LETTER TO THE EDITOR

Quantum dynamics of a diatomic molecule under chirped laser pulses

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Abstract.   The photodissociation probability of a diatomic molecule is usually very small even under a strong field due to its anharmonicity. However, the progress in laser technology provides a chirped laser pulse to lower the threshold of the dissociation intensity. We investigate the quantum dynamics of a diatomic molecule under such a kind of pulse. It is found that there is a significant dissociation probability at moderate intensity for a diatomic molecule under a chirped pulse. The quantum dissociation probability is found to be suppressed with respect to the classical one for intensities above the dissociation threshold. Therefore the chirped pulse can efficiently dissociate a diatomic molecule.

Photodissociation of molecules has been an interesting area for both theoretical and experimental physicists since the initial era of quantum mechanics (Bloembergen and Yablonovitch 1978). Among various kinds of molecules, the diatomic molecules usually serve as the paradigm of this subject for their simplicity. Recent studies (Bloembergen and Zewail 1984, Goggin and Milonni 1988, Chelkowski and Bandrauk 1990) show that diatomic molecules are resistant to dissociation even under intense lasers due to their anharmonicity and nonlinear interaction with the field. On the other hand, as the intensity goes beyond 10^{13} W cm^{-2}, the ionization processes dominate the dissociation ones. So for moderate laser intensities, it seems difficult to have a significant dissociation probability. There have been several methods proposed to excite the molecules to highly excited states efficiently and to control the molecular dissociation probability. Theoretically, Chelkowski *et al* (1990) designed a kind of stepwise π-pulse that fulfils the population inversion between successive energy levels by the π-pulse criterion (Allen and Eberly 1975). This ladder-climbing mechanism is rather efficient in molecular vibrational excitations. A chirped, ultra-short pulse was used to selectively excite the molecular wavepacket motion (Bardeen *et al* 1995). Guérin (1997) analysed the complete dissociation of a Morse oscillator under a chirped pulse by the adiabatic Floquet theory. Liu *et al* (1995) and Yuan and Liu (1997) used a linear chirped pulse and employed a Morse oscillator as a model NO molecule to study the dissociation. The Chirikov nonlinear resonance theory (Chirikov 1979) and bucket dynamics (Hsu *et al* 1994) are used to explore the dissociation process. Although the stepwise chirped π-pulse is slightly more efficient to excite the molecules than the linear chirped pulse, it is actually not easy to construct in practice. Also, the relationship between the dissociation mechanism and the field parameters remains to be explored. Experimentally, the chirped

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pulses which could be used to climb the vibrational ladders are currently available from free-electron lasers (Vrijen *et al* 1997). In this letter, we will use the linear and quadratic chirped pulses to study the dissociation process and its associated dynamical mechanism. We find that the quantum dissociation is suppressed with respect to the classical dissociation for field intensity which goes above the dissociation threshold. The phenomenon resembles that found in microwave ionization of hydrogenic Rydberg states. The dependence of the dissociation probability on the chirp constants, the initial excitation frequency, and the pulse duration are investigated. We found that the chirp pulse can efficiently dissociate a diatomic molecule under a moderate intensity.

This letter is organized as follows. First, we describe our numerical method. An adaptive grid method was developed to avoid the boundary reflection problem and to save computing time. Then, we present our results and discussion. Finally, a summary is given.

We will briefly describe our method of calculation here, readers are referred to some references (Feit *et al* 1982, Kosloff and Kosloff 1983, Feit and Fleck 1984) for more details. The time-dependent Schrödinger equation for the interaction of a diatomic molecule with an external field can be written as

$$i\hbar \frac{\partial}{\partial t}|\psi\rangle = \left\{ \frac{(\hat{p} - q_e A(t))^2}{2m} + \hat{V}(r) \right\} |\psi\rangle \tag{1}$$

where the vector potential $A(t) = -\int_0^t E(t')\,\mathrm{d}t'$ and $E(t) = E_m U(t) \sin[\Omega(t)\,t]$ is the electric field with chirping frequency $\Omega(t)$, where

$$\Omega(t) = \Omega_0 \left[1 - \alpha_n \left(\frac{t}{T_0} \right)^n \right]. \tag{2}$$

