Efficient Molecular Dissociation by a Chirped Ultrashort Infrared Laser Pulse

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Dissociation probabilities and populations of excited vibrational states are calculated numerically for interaction of a Morse oscillator with a chirped, ultrashort ($t_p < 10^{-11}$ sec), intense laser pulse. It is shown that if the pulse frequency $\omega(t)$ decreases at a specific rate, adapted to the molecular anharmonicity, the dissociation probability is many orders of magnitude higher than for a monochromatic pulse of the same intensity. Such pulses should be useful for more efficient multiphoton dissociation of molecular bonds.

This paper introduces a new and practical approach to the control of molecular dissociation. We show that an appropriately chirped pulse can selectively excite a diatomic molecule to high vibrational levels. We also show that dissociation rates are sensitive to the form of the excitation pulse. Both selective excitation and dissociation are experimentally accessible as a result of recently developed ultrashort-pulse techniques[1] to generate broad-bandwidth midinfrared radiation[2-4] which can be phase and amplitude controlled with sufficient precision to follow the level spacing of a diatomic molecule.

The anharmonicity of molecular vibrations has been the major obstacle to dissociation of small molecules both in theoretical calculations[5-7] and in experiment.[8] Recent numerical studies[5] of dissociation of HF using monochromatic subpicosecond pulses show a dissociation probability smaller than 10^{-5} for intensities less than 10^{14} W/cm^2. Although such calculations often proceed to still higher intensities,[5,6] judging from atomic experience[9] an intensity of only 3×10^{13} W/cm^2 may be unrealistically large since, for $I > 3 \times 10^{13}$ W/cm^2, the ionization rates will exceed dissociation rates for many molecules. In other words, models in which only vibrational degrees of freedom are considered cannot be used for such high intensities. The only possible conclusion from these models is that monochromatic dissociation without ionization is unlikely. In contrast, we show that a pulse whose frequency is decreasing as a function of time, in such a way that the pulse is resonant with transitions between higher levels for later times, increases the dissociation probability by many orders of magnitude.

The behavior of two-level systems[10-12] suggests how to devise appropriately shaped pulses. The transition amplitudes, in such systems, are functions of the pulse area defined by

$$\sigma(t) = (p/\hbar) \int_{-\infty}^{t} \varepsilon(t')dt', \tag{1}$$

where p is the transition dipole moment and $\varepsilon(t)$ is the slowly varying electric-field envelope. The complete inversion of population occurs when the pulse area is equal to π. Thus one might expect that a series of N pulses each of frequency $\omega_{n,n+1} = (E_{n+1} - E_n)/\hbar$, where E_n are

vibrational levels of the molecule, and each having the area [defined by (1) in which $p = p_{n,n+1}$] equal to π should completely transfer the population from the ground state ($n = 0$) to the Nth excited state.

Such pulse sequences can probably be constructed using emerging experimental techniques.[1] For low-intensity radiation, dissociation would require many components to the pulse sequence, each satisfying exact resonance and constant-area conditions. Since the transition frequencies and transition dipole moments between higher excited states are usually not well known, this may be impractical. Moreover, at low intensities the whole sequence could take longer than the various relaxation times in the molecular medium. Thus we concentrate on sufficiently high intensities that the dynamic Stark effects overwhelm these problems and a continuously chirped pulse can be used. Such chirped pulses can be comparatively easily generated using modern laser technology.[2-4]

Our calculation scheme describing the interaction of radiation with a Morse oscillator is based on the time-dependent Schrödinger equation with the Hamiltonian

$$H = H_0 + V(x,t), \quad H_0 = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2}, \tag{2}$$

$$V(x,t) = D[1 - \exp(-ax)]^2 - d_1 x E_M U(t) \cos[\omega(t)t],$$

where $x = r - r_0$, r_0 is the equilibrium separation of nuclei, m is the molecule's reduced mass, d_1 is the effective charge or dipole gradient, E_M is the maximum value of the radiation electric field, and $U(t)$ is the pulse envelope chosen equal to 1 at the maximal value of the electric field. The energy eigenvalues E_n of the Morse oscillator are[6,13,14]

$$E_n = \hbar\omega_0(n + \tfrac{1}{2})[1 - B(n + \tfrac{1}{2})/2], \tag{3}$$

where

$$\hbar\omega_0 = 2BD, \quad B = \left[\frac{\hbar^2 a^2}{2mD}\right]^{1/2}, \tag{4}$$

$$n = 0, 1, \ldots < 1/B - 1/2.$$

Our task now is to find such a pulse shape $\varepsilon(t) = E_M U(t)$ and pulse frequency $\omega(t)$ that the resonance and area conditions mentioned in the introduction are satisfied; i.e., we require that

