t)/m. \tag{10}$$

Near the mth resonance, we expect that the motion is approximately determined by the resonant Hamiltonian

$$H_r^m=H_0(i)+BG_m\cos[m\theta-\Phi(t)]. \tag{11}$$

We next carry out a canonical transformation to the new variables (ϕ,I) in the moving frame,

$$\phi=\theta-\frac{\Phi}{m}, \quad i=I+i_r^m(t), \tag{12}$$

using the generator

$$F_2(\theta,I,t)=I\left(\theta-\frac{\Phi}{m}\right)+i_r^m(t)\theta+h(t). \tag{13}$$

If $h(t)$ is chosen to satisfy

$$\dot{h}(t)+\frac{\Phi}{m}\frac{di_r^m(t)}{dt}+H_0(i_r^m(t))=0, \tag{14}$$

the new resonant Hamiltonian becomes

$$\overline{H}(\phi,I)=H_r^m+\frac{\partial F_2}{\partial t}=\frac{1}{2}H_0''(i_r^m)I^2+\frac{di_r^m(t)}{dt}\phi$$
$$+BG_m(i_r^m)\cos(m\phi), \tag{15}$$

where an expansion of $H_0(i)$ about i_r^m up to second order in I is made. For the Morse oscillator, $H_0''=-1$, $di_r^m(t)/dt=-\ddot{\Phi}$, and making a final canonical transformation to $J=I$ and $\psi=-\phi$ [12], we obtain

$$K(\psi,J)=-\overline{H}(-\psi,J)=\frac{J^2}{2}+V_m(\psi), \tag{16}$$

where

$$V(\psi)=-BG_m\cos m\psi-\frac{\ddot{\Phi}}{m}\psi. \tag{17}$$

When $\dot{\Phi}$(t) is slowly varying, $\ddot{\Phi}$ is approximately constant over the time scale of a period of the laser oscillation, and $K(\psi,J)$ can be treated as time independent over this time scale. If the laser intensity is high enough to satisfy

$$\left|\frac{\ddot{\Phi}}{m^2BG_m}\right|<1, \tag{18}$$

buckets exist and the system can be trapped and oscillates about $i_r^m(t)$. For negatively chirped laser pulses, $i_r^m(t)$ increases with time, and the system can be excited to higher values of the action by this convective process. Examples of such bucket dynamics for the case of nonlinear chirping with a realistic dipole moment for NO have been demonstrated [12]. The Hamiltonian governing the bucket dynamics as given by Eqs. (14) and (15) differs from the one derived in Refs. [10,12] only in that $\ddot{\Phi}$ takes the place of $\dot{\Omega}$ for $n_p=1$, a general Fourier coefficient G_m is used instead of the analytic expression for the linear dipole moment, and $i_r^m(t)$ is denoted by $i_B(t)$ there.

III. RESULTS

In this section, we study the excitation and dissociation probabilities of the diatomic molecule NO as functions of various laser characteristics. The dipole moment function for NO used here is the same as in Refs. [10,12]:

$$\mu(x)=\kappa y e^{-y/b}, \quad y=(\alpha'/\alpha)x+a, \tag{19}$$

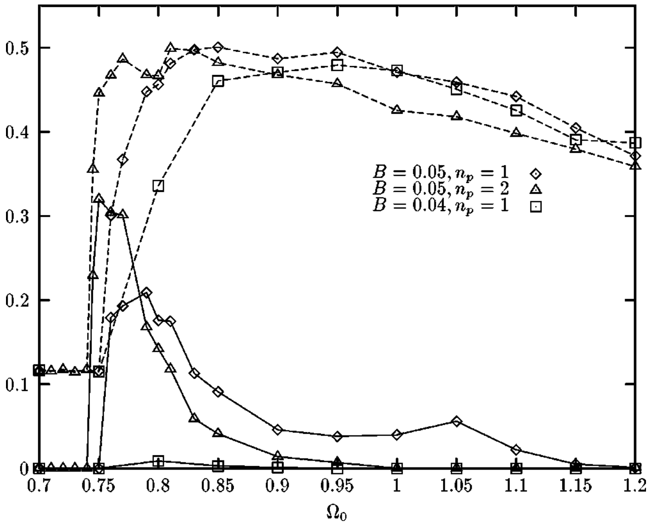

FIG. 1. Final dissociation probability P_d (solid lines) and average action $\langle i_d\rangle$ (dashed lines) as functions of the initial frequency Ω_0 of the chirped laser with $\alpha_c=0.5$ and $T_p=1000$. The NO molecule is initially in the $n=6$ state.

where $\alpha'=1.29$ Å^{-1}, $a=0.1058$, $b=0.6017$, and κ is chosen to satisfy $d\mu(0)/dx=1$.