The pulse duration is T_0 and the peak field is E_m. We define the parameter α_n as the chirping constant of the linear (quadratic) chirped pulse for $n = 1$ (2). In our calculation, we choose Ω_0 to be $1.1\omega_{01}$ and ω_{01}, where ω_{01} is the resonance frequency between the unperturbed ground state and the first excited state. The optical cycle is defined as $2\pi/\Omega_0$. Since the energy level spacings of a Morse oscillator decrease from lower to high states. The blue to red chirping will provide a climbing ladder for the pumping process. Besides, there is an AC Stark shift for each level, and the π-pulse based upon unperturbed states may not assume exact population inversion between two states. Thus we use the linear and quadratic chirping as given by equation (2). The $U(t)$ is a slowly varying envelope function given by

$$U(t) = \begin{cases} t/t_0 & \text{for} \quad t \leqslant t_0 \\ 1.0 & \text{for} \quad t_0 < t \leqslant T_0 - t_0 \\ (T_0 - t)/t_0 & \text{for} \quad T_0 - t_0 < t \leqslant T_0. \end{cases} \tag{3}$$

The rising time and switching-off time t_0 is set to 10 cycles. For simplicity we consider only the vibrational excitation of the ground electronic state. The Morse potential is

$$V(r) = D_e \{1 - \exp[-\alpha(r - r_0)]\}^2. \tag{4}$$

We fit the potential parameters to the HF molecular vibrational spectrum such that $D_e = 0.225, \alpha = 1.1741$, equilibrium nuclei separation $r_0 = 1.7329$, reduced mass $m = 1744.8423$ and effective charge $q_e = 0.31$ (atomic units are used unless otherwise stated). There are 24 bound vibrational levels for the HF molecule.

The time-dependent Schrödinger equation is propagated by the split-operator algorithm,

$$\psi(p, t + \Delta) = \exp\left\{-i\frac{[\hat{p}^2 - 2q_e\alpha_A(t + \Delta)\hat{p}]\Delta}{4m}\right\}\exp[-i\hat{V}(r)\Delta]$$

$$\times \exp\left\{-i\frac{[\hat{p}^2 - 2q_e\alpha_A(t + \Delta)\hat{p}]\Delta}{4m}\right\}\psi(p, t) + \mathcal{O}(\Delta^3) \tag{5}$$

where $\alpha_A(t + \Delta) = \int_t^{t+\Delta} A(t')\,dt'$. The state function is transformed alternatively between the coordinate and momentum spaces. The calculation is performed using a fast-Fourier transform (FFT) (Jiang and Chu 1992). Generally speaking, the wavefunction is localized in the momentum space but spreads in the coordinate space with time. When the system is excited to higher or continuum states, the wavefunction will eventually hit the coordinate grid boundary. The aliased boundary reflection will contaminate the correct wavefunction. However, the moving apart velocity of the system is finite, so under the duration of a short pulse, the extent of wavefunction travelling is controllable. Here we used the adaptive grid
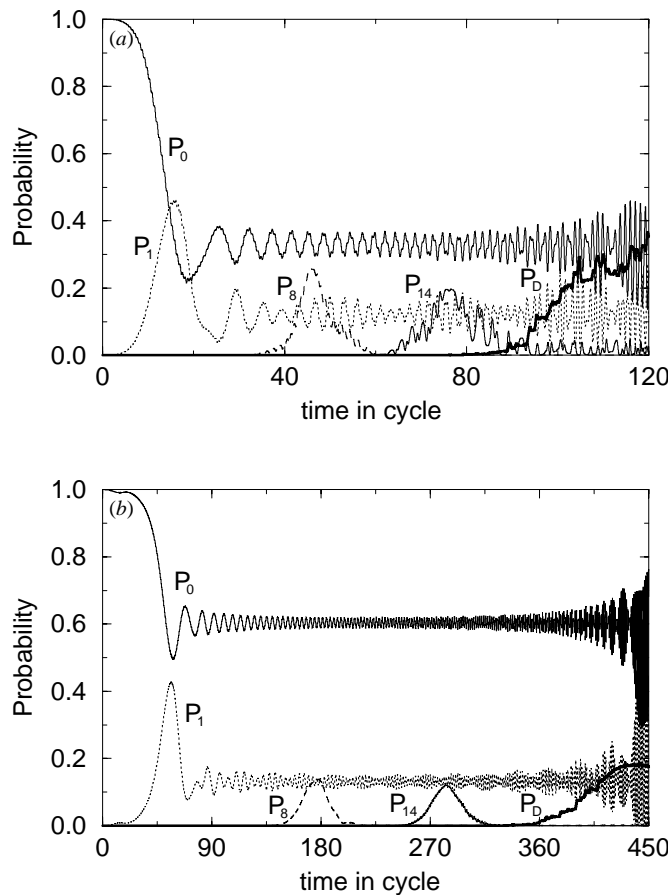

