Nonlinear Dynamics of Chirped Pulse Excitation and Dissociation of Diatomic Molecules

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The classical dynamics of a diatomic molecule modeled by a Morse oscillator interacting with a chirped infrared laser pulse is studied. When the chirping rate is small, the system can be described approximately in the moving frame by a time-independent Hamiltonian, which produces single-node separtrices (buckets) in phase space. Systems trapped in the buckets undergo convection to dissociation. This route to dissociation is different from the chaotic diffusion route for monochromatic excitation and requires a much lower threshold laser intensity to achieve dissociation.

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The study of excitation and dissociation of molecules by infrared lasers has been a subject of interest for many years [1]. Up to now, experimental results are available only for polyatomic molecules. Because of their simplicity, much of the theoretical effort has been directed towards diatomic molecules, and classical mechanics provided much insight into the analysis. The dynamics for fixed frequency excitation of diatomic molecules is now quite well understood: The motion undergoes a transition from quasiperiodicity at low excitation intensity to chaos at higher intensity via overlapping of resonance, and then the system diffuses towards dissociation after the breakup of the last bounding tori [2–4]. Furthermore, the threshold intensity can be estimated by applying the Chirikov resonance overlap criterion [3–5]. However, it has been shown that at the high laser intensity required to achieve significant dissociation of diatomic molecules the ionization process dominates, making monochromatic dissociation without ionization unlikely [6].

Recently, it was demonstrated by quantum mechanical calculations that chirped lasers can be used to reduce the intensity required for infrared multiphoton dissociation of diatomic molecules to an intensity range that is achievable in present-day laboratories [6–9]. In view of the importance of chirped lasers, it would be useful to provide a classical, intuitive picture of the excitation and dissociation mechanisms. This is the objective of the present paper.

Frequency chirping also occurs in plasma physics, and particle motion in a wave with time-dependent frequency has been analyzed in terms of bucket dynamics [10]. Similar ideas can be applied to the present situation. As in previous work [3,4,6–9], the diatomic molecule is represented by a Morse oscillator, so that the Hamiltonian of the driven system in dimensionless units is given by

$$\begin{aligned} H(x,p,t) &= H_0(x,p) - Bx\cos[\Omega(t)t], \\ H_0(x,p) &= \tfrac{1}{2}p^2 + \tfrac{1}{2}(e^{-2x} - 2e^{-x}). \end{aligned} \tag{1}$$

Here, energy is measured in terms of $2D$, where D is the dissociation energy of the diatomic molecule, length is measured in terms of $1/\alpha$, the range of the Morse oscillator, and angular frequency is measured in terms of the harmonic frequency of the Morse oscillator $\omega_0 = \alpha\sqrt{2D/M}$, where M is the reduced mass of the molecule. It is assumed that the dipole moment of the molecule can be written as $q_e x/\alpha$, so that the driving amplitude B is related to the electric field E of the laser by $B = q_e E/2\alpha D$. The driving frequency is assumed to be of the form

$$\Omega(t) = \Omega_0\left[1 - \frac{1}{2}\left(\frac{t}{\tau_{sw}}\right)^{n_p}\right], \tag{2}$$

and we shall study the linear chirping case with $n_p = 1$ in detail. In terms of the action-angle variables (i,θ), the molecular Hamiltonian takes the simple form $H_0(i) = -\frac{1}{2}(1-i)^2$ so that the frequency of unperturbed motion is given by $\omega(i) = \partial H_0/\partial i = 1 - i$, and the Cartesian coordinate x can be expanded in a Fourier series in θ [3,4,11]. When $\Omega(t)$ is a slowly varying function of time, adiabatic invariance allows us to define instantaneous resonance frequencies and action satisfying $\Omega(t) = m\omega(i_m)$, $m = 1,2,\ldots$, yielding $i_m = 1 - \Omega(t)/m$. Expanding the total Hamiltonian about i_m and keeping only the resonant excitation term, we obtain the Chirikov Hamiltonian

$$H(\theta,j,t) = -\frac{j^2}{2} + \frac{\Omega}{m}j + BG_m\cos[m\theta - \Omega(t)t], \tag{3}$$

where $j = i - i_m$, $G_m = m^{-1}[i_B/(2-i_B)]^{m/2}$, and i_B is the value of i at the stable fixed point of the system. For fixed frequency excitation, $i_B = i_m$. For chirped pulse excitation, the value of i_B will be discussed below. Finally, a time-independent Hamiltonian can be obtained by making a canonical transformation to the "moving frame" with $\psi = \frac{\Omega}{m}t - \theta$ and $J = j + \frac{\dot{\Omega}}{m}t$:

$$\begin{aligned} K(\psi,J) &= \frac{J^2}{2} + V(\psi), \\ V(\psi) &= -BG_m\cos m\psi - \frac{\dot{\Omega}}{m}\psi, \end{aligned} \tag{4}$$