$$(p_{0,1}/\hbar) \int_0^{t_1} \varepsilon(t)dt = S_0 ,$$

$$(p_{n,n+1}/\hbar) \int_{t_n}^{t_{n+1}} \varepsilon(t)dt = S , \qquad (5)$$

$n = 1, \ldots, N-1$, where S_0, S are area values, and N is

$$U(t) = \begin{cases} [1 - \text{sech}(\alpha_0)]^{-1}\{\text{sech}[\alpha_0(t - t_0)/t_0] - \text{sech}(\alpha_0)\} & \text{for } t < t_0 , \\ 1 & \text{for } t_0 < t < t_c , \\ [1 - \text{sech}(\alpha_F)]^{-1}\{\text{sech}[\alpha_F(t - t_c)/t_0] - \text{sech}(\alpha_F)\} & \text{for } t > t_c , \end{cases} \qquad (7)$$

allows us to integrate analytically conditions (5). In Eq. (7) α_0, α_F, t_c, and t_0 are free parameters determining the pulse switching on and switching off. They are chosen here to be $\alpha_0 = 2.5$, $\alpha_F = 6.25$, $t_c = t_N + 0.2t_0$. We assumed that chirping starts at $t = t_0$, i.e., when the pulse achieved its maximal value. Thus

$$\omega(t) = \omega_{0,1} \text{ for } t < t_0 . \qquad (8)$$

Equations (5)–(8) determine $t_0, t_1, \ldots, t_N$ uniquely and the function $\omega(t)$ can be found by interpolation. An analytical expression for $\omega(t)$ can be found when the harmonic-oscillator formula for dipole moments

$$p_{n,n+1} = (n+1)^{1/2}p_{0,1} \qquad (9)$$

holds. For HF Eq. (9) is a good approximation up to the twelfth level. Using Eq. (9) the second part of (5), with $U(t)$ given by (7), becomes

$$t(n+1) - t(n) = Q(n+1)^{-1/2} , \qquad (10)$$

where $n = 1, 2, \ldots, N$, $t(n) \equiv t_n$, and

$$Q = S\hbar/p_{0,1}E_M . \qquad (11)$$

The function $t(n)$ can be easily found from (10) if one uses the Taylor expansion $t(n+1) \simeq t(n) + dt/dn$. Thus one gets

$$t(n) = 2Q[(n+1)^{1/2} - 2^{1/2}] + t_1 \qquad (12)$$

and from (6) $\omega(t_n) \equiv \omega(n) = \omega_0(1 - Bn - B/2)$. Thus after calculating from Eq. (12) n as a function of t one gets the following form of a chirp, which approximately satisfies requirements (5) and (6):

$$\omega(t)/\omega_0 = -B[(t - t_1)^2/4Q^2 + 2^{1/2}(t - t_1)/Q + \tfrac{3}{2}] + 1 . \qquad (13)$$

The values of t_0 and t_1, calculated from the first part of Eq. (5) and from Eq. (8), are given by

$$t_0 = Q\frac{S/S_0 - 2[2^{1/2} - (\tfrac{3}{2})^{1/2}]}{A+1} , \quad t_1 = \frac{QS}{S_0} - At_0 , \qquad (14)$$

the level number up to which the approximate resonance conditions

$$\hbar[\omega(t_n) + \omega(t_{n+1})]/2 = E_{n+1} - E_n$$

$$= \hbar\omega_0[1 - B(n+1)] \qquad (6)$$

are imposed. Equations (5) fix the pulse area in the interval (t_n, t_{n+1}) and Eq. (6) ensures that in the center of this interval the pulse is resonant with the transition from the nth to $(n+1)$th level. The following choice of pulse shape $U(t)$,

where

$$A = \frac{2\{\pi/4 - \tan^{-1}[\exp(-\alpha_0)]\}/\alpha_0 - 1}{1 - \text{sech}(\alpha_0)} .$$

The pulse shapes $U(t)$ and chirps $\omega(t)$ resulting from the above formulas, for laser peak intensities $I = (c/8\pi)E_M^2$ (the incident radiation is assumed to be linearly polarized) equal to 10^{12} and 10^{13} W/cm^2, are shown in Figs. 1(a) and 2(a).