Figure 1. State populations and dissociation probability versus time with $\Omega_0 = 1.1\omega_{01}$ and $\alpha_1 = 0.5$. (*a*) $I = 10^{13}$ W cm^{-2}; (*b*) $I = 10^{12}$ W cm^{-2}. Note that the pulse duration in (*b*) is much longer than that in (*a*) in order to have noticeable dissociation probability.

method. Instead of using a large grid throughout the calculation, we start with a smaller grid and double the grid number whenever the wavefunction arrives at the outer boundary of coordinate grids. The initial coordinate range is set to 15.7 au in a mesh of 256 evenly spaced grids. As an example of the adaptive grid, in the case of $\alpha_1 = 0.5$, $\Omega_0 = 1.1\omega_{01}$ and intensity of 10^{13} W cm^{-2}, the number of grids changed from $N = 256$ to 2048 at the end of a chirped pulse consisting of 120 cycles.
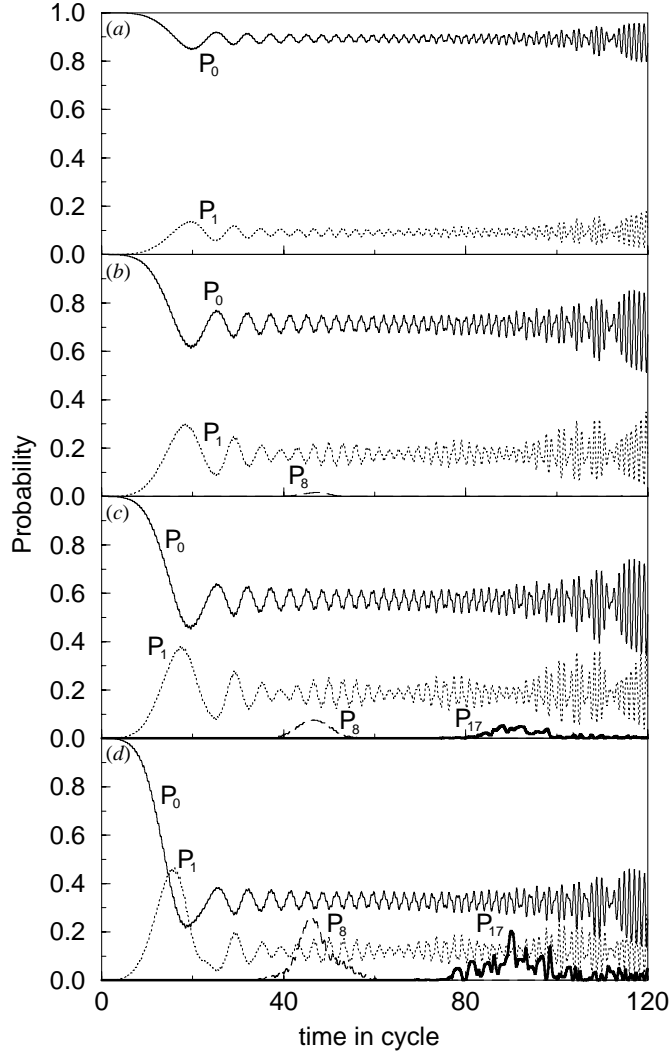

Figure 2. State populations P_n versus time at different field intensities with $\Omega_0 = 1.1\omega_{01}$, $\alpha_1 = 0.5$ and $T_0 = 120$ cycles. (*a*) $I = 10^{12}$ W cm^{-2}; (*b*) $I = 3 \times 10^{12}$ W cm^{-2}; (*c*) $I = 5 \times 10^{12}$ W cm^{-2} and (*d*) $I = 10^{13}$ W cm^{-2}.