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where, for linear chirping with $n_p = 1, \dot{\Omega} = -\Omega_0/2\tau_{sw}$ is a constant. $V(\psi)$ will have local maxima and minima and thus creating "buckets" if

$$|\dot{\Omega}|/m^2 BG_m < 1\,. \tag{5}$$

Then the centers or stable fixed points of K occur at $J = 0$ and $\psi_c^l = (2l\pi - \delta)/m$, where $\delta = \sin^{-1}\{|\dot{\Omega}|/m^2 BG_m\}, l = 0, \pm 1, \pm 2, \ldots$; and the saddle points are given by $J = 0$, $\psi_s^l = [(2l + 1)\pi + \delta]/m$.

The buckets are defined by the trapped regions of the separatrices passing through the saddle points. In Fig. 1 we sketch the potential $V(\psi)$ and the phase space trajectories for $K(\psi, J)$, which are similar to those in [10]. As in [10], trajectories inside the buckets will oscillate about the centers whose actions increase in time according to $i_B(t) = i_m - \dot{\Omega} t/m = 1 - \Omega_0/m + \Omega_0 t/m\tau_{sw}$ and dissociate when $i_B \sim 1$. The trajectories located initially far from the separatrices will not be confined by the buckets; they will oscillate about constant (negative) values of j asymptotically and will not dissociate.

In Figs. 2(a) and 2(b), we show the trajectories obtained by numerically integrating Hamilton's equations for the Hamiltonian of Eq. (1) for $\Omega_0 = 0.9$ and 1.1, respectively, and observe that their behavior did fall into these two categories. For $\Omega_0 = 1.1$, the lowest initial resonant action is $i_2 = 0.45$, and the trajectory with initial action $i(0) = 0.1$ simply oscillates about a constant value until $\Omega(t)$ decreases sufficiently to trap it in the first resonance zone and carry it upwards. The slopes of the dissociating trajectories all have numerical values very close to $\Omega_0/m\tau_{sw}$ and the slope of $i_B(t)$.

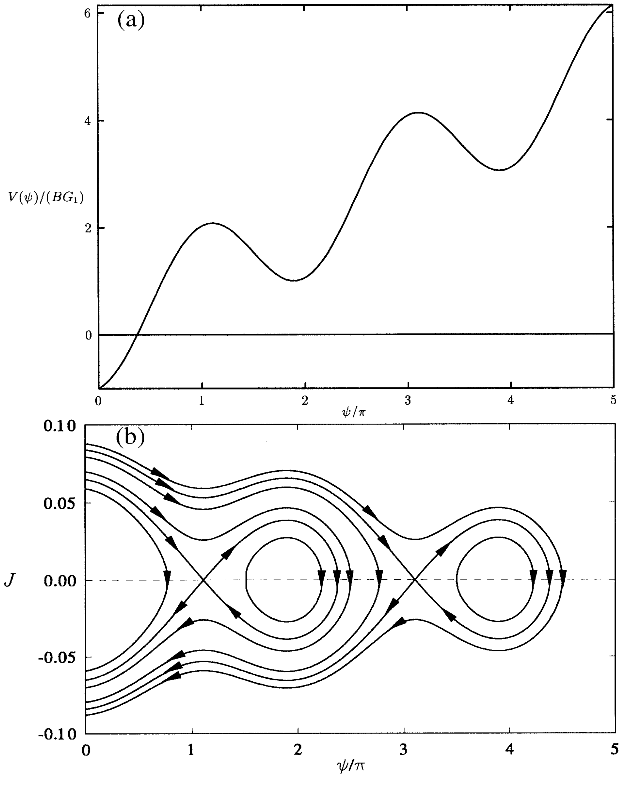

FIG. 1. (a) The potential $V(\psi)$, and (b) phase space portrait in the moving frame for $B = 0.003$, $m = 1, \Omega_0 = 0.9$, and $\tau_{sw} = 2000$.