We have integrated numerically the time-dependent Schrödinger equation, using the Hamiltonian given by Eq. (2), pulse shapes and chirps we have just found, and the following values of parameters,[6,13] corresponding to
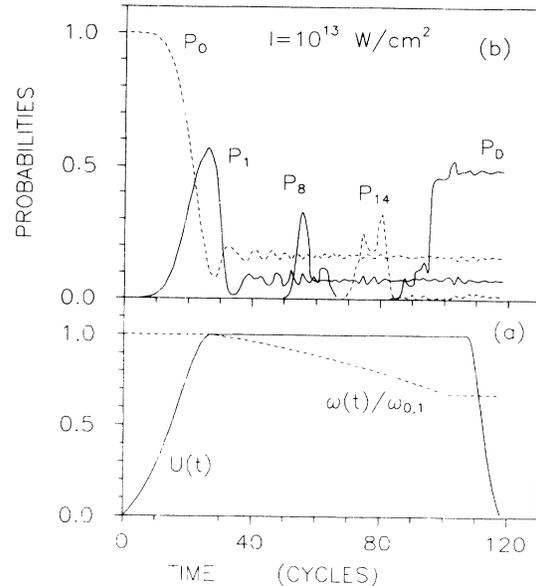
FIG. 1. Time dependence of (a) pulse shapes (——) $U(t) = \varepsilon(t)/E_M$, (---) chirps $\omega(t)/\omega_{0,1}$, and (b) the resulting populations (---) $P_0(t)$, (——) $P_1(t)$, (——) $P_8(t)$, (---) $P_{14}(t)$, and dissociation probability (——) $P_D(t)$, at the intensity $I = 10^{13}$ W/cm^2, $N = 8$, $S = S_0 = 1.5\pi$. 1 cycle = 8.41 fm.
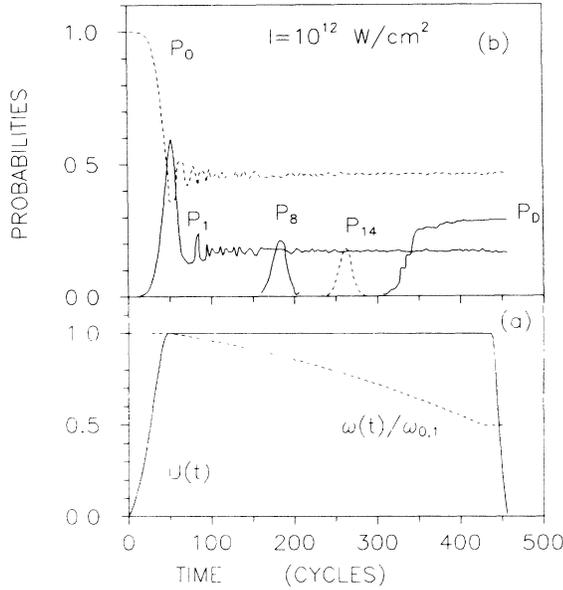
FIG. 2. The same as in Fig. 1 but for the intensity $I = 10^{12}$ W/cm^2, $N = 12$, $S = 1.8\pi$, $S_0 = 1.2\pi$.

HF: $B = 0.0419$, $D = 6.125$ eV, $a = 1.1741a_0^{-1}$, $d_1 = 0.786$ Db/a_0, $r_0 = 1.7329a_0$. The molecule was assumed to be in its vibrational ground state ($n = 0$) at $t = 0$. The transition dipole moment $p_{0,1}$ for HF was calculated with the help of the following expression:

$$p_{01} = d_1 \langle \psi_1 | x | \psi_0 \rangle \cong d_1 (B/2)^{1/2}/a = 0.097 \text{ Db}, \quad (15)$$

where ψ_n are Morse eigenfunctions.[6,14] For these parameters the Morse potential supports 24 bound states and its characteristic vibrational period is $t_c = 2\pi/\omega_{0,1} = 8.41 \times 10^{-15}$ sec, which is equal to the radiation cycle for $t < t_0$.

The calculations were performed with the help of the split-operator technique,[15,16] in which the evolution of the wave function over the time interval δt is given by

$$\psi(x, t + \delta t) = \exp \left[\frac{-iV(x, t')\delta t}{2\hbar} \right] \exp \left[\frac{-iH_0\delta t}{\hbar} \right]$$

$$\times \exp \left[\frac{-iV(x, t')\delta t}{2\hbar} \right] \psi(x, t), \quad (16)$$