The dissociation probability P_D is defined as

$$P_D(t) \equiv 1 - \sum_{\nu=0}^{23} P_\nu(t) \tag{6}$$

with $P_\nu(t) = |\langle \phi_\nu | \psi(t) \rangle|^2$ as the population of the νth bound state ϕ_ν of the Morse oscillator at time t.

It is instructive to compare the quantum results with the classical ones that had revealed the bucket dynamics and dynamical barrier scenarios (Brown and Wyatt 1986). The classical dissociation probability is defined from those trajectories that have total energy greater than zero after the field is turned off. In our calculation, we use an ensemble of 1000 points (r, p) as the initial values satisfying some specified energy value. These trajectories are calculated from the Hamiltonian–Jacobi equation:

$$\frac{\partial r}{\partial t} = \frac{p - q_e A(t)}{m} \qquad \frac{\partial p}{\partial t} = -\frac{\partial V(r)}{\partial r}. \tag{7}$$

In this study, we use the frequency chirping form as described in equation (2). Our system is initially prepared in the ground state. The laser intensity runs from 10^{12} to 10^{13} W cm^{-2}. The ionization processes are not important within this field range. From the corresponding ponderomotive potential U_p and dissociation energy I_p of HF, the Keldysh parameter $\gamma = \sqrt{I_p/U_p} \gg 1$, so we expect that the multiphoton process strongly dominates the tunnelling one in our calculation. During the multiphoton process, the dissociation occurs only when the system has been pumped up to some νth excited states such that $E_\nu + \hbar\Omega(t) \geqslant 0$. It means that, during the interaction time, once the system has been pumped to the state with energy greater than $-\hbar\Omega_0$, it probably dissociates. From the π-pulse criterion (Allen and Eberly 1975), the stepwise transition amplitude depends on the
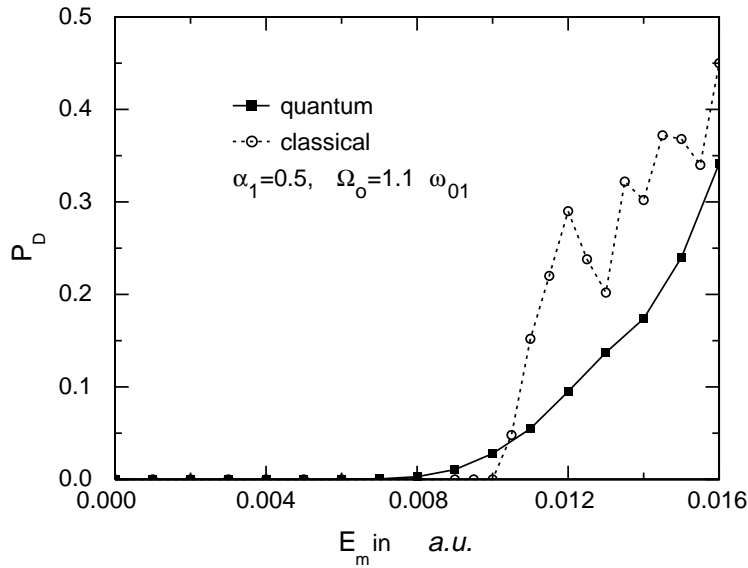

Figure 3. The dissociation probability versus field strength E_m. Full squares represent the quantum results and open circles represent the classical simulation. The pulse duration T_0 is 120 cycles. Above the onset of threshold, quantum dissociation suppresses the classical result.

field strength E_m, the dipole moment between neighbouring states $M_{v,v+1} = \langle \phi_{v+1} | r | \phi_v \rangle$, and the chirping constant α_n. On the other hand, for a successful dissociation, the time T_{ex} required to pump the ground state into the described vth state should be less than the pulse duration T_0, where

$$T_{ex} = \sum_{i=0}^{i=v} T_i \qquad \text{with} \qquad \int_{T_v}^{T_{v+1}} U(t)\, dt = \pi / E_m M_{v,v+1}. \tag{8}$$