The Poincaré maps of the dissociating trajectories, obtained by recording the values of the action-angle variables before dissociation at times t_n given by $\Omega(t_n)t_n = 2n\pi, n = 0, 1, 2, \ldots,$ are presented in Figs. 3(a) and 3(b) for $\Omega_0 = 0.9$ and 1.1, respectively. Note that at $t_n \bmod(\theta, 2\pi) = 2\pi \bmod(\psi, 2\pi)$. These phase portraits indeed correspond to those for $K(\psi, J)$, and resemble those for fixed frequency excitations [3,4]. Thus for trajectories near the resonant actions i_m and trapped by the buckets the approximate Hamiltonian Eq. (4) provides a good description of the dynamics.

The physical picture that emerges from the above studies on chirped pulse dissociation is the following: Dissociation occurs when the system is trapped by the bucket in phase space and transported convectively upwards in

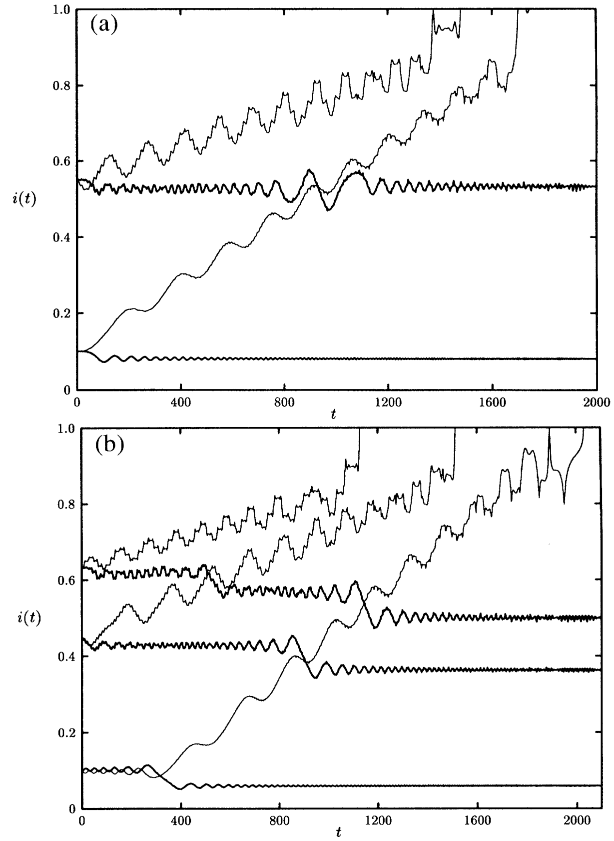

FIG. 2. Exact trajectories for $B = 0.003$ and $\tau_{sw} = 2000$. (a) $\Omega_0 = 0.9$. The initial conditions for the bound trajectories are $(i(0), \theta(0)) = (0.1, \pi), (0.55, 0.5\pi)$, while those for the dissociating trajectories are $(i(0), \theta(0)) = (0.1, 0), (0.55, 0.8\pi)$. (b) $\Omega_0 = 1.1$. The initial conditions for the bound trajectories are $(i(0), \theta(0)) = (0.1, \pi), (0.45, 1.6\pi), (0.633\,33, \pi)$, while those for the dissociating trajectories are $(i(0), \theta(0)) = (0.1, 1.8\pi), (0.45, 1.8\pi), (0.633\,33, 0.8\pi)$.