For the NO molecule, results from classical calculations have been found to agree well with the quantum mechanical results, and the classical trajectory method will be used in this study. The vibrational quantum number of the molecule is related to its classical action by the semiclassical quantization condition

$$i_n=\left(n+\frac{1}{2}\right)\hbar_{eff}, \quad n=0,1,2,\ldots, \tag{20}$$

where the effective Planck's constant is given in terms of the Morse parameters by $\hbar_{eff}=\hbar\alpha/\sqrt{2MD}$. From Table I, $\hbar_{eff}=0.018$ for the NO molecule. Here 1000 trajectories are generated with initial angles θ uniformly distributed between 0 and 2π, and the initial action corresponding to an initial vibration quantum number n using Eq. (18). Hamilton's equations corresponding to the Hamiltonian of Eq. (1) are integrated numerically. The dissociation probability $P(t)$ is then given by the fraction of trajectories which by time t have already attained energies greater than 0 and interatomic separations greater than 10. The excitation is measured by the average action $\langle i(t)\rangle$ at time t. (For dissociated trajectories, the action is assigned the value 1.) The final values of the dissociation probability and the average action after the laser pulses are switched off are denoted by P_d and $\langle i_d\rangle$, respectively.

A. Single-pulse excitation

We first study the excitation characteristics of the NO molecule by a single chirped pulse of Eqs. (5)–(7). In all of our studies, the motion of the molecular system is followed for a time period of 100 units after the laser pulses are terminated. In Fig. 1, we plot as a function of the initial frequency Ω_0 the final dissociation probability P_d and the final average action $\langle i_d\rangle$ after the laser pulse is completely switched off. Initially the molecule is assumed to be in the

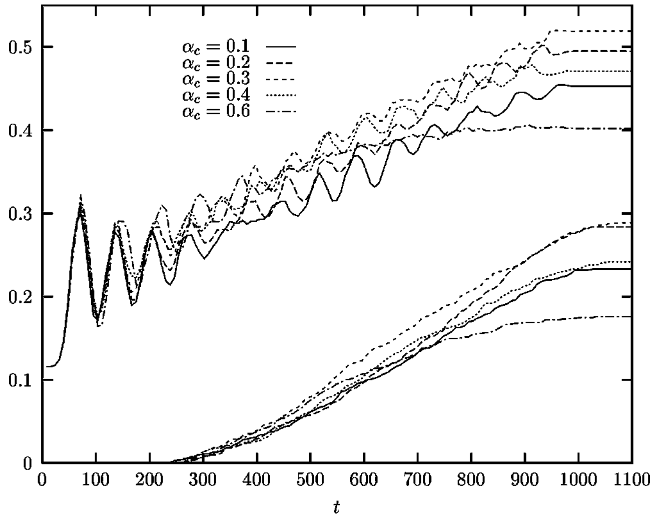

FIG. 2. Time evolution of the dissociation probability $P(t)$ (lower curves) and average action $\langle i(t) \rangle$ (upper oscillatory curves). The chirped laser parameters are $T_p = 1000$, $B = 0.05$, and $\Omega_0 = 0.79$. The NO molecule is initially in the $n = 6$ state.

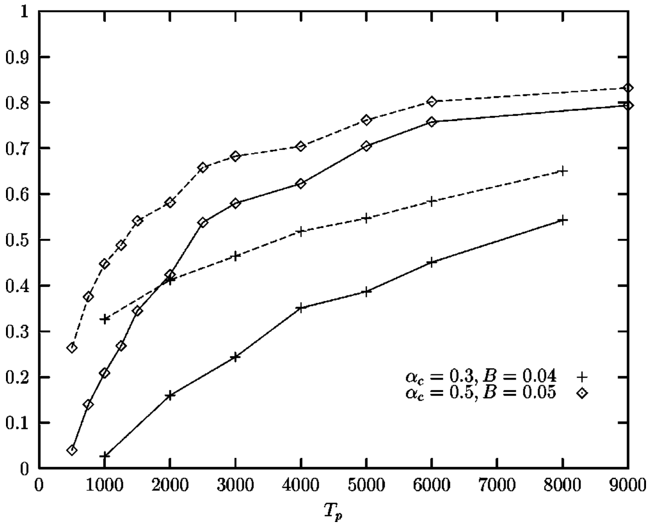

FIG. 3. Final dissociation probability P_d (solid lines) and average action $\langle i_d \rangle$ (dashed lines) as functions of the chirped pulse duration T_p. The NO molecule is initially in the $n = 6$ state.