In fact, T_{ex} is only an estimate due to (i) the shift of the energy levels in the presence of an electromagnetic field; (ii) the necessity of a larger area to compensate the approximation of the derivation of this formula and the nonresonance effects of a continuously chirped pulse (Chelkowski *et al* 1990); (iii) the importance of the non-negligible hopping dipole
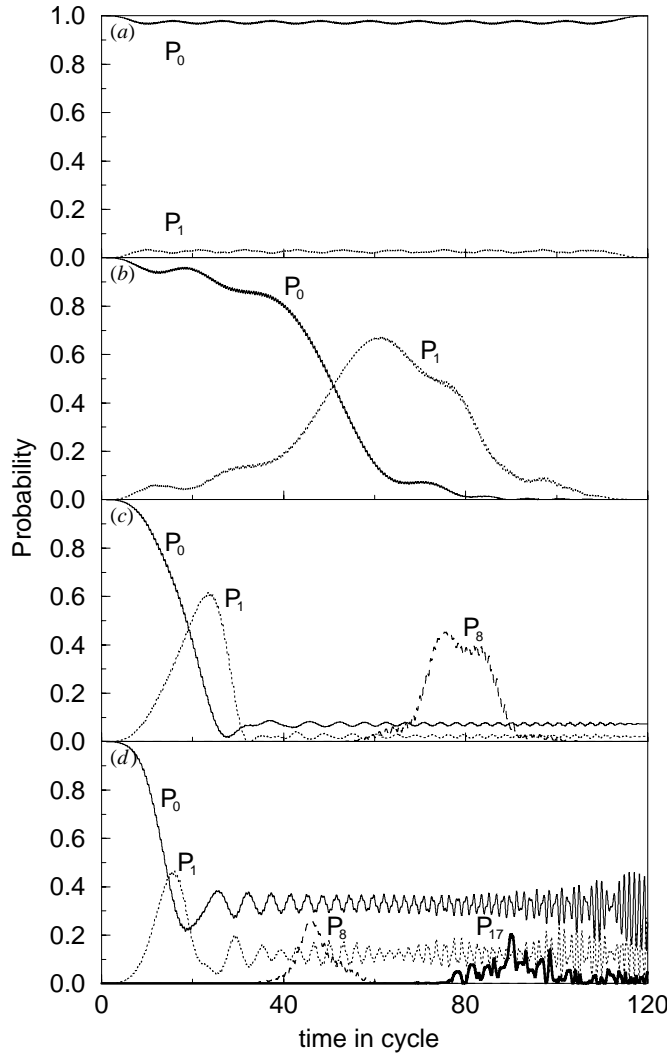

Figure 4. State population P_n versus time for different chirpings at field intensity $I = 10^{13}$ W cm^{-2}, $\Omega_0 = 1.1\omega_{01}$ and pulse duration $T_0 = 120$ cycles, for (a) $\alpha_1 = 0.0$, (b) $\alpha_1 = 0.1$, (c) $\alpha_1 = 0.3$, (d) $\alpha_1 = 0.5$.

transition with moment $M_{v,v' \neq v+1}$, especially when the system is in highly excited states and (iv) the decay rates among states. In the case of $I = 10^{13}$ W cm^{-2}, $\alpha_1 = 0.5$ and the total pulse duration contains 120 cycles, theoretically the pulse can excite the ground state up to the 22th state according to equation (8). However, in the numerical experiment, the actual highest bound state reached is the 20th. Also for HF we have $E_{17} + \hbar\Omega(t) \geqslant 0$. So there is a finite probability to dissociate for a system which has been pumped up over the 20th. Our calculation shows that a dissociation probability of 0.4 is achieved in this case, which is just slightly less than that of Chelkowski *et al* (1990) where a complicated chirped pulse was used. For a lower field, e.g. $I = 10^{12}$ W cm^{-2}, a much longer time is necessary to arrive at the dissociation limit as mentioned above. The dissociation probabilities of the two cases are shown in figures 1(*a*) and (*b*).

Figure 2 shows the population history of some states under a chirped pulse of duration 120 cycles, $\Omega_0 = 1.1\omega_{0,1}$ and $\alpha_1 = 0.5$. The field intensities are 1, 3, 5 and 10×10^{12} W cm^{-2}, respectively. The different field intensity will excite the ground state to different highest possible bound states during the pulse. The highest states arrived at for the corresponding fields are the 4th, 8th, 12th and 22nd, respectively. Thus, with this pulse duration, noticeable dissociation is possible only if the field strength goes above 5×10^{12} W cm^{-2}. Also, the time spent in populating from the ground state into the first excited state reduces as the field strength increases. Similar situations occur for populating other higher states. This agrees with the population flip equation (8).