where $t' = t + \delta t/2$. The second exponential from this expression containing the second derivative with respect to x was evaluated in momentum space, using fast-Fourier-transform techniques. The wave function was confined in a box of size $L = 130$ a.u. and 2048 space steps were used. The size of the box was chosen so that the wave function was rapidly decreasing well before the edges of the box. The time step δt was equal to $0.001t_c = 8.41 \times 10^{-18}$ sec. We calculated the populations $P_n(t)$ of all vibrational levels and the dissociation
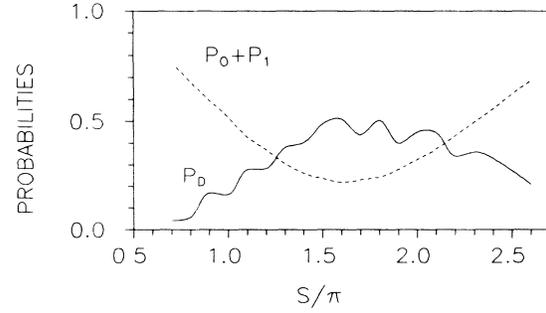
FIG. 3. Dissociation probability (——) P_D and (---) $P_0 + P_1$ at the end of chirped pulse for the laser intensity $I = 10^{13}$ W/cm^2, $N = 8$ as a function of the area S ($S_0 = S$).

probability $P_D(t)$ using the following formulas:

$$P_n(t) = |\langle \psi_n | \psi(t) \rangle|^2, \quad P_D(t) = 1 - \sum_{n=0}^{23} P_n(t). \quad (17)$$

The time evolution of the populations $P_0(t)$, $P_1(t)$, $P_8(t)$, and $P_{14}(t)$ and of the dissociation probability are shown in Fig. 1(b) ($I = 10^{13}$ W/cm^2) and in Fig. 2(b) ($I = 10^{12}$ W/cm^2) for the pulses displayed in Figs. 1(a) and 2(a), respectively [for comparison, the dissociation probability at the end of a pulse having no chirp, resonant with $\omega_{0,1}$, but otherwise similar to that in Fig. 1(a), is less than 10^{-10}]. One sees clearly that the frequency $\omega(t)$, decreasing according to Eq. (13), constitutes the "force" driving populations upward much beyond the $N = 8$ level [the chirp from Fig. 1(a) stops at the frequency corresponding to the transition from level 7 to 8] yielding 50% dissociation. The fact that such a small chirp is sufficient to give such efficient dissociation results from dynamic Stark shifts[5,10] of higher vibrational levels. Already for the $0 \to 1$ transition, the Rabi frequency exceeds the detuning $\Delta = 2B^2D$ at an intensity of 10^{13} W/cm^2.[5] This implies that for high intensities, our predictions are insensitive to the asymptotic behavior of the molecular potential.

The area $S = S_0 = 1.5\pi$, chosen for the case shown in Figs. 1(a) and 1(b), gives the largest probability, as seen from Fig. 3. There are two reasons why S is greater than π: (i) The larger area compensates the error introduced by using a Taylor expansion for small values of n in solving Eq. (10), and (ii) increasing the area compensates for the less efficient population transfer with a continuously chirped pulse due to nonresonance effects. Figure 3 also shows that greater than 25% dissociation is obtained over a factor of 2 in pulse area (equivalent to a factor of 4 in pulse intensity or a factor of 2 in chirp rate). Although the concept of chirped-pulse dissociation requires that dissociation be sensitive to the phase structure $[\omega(t) \cong d\Phi(t)/dt]$ of the pulse, the dynamic Stark effect ensures that there will be no practical difficulty with pulse preparation.

In order to obtain similar dissociation probabilities [actually slightly smaller, Fig. 2(b)] for $I = 10^{12}$ W/cm^2, we must choose different values of the area S_0 and S and continue the pulse chirp down to the transition frequency $\omega_{11,12}$. Such an intensity is well below multiphoton-ionization intensities.

We have presented our results for the parameters of HF in order to compare to previous calculations for diatomic molecules. However, the parameters appropriate to the excitation and dissociation of DCl are more accessible to the current laser technology since its vibrational frequency is close to the second harmonic of currently available ultrashort-pulse CO_2 lasers. The predictions are qualitatively similar.

In conclusion, we have introduced a new method of molecular control[17] in which only phase variation of the pulse, not of its amplitude, determines the level of excitation or dissociation. The control implicit in chirped-pulse dissociation is very strong. This statement is intuitively clear if we consider two pulses which are identical except for an opposite frequency chirp, i.e., $\omega(t)$ being an increasing function of time in the second pulse. Of the two pulses, one will leave little or no excitation above the first excited state, while the other, as we have shown, can lead to at least 50% dissociation. It is important to consider whether this approach can be applied to a polyatomic molecule in view of exciting selectively a particular molecular bond. High intensities, $I > 10^{12}$ W/cm^2, are still necessary to achieve excitations faster than a picosecond, which is the order of intramolecular relaxation in polyatomic molecules. Chirping according to Eq. (13) achieves this goal, so that single bond excitation should be possible in polyatomic molecules, while working at intensities below ionization thresholds.

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