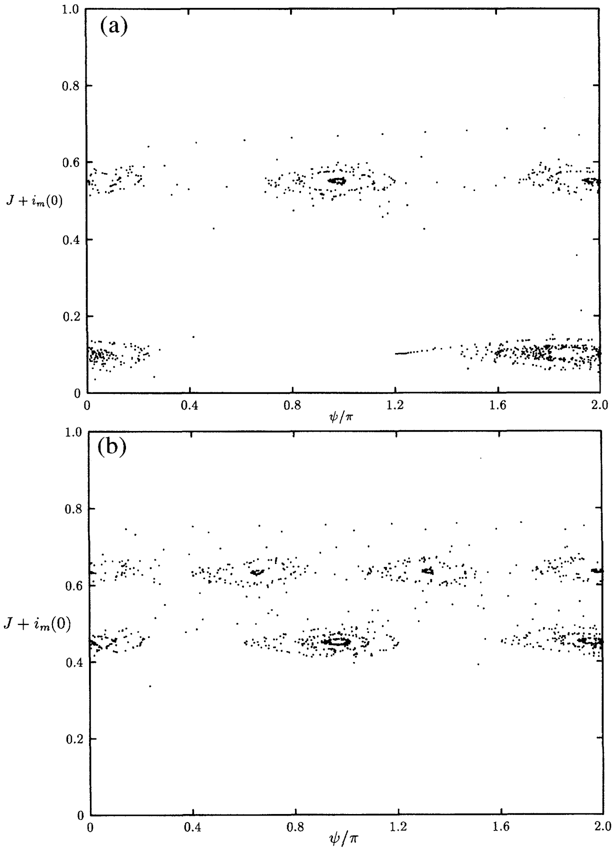

FIG. 3. Poincaré maps of the dissociating trajectories for $B = 0.003$ and $\tau_{sw} = 2000$. To aid visualization, we plot $J + i_m(0)$ vs ψ/π, where $i_m(0) = 1 - \Omega_0/m$ is the initial resonance action closest to $i(0)$. (a) $\Omega_0 = 0.9$. The initial angles for the trajectories with initial action $i(0) = 0.1$ are $\theta(0)/\pi = 0, 0.4, 0.8$, while those with initial actions $i(0) = 0.55$ are $\theta(0)/\pi = 0, 0.2, 0.8$. (b) $\Omega_0 = 1.1$. The initial angles for the trajectories with initial action $i(0) = 0.45$ are $\theta(0)/\pi = 1.0, 1.2, 1.8$, while those with initial actions $i(0) = 0.633\,33$ are $\theta(0)/\pi = 0, 1.2, 1.6$.

action at a rate of $\Omega_0/m\tau_{sw}$, which is proportional to the chirping rate. This route to dissociation is very different from the case of fixed frequency excitation, where neighboring resonance zones begin to overlap and the system becomes chaotic and diffuses in phase space to dissociation.

Associating with each value of B satisfying the existence condition of (5) is a bucket or resonance zone, whose width Δi centered at i_B is given by $\frac{1}{2}(\Delta i)^2 = V(\psi_s^l) - V(\psi_c^{l+1})$, where the right hand side is the depth of the bucket. The system will be trapped in the bucket if its initial action lies within Δi, which allows us to estimate the threshold field strength for dissociating a diatomic molecule. Using the Einstein-Brillouin-Keller (EBK) quantization rule [12], the action for a Morse oscillator in the ground vibrational state is given by $i(0) = \frac{1}{2}\hbar\alpha/\sqrt{2MD}$. For the NO molecule with $D = 6.4968$ eV and $\alpha = 2.768\,06$ Å^{-1} [13], we obtain $i(0) = 0.0091$. Thus the relevant resonant action is i_1, and we only have to consider the approximate Hamiltonian Eq. (4) with $m = 1$. Then the threshold amplitude B_{th} is estimated by finding the minimum value of B satisfying $|i_B - i(0)| = \Delta i$. This theoretical value of B_{th} can be compared with the corresponding one determined numerically by the following procedure: For each value of Ω_0 and B, the dissociation probability P_D can be computed from the fraction of dissociating trajectories when 100 trajectories with evenly distributed initial angles are integrated. The numerical threshold amplitude at which $P_D \rightarrow 0^+$ can then be determined using the bisection method. In Table I, we present the values of B_{th} determined by these two methods. The qualitative behavior of the numerical results is similar to those calculated from bucket dynamics especially for $\Omega_0 > 1$, although the optimal Ω_0 is determined numerically to be 1.02, while the bucket dynamics consideration yields the value 0.98.