In figure 3, we show both the quantum and classical dissociation probability versus the peak field at $\alpha_1 = 0.5$ and $\Omega_0 = 1.1\omega_{0,1}$. It is interesting to note that above the onset of the classical dissociation threshold, the quantum results are suppressed with respect to the classical ones. The results are consistent with the study of microwave ionization of the hydrogenic (MIH) Rydberg state. The MIH experiments confirmed that for field
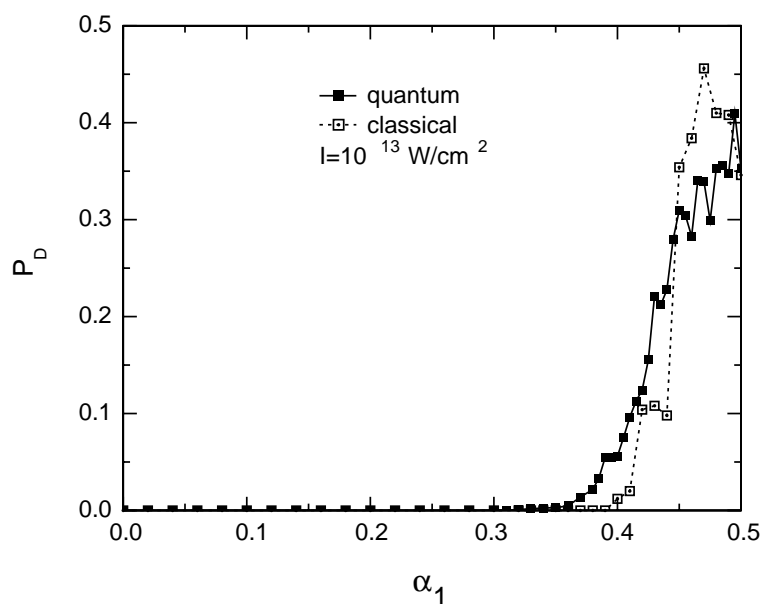

Figure 5. Dissociation probability versus linear chirping constant α_1 at frequency $\Omega_0 = 1.1\omega_{01}$ and $T_0 = 120$ cycles for quantum (full squares) and classical calculations (open squares). The dissociation probability for $\Omega_0 = \omega_{01}$ is negligible and not drawn.

frequencies higher than the neighbouring level spacing of the initial state, the suppression does happen (Galvez *et al* 1988, Bayfield *et al* 1989). Theoretically, the classical motion of an integrable system is restricted to invariant tori. The Kolmogorov–Arnold–Moser theorem (Tabor 1989) stated that some tori will survive when the system is perturbed, but when the external perturbation exceeds a critical value, the last persistent torus is destroyed and the remnant consists of a Cantor set. The classical orbits nearby will eventually diverge from them; while quantum transport inhibits the escaping of the phase area with value larger than $\hbar$ (MacKay and Meiss 1988).