vibrational state $n = 6$, whose action corresponds to the resonant action of Eq. (8) for $\Omega_0 = 0.88$. At the field strength $B = 0.05$, corresponding to a laser intensity of $I = 2.38 \times 10^{14}$ W/cm^2, excitation and dissociation are abruptly turned on near $\Omega_0 = 0.74$, at which the primary resonant zone (bucket) begins to overlap with the initial action. The dissociation probabilities rise rapidly with increase in Ω_0 and reach their peaks at $\Omega_0 = 0.79$ and 0.75 for $n_p = 1$ and 2, respectively, and then fall off more gradually, with full widths of the order of 10% of the natural frequency of the oscillator. The peak of P_d for the nonlinear chirping case of $n_p = 2$ is about 50% higher than that of the linear chirping case of $n_p = 1$, but it falls off faster as Ω_0 is increased. At the beginning of the excitation, the chirping rate $\dot{\Omega}_{ins}$ for $n_p = 2$ is smaller than that for $n_p = 1$, and hence the adiabaticity requirement is better satisfied initially for nonlinear chirping. This appears to give rise to a more efficient initial excitation and, hence, a higher dissociation probability. When the field strength B is lowered to 0.04 ($I = 1.52 \times 10^{14}$ W/cm^2), the dissociation probability is dramatically reduced.

The excitation $\langle i_d \rangle$ is also turned on abruptly near $\Omega_0 = 0.74$ and rises rapidly as Ω_0 is increased. Unlike P_d, however, it falls off much more slowly, showing that the system still attain a high level of excitation at blue shifted frequencies even when the dissociation probability becomes negligibly small. At $B = 0.05$, $\langle i_d \rangle$ rises a little more rapidly for $n_p = 2$ than for $n_p = 1$, but it also falls off slightly faster. The peak values of $\langle i_d \rangle$ for linear and nonlinear chirping are quite similar. For $B = 0.04$, $\langle i_d \rangle$ rises somewhat more slowly than for $B = 0.05$, but the peak value is similar to that of the higher intensity case. Thus, in contrast to P_d, $\langle i_d \rangle$ is less sensitive to the field strength B, and the molecular system can attain similar level of exciation as measured by $\langle i_d \rangle$ at lower intensities.

Next we study the excitation process as a function of the chirping parameter α_c, which represents the fractional decrease of the laser frequency at the end of the pulse. We show in Fig. 2 the time dependence of the dissociation probability $P(t)$ and the excitation $\langle i(t) \rangle$ during the interaction with the laser for pulses with duration $T_p = 1000$ and different values of α_c. The oscillations in $\langle i(t) \rangle$ are signatures of the bucket dynamics where the system is trapped in the potential of Eq. (17) in the moving frame. It is interesting to observe that for the smaller values of $\alpha_c = 0.1$, 0.2, and 0.3, the excitation $\langle i(t) \rangle$ increases with increasing value of the chirping constant α_c (which is proportional to the chirping rate for fixed T_p), as expected from bucket dynamics analysis. For the larger values $\alpha_c = 0.4$ and 0.6, this trend is observed only initially, up to $t \sim 300$, after which $\langle i(t) \rangle$ falls below some of those with smaller α_c. This could be an indication that the adiabaticity required for bucket dynamics is less well satisfied for these values of α_c. The dissociation probabilities reflect the same trend, and we obtain the largest values of P_d for $\alpha_c = 0.3$.

Figure 3 shows the excitation as a function of the pulse duration T_p for $\alpha_c = 0.5$. Note that for a fixed value of α_c, the chirping rate decreases with increasing T_p, and the excitation becomes more adiabatic. We observe that for the smaller values of T_p, the excitation increases with T_p, but levels off to an asympototic value for larger T_p when the adiabaticity requirement is fully satisfied. However, experimental considerations would limit the pulse duration employed, and we shall study pulses of shorter durations.

In the above studies, the electric field strength of the laser for appreciable dissociation is very high and one might have to worry about the molecule being ionized before dissociation, a process we have not taken into account. Furthermore, the initial vibrational state of the NO molecule is assumed to be $n = 6$, while usually the molecule is in its ground state $n = 0$. At lower laser intensities with the molecule in its ground state, dissociation hardly occurs, but we can still study its excitation. Figure 4 represents one of such investigation, where we use $\alpha_c = 0.3$. The field strengths used in the calculation are insufficient to dissociate the NO molecule initially in its ground vibrational state. However, the molecule can easily be excited, and the amplitudes of the oscillation of $\langle i(t) \rangle$ increase with B initially. Substantial excita-