In Fig. 4 we present dissociation trajectories for four different cases to illustrate the effects of changing the time dependence of the driving frequency and of using a more realistic dipole moment function. We see that the trajectories of a nonlinear chirped pulse [with $n_p = 2$ in Eq. (2)] oscillate about $i_B(t)$, which now increases quadratically with time, showing that the picture of bucket dynamics applies to this case as well. A realistic dipole moment function for NO has been obtained from a fit with *ab initio* calculations [14]

$$\mu(x) = \kappa y e^{-y/b}, \qquad y = (\alpha'/\alpha)x + a, \tag{6}$$

where $\alpha' = 1.29$ Å^{-1}, $a = 0.1058$, $b = 0.6017$, and κ is chosen to be $(\alpha/\alpha')[e^{a/b}/(1 - a/b)]$ so that $d\mu/dx = 1$ at $x = 0$. The trajectories using $\mu(x)$ initially follow closely those using the linear dipole function [Eq. (1)], but begin to get out of phase when x becomes large and $\mu(x)$ is no longer linear in x, and reaches a plateau before finally dissociating. Nevertheless, the initial excitation of the molecule to a highly excited state is well described by the convectional mechanism discussed above. Also, the dissociation threshold using $\mu(x)$ is found to be about a factor of 2 higher than the linear dipole case.

Finally, we have calculated classically the dissociation probabilities P_D for the chirped pulse of Ref. [6], employing 1000 trajectories. Our results are very similar to the quantum results shown in their Fig. 1, with P_D rising rapidly at about 96 cycles to reach an asymptotic value, except that our P_D approaches 0.4 instead of 0.5. Furthermore, we have calculated P_D as a function of the pulse area S (Fig. 3 of Ref. [6]). Again the classical results are similar to the quantum ones, except the peak P_D occurs at $S = 1.3\pi$ instead of 1.6π. Similar agreement between quantum and classical results has also been observed in Ref. [9].

In summary, we have analyzed the classical dynamics of chirped pulse excitation of a diatomic molecule where the excitation frequency is a linearly decreasing function

TABLE I. Threshold amplitudes as a function of Ω_0.

Ω_0	0.90	0.95	0.98	1.00	1.02	1.05	1.10
$100B_{\text{th}}$ (theory)	1.05	0.47	0.31	0.32	0.32	0.33	0.34
$100B_{\text{th}}$ (numerical)	1.81	0.86	0.45	0.32	0.27	0.29	0.31

of time. When the rate of frequency chirping is small, adiabatic invariance allows us to reduce the Hamiltonian of the system to a time-independent Hamiltonian in a moving frame governing bucket dynamics. The route to dissociation is now clear: When the trajectory of the system in phase space is trapped by the bucket in the moving frame, it will be carried upwards convectively until it dissociates. The threshold amplitude for photodissociation of molecules in the their ground vibrational states is then determined by the existence condition of the bucket and the overlap of the initial action with the lowest order resonance action. This is much smaller than the threshold amplitude for fixed frequency excitation, which requires the overlap of adjacent resonance zones to initiate diffusive chaotic motion. For the NO molecule, $q_e = 0.25e$, the threshold amplitude at $\Omega_0 = 1.05$ is determined numerically to be $B = 0.0065$ using $\mu(x)$ of Eq. (6), which corresponds to a laser intensity of 1.16×10^{13} W/cm^2. Lower threshold intensity could be obtained by optimizing the pulse shape [6,9], and it should be possible to photodissociate such a molecule using infrared chirped laser pulses in the laboratory.

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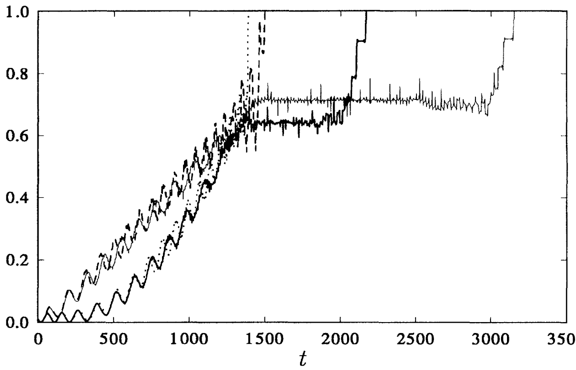

FIG. 4. Dissociating trajectories for the molecule NO initially in its ground vibrational state with $i(0) = 0.0091, \theta(0)/\pi = 1.6$, $B = 0.014$, $\tau_{sw} = 2000$, and $\Omega_0 = 1.05$. Dashed line: linear dipole moment, $n_p = 1$; dotted line: linear dipole moment, $n_p = 2$; thin solid line: nonlinear dipole moment, $n_p = 1$; thick solid line: nonlinear dipole moment, $n_p = 2$.

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