To find the optimal condition for dissociation, we investigate the change of dissociation probability with the field parameters. First, we vary the linear chirping constant α_1 from 0 to 0.5 with fixed field intensity $I = 10^{13}$ W cm^{-2} and frequency $\Omega_0 = 1.1\omega_{01}$. Figure 4 depicts the time history of the populated states. Without chirping, almost no excited state can be populated in a pulse of 120 cycles duration. The larger the α_1, the higher the state populated. The onset of dissociation occurs at about $\alpha_1 = 0.35$. Figure 5 shows the dependence of the dissociation probability on α_1 for both classical and quantum results.
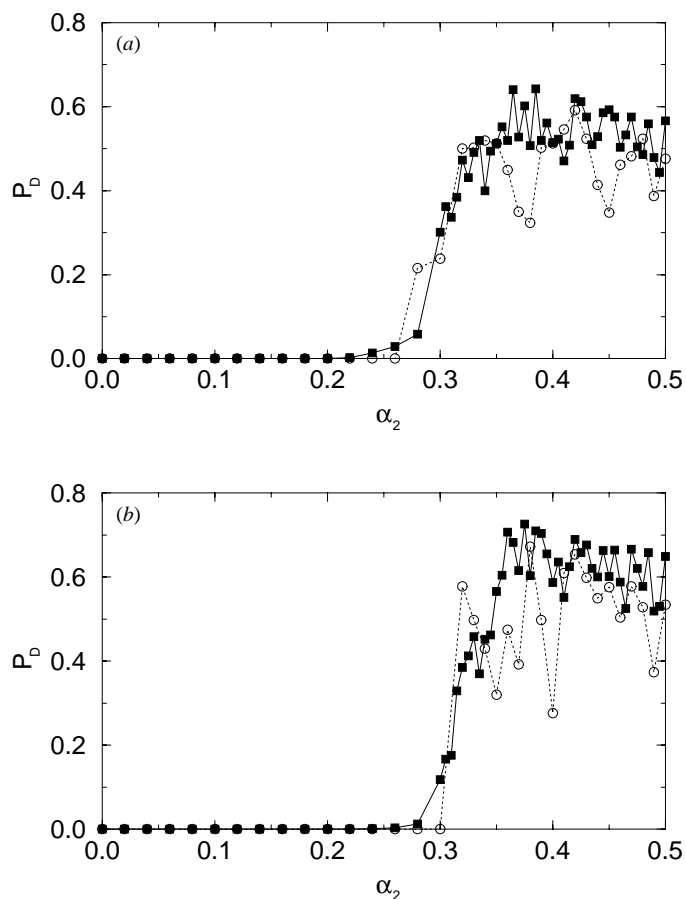

Figure 6. Dissociation probability versus quadratic chirping α_2 at $T_0 = 120$ cycles and $I = 10^{13}$ W cm^{-2} for (*a*) $\Omega_0 = \omega_{01}$, (*b*) $\Omega_0 = 1.1\omega_{01}$. Full squares denote the quantum results and open circles denote the classical simulations.

The dissociation probability corresponding to the case of $\Omega_0 = \omega_{01}$ is negligible and is not plotted. We can see from the results that the dissociation probability increases with the value of α_1. Second, we study the effect of the initial field frequency and the quadratic chirping constant on the dissociation. Figure 6(a) shows the results of a chirped pulse at $I = 10^{13}$ W cm^{-2} for initial frequency $\Omega_0 = \omega_{01}$ in a time duration of 120 cycles. The dissociation probability for the $\Omega_0 = \omega_{01}$ case is rather small in the linear chirping case. But in the corresponding case of quadratic chirping, the dissociation probability is important. Figure 6(b) shows the dissociation probability for $\Omega_0 = 1.1\omega_{01}$. Comparing with the linear chirping case in figure 5, we can see that the dissociation threshold of quadratic chirping is lowered, and the dissociation probabilities are larger. Above threshold, the dissociation rises rapidly and fluctuates around some value higher than the linear one. Note that even in the resonant case of initial frequency $\Omega_0 = \omega_{01}$, there is a significant dissociation probability. Since the chirp is from blue to red, one may question how the first step of the quantum ladder was climbed. However, as shown by Vrijen *et al* (1997), the field intensity used to achieve significant transfer has already distorted the unperturbed bound levels, and the initial resonance frequency between the ground state and the first excited state is no longer the dominant role in the excitation process. The results also show that the method of chirping is important to the dissociation and that quadratic chirping is more efficient than linear chirping.

In summary, we have studied diatomic molecules under the chirped pulse and its related dynamics. We find that the chirp significantly enhances the dissociation probability even under moderate field intensity. Besides the population mechanism, we find that the quantum dissociation probability is suppressed with respect to the classical one when the field strength is stronger than the classical dissociation threshold. The corresponding phenomenon has been of much interest in connection with the microwave ionization of hydrogenic Rydberg states. The dissociation probability is also found to increase with increasing value of the chirping constant. Also, the resonance of the initial field frequency with the unperturbed ground and the first excited states no longer plays the decisive role in vibrational ladder climbing. For simplicity, this letter only deals with the vibrational states of the Morse oscillator. The coupling of the rotational levels and the higher electronic states is now under investigation and will be reported elsewhere.

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