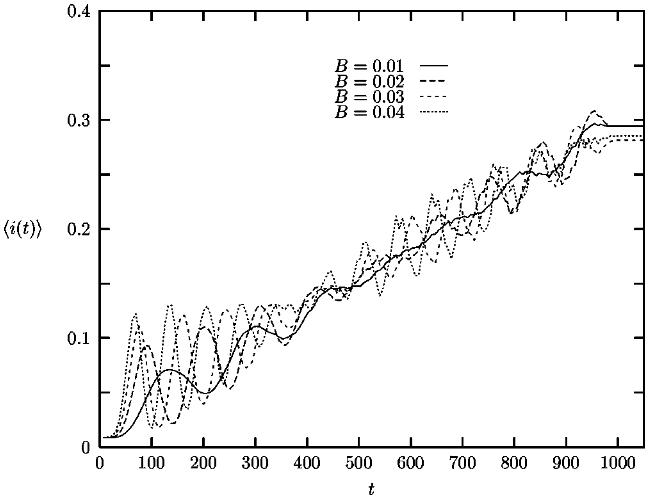

FIG. 4. Time evolution of the average action $\langle i(t)\rangle$ for $\alpha_c = 0.3$, $T_p = 1000$, and $\Omega_0 = 1.0$. The NO molecule is initially in the ground state $n = 0$.

tion is observed at the end of the laser pulses, but the final values of the average action $\langle i_d\rangle$ become almost independent of the field intensity B.

B. Two-laser excitation

It is clear from Sec. III A that it is difficult to dissociate the molecule by a single short laser pulse without using too high an intensity. In our earlier study of classical and quantum dynamics of chirped pulse dissociation [12], we have used a somewhat unrealistic chirping scheme in which frequency chirping is terminated at T_p and the driving frequency is kept constant at $\frac{1}{2}\Omega_0$. In many cases, the dissociation probability $P(t)$ exhibited a double-plateau behavior: $P(t)$ reached the first plateau during the chirping period, but it rose again, sometimes substantially, after chirping was terminated, eventually reaching a second plateau under the fixed-frequency excitation. Such a chirping scheme is equivalent to an excitation by two lasers: first a chirped pulse for a period T_p, then a fixed frequency laser with the same intensity and matching phase. This scheme suggests that the use of two lasers, one chirped and one fixed frequency, with different intensities and frequencies, may provide a more efficient method for dissociation. Thus, in the calculation below, we include the additional interaction in the Hamiltonian of Eq. (2):

$$V_2(x,t) = -\mu(x) B_2 U(t - t_d; T_{p2}) \cos \Omega_2 t, \tag{21}$$

where t_d is the time delay between the turning on the first chirped laser and the switching on of the second fixed-frequency laser, B_2 and T_{p2} are the field strength (in reduced unit) and the duration of the second laser, respectively, and $U(t;T_p)$ is the envelope function of Eq. (3). We assume that both lasers have the same rise time t_r since the dynamics is found to be insensitive to this parameter.

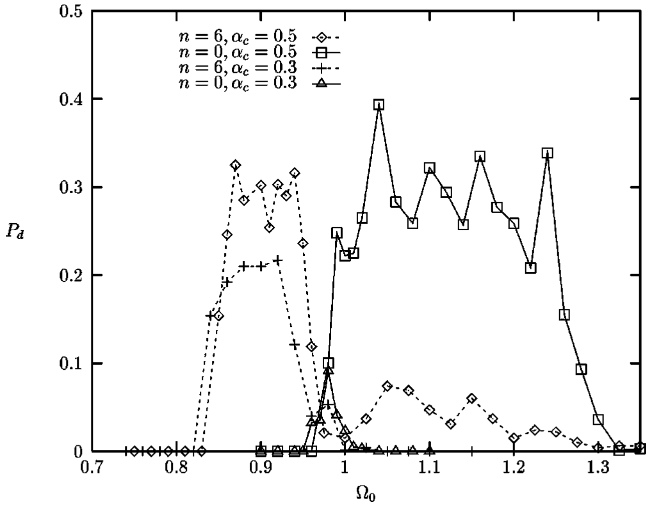

FIG. 5. Final dissociation probability as a function of the initial frequency Ω_0 of the first chirped laser with field strength $B = 0.01$, in the presence of a second laser with fixed frequency $\Omega_2 = 1.80$, field strength $B_2 = 0.02$, and time delay $t_d = 500$. Pulse durations $T_p = T_{p2} = 750$.

In Fig. 5, we show the dissociation probabilities as a function of the initial frequency Ω_0 of the chirped laser, while the frequency of the second laser is kept constant at $\Omega_2 = 1.8$. Note that at $B = 0.01$ and $B_2 = 0.02$, corresponding to intensities of 0.95×10^{13} W/cm^2 and 3.80×10^{13} W/cm^2, respectively, neither laser by itself can dissociate the molecule. When the molecule is initially in the vibrationally excited state $n = 6$, dissociation is turned on rather abruptly similar to the single laser case of Fig. 1, except around the larger value of $\Omega_0 \sim 0.85$. This is due to the fact that at $B = 0.01$, the resonance zone is smaller than that of Fig. 1, and Ω_0 must get closer to the molecular frequency of 0.88 before the resonance zone overlaps with the initial action. Again the peaks have full widths about 10% of the fundamental frequency of the oscillator, and decay slowly as Ω_0 is increased, with minor peaks occurring at higher frequencies. Unlike the single-laser case, the peak dissociation probability is higher for $\alpha_c = 0.5$ than for $\alpha_c = 0.3$, but now it is the second laser that promotes dissociation. When the molecule is initially in its ground vibrational state $n = 0$, dissociation is turned on when Ω_0 approaches the fundamental oscillator frequency of 1.0. It is surprising that for $\alpha_c = 0.5$, the dissociation probabilities could become larger than those when the molecule is initially at the excited state $n = 6$, and the peak is much broader. For $\alpha_c = 0.3$, the peak is sharper and smaller, but still reaching $P_d = 0.09$ at $\Omega_0 = 0.98$. Thus it is clear that with two lasers, it is possible to dissociate the molecule NO in its ground state, without using too high intensities.

In Fig. 6(a) we study the time development of the excitation $\langle i(t)\rangle$ and the dissociation probability $P(t)$ when the NO molecule is initially in the $n = 6$ state, for $\alpha_c = 0.5$ and various time delay t_d between the switching on of the first and second lasers. From the behavior of $\langle i(t)\rangle$, we observe that before the second laser is switched on, the system oscillates about the resonance action which slowly increases, as described by the bucket dynamics, but it remains bound. Dissociation occurs after the application of the second laser, and $P(t)$ reaches its asymptotic value before the second laser is turned off. While dissociation appears earlier when t_d is shorter, the asymptotic value of $P(t)$ at the end of the second laser pulse, P_d, generally increases with increasing t_d. When t_d is increased beyond the duration of the first pulse

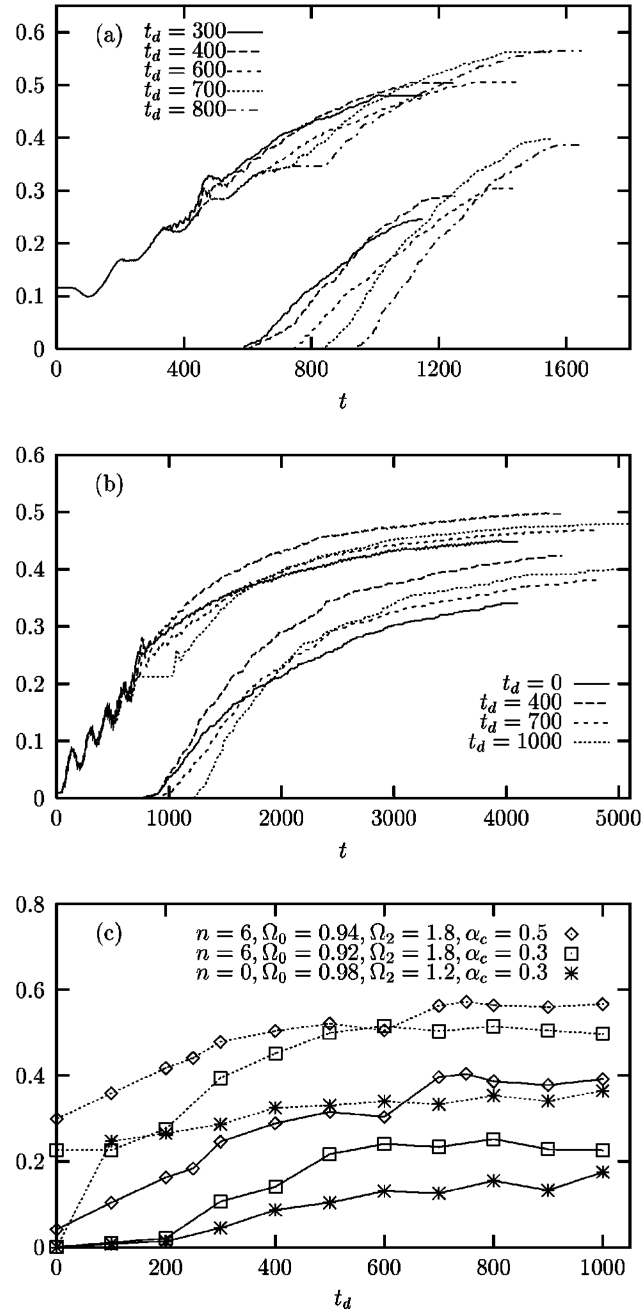

FIG. 6. Excitation of the NO molecule by two lasers with field strengths $B = 0.01$ and $B_2 = 0.02$ for different time delay t_d. (a) Time evolution of the dissociation probability $P(t)$ (lower curves) and average action $\langle i(t) \rangle$ (upper oscillatory curves) for $\Omega_0 = 0.94$, $\Omega_2 = 1.80$, $\alpha_c = 0.5$ with the molecule initially in the $n = 6$ state. (b) Same as (a) except that $\Omega_0 = 0.98$, $\Omega_2 = 1.20$, $\alpha_c = 0.3$, and $n = 0$. (c) Final dissociation probability P_d (solid lines) and average actions $\langle i_d \rangle$ (dotted curves) as functions of t_d when the two lasers have pulse durations $T_p = T_{p2} = 750$.

T_p, P_d levels off. There is no advantage of choosing $t_d > T_p$ since other relaxation mechanism not included in the present model will further reduce the excitation before the second laser becomes effective.

The t_d dependence for $\alpha_c = 0.3$ is shown in Fig. 6(b). While the short time behavior is similar to the $\alpha_c = 0.5$ case, $P(t)$ and $\langle i(t) \rangle$ for $\alpha_c = 0.3$ take much longer to reach their asymtoptic values. Furthermore, at the end of the second laser with duration $T_{p2} = 5000$, P_d is maximun at $t_d = 400$. It is interesting to observe that for such long T_{p2}, the molecule can dissociate even for $t_d = 0$. In fact, the final P_d is not too sensitive to t_d, lying between 0.3 and 0.43 for t_d between 0 and 1000. However, for shorter T_{p2}, the behavior of P_d is similar to the $\alpha_c = 0.5$ case. This is demonstrated in Fig. 6(c), in which the final dissociation probability P_d and excitation $\langle i_d \rangle$ are plotted as a function of the time delay t_d, when both laser pulses have the same duration $T_p = T_{p2} = 750$. For short laser pulses, substantial excitation will be observed when t_d falls in the range between 300 and 1000.

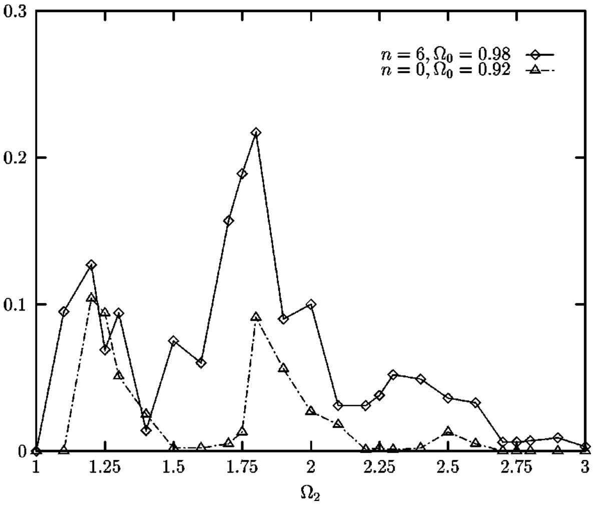

FIG. 7. Final dissociation probability as a function of the frequency Ω_2 of the second laser with field strength $B_2 = 0.02$ and time delay $t_d = 500$. The parameters for the first chirped laser are $\alpha_c = 0.3$ and $B = 0.01$. Pulse durations $T_p = T_{p2} = 750$.

We have studied the dependence on the chirped pulse duration by setting the chirping parameter to $\alpha_c = 0.3$, and switching on the second laser of duration $T_{p2} = 750$ at the end of the first pulse. For $T_p = 500$, 750, and 1000, we obtain the final dissociation probabilities $P_d = 0.092$, 0.127, and 0.093, respectively, for the NO molecule initially in the $n = 0$ state. Hence, while a short chirped pulse would not be very effective in exciting the molecule (as we expect from Fig. 4), too long a pulse may not necessarily enhance the dissoication probability.

We next study in Fig. 7 the dependence on the frequency of the second laser, Ω_2, with $\alpha_c = 0.3$ and $t_d = 500$, when the NO molecule is in the initial states $n = 0$ and 6. For both initial states, three broad peaks are observed. For $n = 6$, these occur at $\Omega_2 = 1.2$, 1.8, and 2.3, and there is some overlapping among them, especially between the second and third peaks. For $n = 0$, the peaks are more isolated, with the first two peaks also appearing at $\Omega_2 = 1.2$ and 1.8, while the third is located at 2.5. (Note the difference in scale of the x coordinates of Figs. 5 and 7.) In both cases, there is a wide range of Ω_2 for which dissociation is detectable.

We have also studied the dependence of the dissociation on the field strength of the two lasers. We set $\alpha_c = 0.3$, $t_d = 500$, $\Omega_0 = 0.98$, $\Omega_2 = 1.2$, and $T_p = T_{p2} = 750$. The molecule is assumed to be initially in the $n = 0$ state. We first fix $B = 0.01$ and vary B_2. Then we set $B_2 = 0.02$ and change B. Our results are summarized in Table II. As expected, the dissociation probability decreases with a decrease in either

TABLE II. Dependence of P_d and $\langle i_d \rangle$ on B and B_2 for $n=0$, $\alpha_c=0.3$, $\Omega_0=0.98$, $\Omega_2=1.20$.

B	B_2	P_d	$\langle i_d \rangle$
0.010	0.025	0.276	0.436
	0.020	0.104	0.331
	0.015	0.003	0.250
	0.010	0.000	0.225
0.015	0.020	0.167	0.480
0.008		0.080	0.247
0.006		0.004	0.079

laser field strength. It appears that a higher intensity is required for the second fixed-frequency laser than the chirped pulse, although dissociation can be detected for relatively low field strengths. Finally, we show in Fig. 8 the Poincaré map for a dissociating trajectory, i.e., a plot of $(\theta(t_n),i(t_n))$ at each period of the second fixed-frequency laser *after* the first chirped laser has been completely switched off, for $B=0.008$, $\alpha_c=0.3$, $T_p=750$, $t_d=700$, and $B_2=0.015$ with the molecule initially in $n=0$. The intensities of the first and second lasers are thus 0.61×10^{13} W/cm^2 and 2.14×10^{13} W/cm^2, respectively. Although the remnant of a $m=2$ resonant zone is still discernible, the motion is chaotic and the molecule dissociates when the action approaches unity. At such low field strengths, the second laser must be turned on for a longer period to achieve dissociation, and with $T_{p2}=6000$, we obtain $P_d=0.053$. We have also shown in Fig. 8 the Poincaré map in the *absence* of the first chirped laser, which shows up as minute oscillations around the initial action $i_0\simeq0.01$. The motion is obvious quasiperiodic and no dissociation is possible at such low field strengths. Thus, it is clear that the two-laser dissociation process is achieved in two stages: the first chirped laser promotes the molecule to a highly excited vibrational state by bucket dynamics, and the second fixed-frequency laser then sends the system into a chaotic state which diffuses to dissociation.

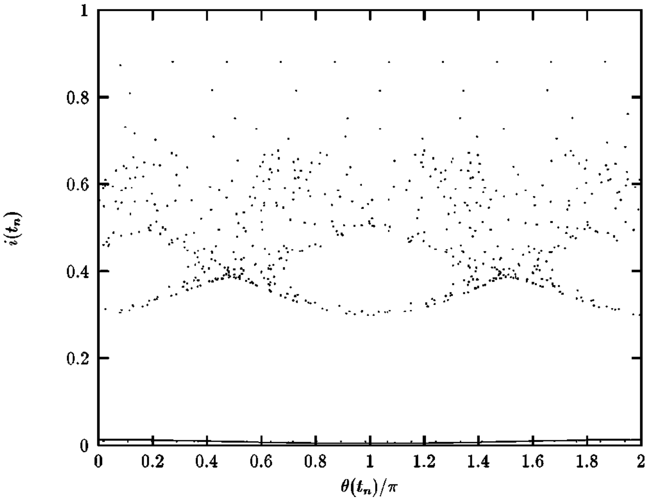

FIG. 8. Poincaré map of a trajectory with initial action $i_0=0.0089$ (ground state $n=0$ of NO) and initial angle $\theta=1.6\pi$ when excited by two relatively weak lasers with $B=0.008$, $\Omega_0=0.98$, $T_p=750$, $\alpha_c=0.3$; $B_2=0.015$, $\Omega_2=1.20$, and $T_{p2}=6000$ (upper scattered plot). Shown also as small oscillations about the initial action $i_0=0.0089$ is the Poincaré map in the absence of the first chirped laser.

IV. SUMMARY AND DISCUSSION

In this paper, we have studied the excitation and dissociation dynamics of the molecule NO as a function of various laser parameters. We have employed the classical trajectory method, which has been proven to give reliable results for this molecule when compared with quantum mechanical calculations. Although we use the NO molecule as a specific example in our study, it should be pointed out that, classically, the reduced Hamiltonian of Eq. (2) applies universally to all diatomic molecules in the linear dipole approximation $\mu(x)\simeq x$. There are only two parameters which are system specific: $\hbar_{\mathrm{eff}}$, which determines the initial action corresponding to a given vibrational state via the semiclassical quantization rule of Eq. (20), and I_0 in Eq. (4), which gives the constant of proportionality between the square of the driving amplitude and the laser intensity.

While it has been demonstrated previously that a frequency-chirped laser can reduce the dissociation threshold, the use of a single chirped laser still requires rather high intensity for direct dissociation. The dissociation probability shows resonant structure, with the optimal initial frequency near but redshifted from the initial molecular frequency. For the same fractional decrease in frequency at the end of the chirped pulse, a slow chirping rate is preferable so that adiabaticity can be maintained throughout the excitation process. However, experimental considerations would limit the length of a pulse, and for the same pulse duration, there is an optimal chirping rate for dissociation. While dissociation is absent at lower laser intensities, substantial molecular excitation by the chirped laser is still achieved, even when the molecule is initially in its vibrational ground state.

When a second laser of fixed frequency is applied to the molecular system with suitable time delay from the first chirped pulse, appreciable dissociation is observed even though each laser by itself could not dissociate the molecule. While the dissociation probability is not too sensitive to the time delay between the two lasers, for short laser pulses, more efficient excitation and dissociation are obtained when the second laser is turned on at the end of the first laser pulse.

Similar to the dissociation by a single chirped laser, the two-laser dissociation process is sensitive to the initial chirped laser frequency Ω_0, peaking at a value near the molecular frequency. While there are optimal values of the frequency of the second fixed-frequency laser for this dynamical process, dissociation is effective over a wide range of Ω_2, blueshifted from the molecular frequency. This has the important experimental implication that selectivity is provided by the first chirped laser, and enhancement of dissociation can be obtained by using a wide range of fixed-frequency lasers.

It is also clear that the dynamics of the excitation of the molecule by the chirped laser is quite different from that of dissociation by the second fixed-frequency laser. Chirped pulse excitation to a highly excited state is well described by bucket dynamics which is a convective process and is nonchaotic. Subsequent application of a fixed frequency laser then induces chaos, as shown in Fig. 8, and the system diffuses to dissociation.

In this paper, we have neglected the possibility of ionization of the molecule by the high intensity lasers. It has been shown that the ionization rates for atoms [22] and molecules [23,24] can be adequately described by the quasistatic tunneling mechanism [25], and based on the barrier suppression model, the threshold intensity for ionization of a neutral molecule can be estimated by the simple formula [22,23]

$$I_{th}=4.00\times 10^9\times E_s^4 \ \ \mathrm{W/cm^2},$$

where E_s is the ionization potential of the molecule in eV. For NO and HF, $E_s=9.25$ eV and 16.0 eV, respectively, yielding the corresponding threshold intensities of 2.9×10^{13} W/cm^2 and 2.6×10^{14} W/cm^2. Thus, the results of Sec. III A show that while dissociation without ionization by a single chirped laser may still be possible for HF [assuming its reduced dipole moment function is qualitatively similar to that of NO in Eq. (19)], this would not be possible for the NO molecule. On the other hand, by adding a second laser as discussed in Sec. III B, dissociation without ionization of NO is possible. Furthermore, the envelope function $U(t;T_p)$ of Eq. (5) and the frequency variation of Eq. (7) are chosen for simplicity. The laser intensities could be reduced and the dissociation probabilities enhanced if $U(t;T_p)$ and/or $\Omega_{\mathrm{ins}}(t)$ can be optimized [9,13,14,16,26]. In conclusion, we have demonstrated theoretically that a second fixed-frequency laser can greatly enhance the photodissociation of a molecule. It would be interesting to see if experiments can be designed to demonstrate this result.

ACKNOWLEDGMENTS

We are grateful to Professor Donna Strickland for helpful discussions. Part of this work was performed when W.K.L. and J.M.Y. visited the Institute of Atomic and Molecular Sciences, Academia Sinica, Taiwan, and we are grateful to the NSC of the Republic of China for its support. This work was also partially supported by a Natural Sciences and Engineering Research Council (NSERC) of Canada Research Grant to W.K.L.

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