Ultrashort laser pulse suppression of dissociation in a molecule

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Abstract. Effect of laser pulse in suppressing the dissociation of a molecule is shown. The time dependent Schrödinger is solved numerically for a molecule in an intense laser pulse whose uppermost state is connected to continuum.

There has been much interest recently in the study of atoms and molecules exposed to intense laser fields [1,2]. A related problem of laser induced stabilization of atomic Rydberg states has also attracted a great deal of attention in recent years [3,4].

Recent theoretical studies have proved that atoms under a very strong high frequency field will be relatively stable against ionization [5]. But the predicted frequency leading to stabilization is much higher than the ionization potential [6]. This kind of laser frequency required for stabilization for systems prepared in the atomic ground states is not available in current laser sources.

Incidentally, the dissociation dynamics of a diatomic molecule under intense laser shows similar characteristics of atomic-strong field phenomena [7,8]. It would then be interesting to study the corresponding molecular stabilization against dissociation with the currently available laser sources. The present problem is oriented along this line.

We report here the results of simulations of interaction of short and long laser pulses with the molecule. We have solved numerically the time dependent Schrödinger equation for the molecule in intense laser pulse with its last level connected to continuum by introducing an irreversible loss from that state.

A point worth mentioning here is that it is found the dissociation can be suppressed by using short laser pulse. This study will be very helpful in exposing the molecule at high intensity without dissociation which in turn will be directly helpful in controlling the transition region of the chemical reaction which exists for a very short time of the order of few picosecond [9].

We consider the interaction of laser pulse with a molecule with the last state being connected to the continuum by introducing an irreversible loss Γ from this state [10]. The

Man Mohan, Vinod Prasad and Rinku Sharma

Hamiltonian for the system describing the coupling of molecule with the laser field in the semiclassical dipole approximation is given by

$$H = H^0 - \vec{\mu} \cdot \vec{\varepsilon}(t), \tag{1}$$

where H^0 denotes the Hamiltonian of the unperturbed molecule, $\vec{\mu}$ denotes the electric dipole moment, $\vec{\varepsilon}(t) = \vec{E}_0 f(t) \cos \omega t$ represents the electric field with $f(t)$ representing the shape of the laser pulse and E_0 is the amplitude and ω is the frequency of pulse. The time dependent Schrödinger equation corresponding to (1) in (a.u.) is given by

$$i\frac{\partial}{\partial t}\psi_p(\vec{r}, t) = H(t)\psi_p(\vec{r}, t). \tag{2}$$

The dressed state wave function of the system $\psi_p(\vec{r}, t)$ can easily be expanded in terms of unperturbed wave function of the system $\chi_q(r)$ satisfying

$$H_0 \chi_q(r) = E_q^0 \chi_q(r)$$

as

$$\psi_p(\vec{r}, t) = \sum_{q=1}^{N} C_{qp}(t)\chi_q(\vec{r})\mathrm{e}^{-iE_q^0 t}, \tag{3}$$

where energy of the last state E_ℓ connected to continuum is denoted by $E^\ell = E^i - i\Gamma/2$, Γ is the decay width responsible for irreversible loss from this state.

On substituting (3) in (2) and using the orthogonality conditions for the molecular states we get a set of first order coupled differential equation

$$i\frac{\partial}{\partial t}C_{qp}(t) = E_0 f(t) \cos \omega t \sum_{s=1}^{N} V_{qs}C_{sp}(t), \tag{4}$$

where N is the total number of quantum states considered.

In (4), the matrix element V_{qs} represents

$$V_{qs} = \langle \chi_q(r)|\mu(r)\cos\theta|\chi_s(r)\rangle, \tag{5}$$

where θ is the angle between the polarization vector of the laser and the axis of the molecular system.

The coefficients C_{qp} in (4) can be assembled as a vector $C(t)$. In matrix notation (4) can be written as

$$i\dot{\mathbf{C}}(t) = \mathbf{H_C}(t)\mathbf{C}(t). \tag{6}$$

$\mathbf{H_C}(t)$ is the time dependent interaction Hamiltonian, which is non-periodic in nature. If $\mathbf{H_C}(t)$ would have been periodic one could solve the coupled equations (6) by an elegant non-perturbative Floquet theory [2], but due to its non-periodic nature one has to solve these equations directly using some numerical technique.

In this letter we have taken the example of HF molecule interacting with the laser pulse. We have included all the vibrational levels which can be supported by electronic ground

state of HF molecule. But after $\nu = 14$ levels the probability variation is not much i.e. results are more or less same even after including all the levels of HF molecule. The last vibrational level is connected to continuum with decay width Γ. The coupling matrix in (6) was calculated using the Morse oscillator wave functions [11]. The Morse parameters for HF molecule are those of Preston and Walker [12]. For solving the time dependent coupled equations we have first decoupled the real and imaginary parts of the equations which results in doubling the number of equations. The resultant coupled equations were solved numerically, using the fourth order Runge Kutta (RK) method assuming initially the molecule to be in the ground vibrational state and by employing at least 1000 time steps per optical cycle $T = 2\pi/\omega$.

We consider the interaction of HF molecule with the laser pulse represented by $\vec{\epsilon}(t) = \vec{E}_0 f(t) \cos \omega t$, with

$$f(t) = \exp \left\{ -\frac{(t - t_0)^2}{2\tau^2} \right\},$$

where τ is the temporal width of pulse and $t = t_0$ is the time at which $f(t)$ is maximum.

Figure 1 shows the results of time variations of the populations of $\nu = 0, 1, 2$ and 3 level (other higher excited levels are taken in the calculations but are not shown here) while the curve E corresponds to the population loss from the last level. It can be seen that the population flows out of state $\nu = 0$ and 1 where it initially resides (shown by the decreasing population as time increases), through the excited states, to the uppermost
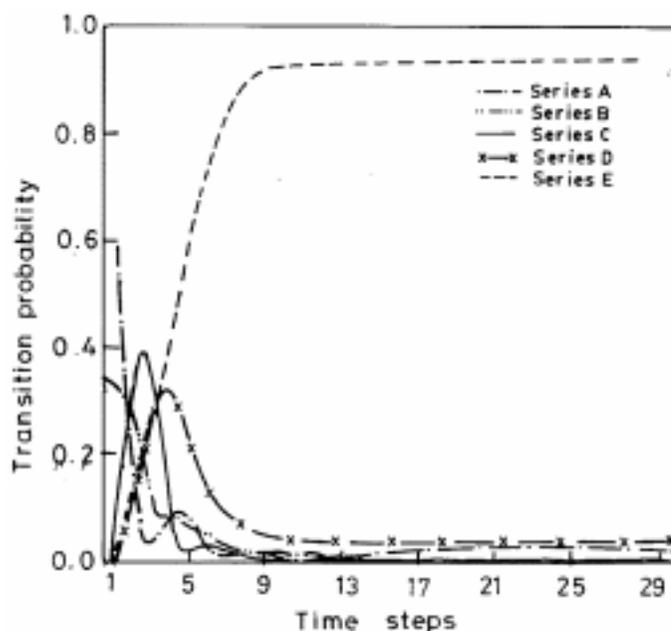

Figure 1. Population histories of $P_0(t)$ (Series A), $P_1(t)$ (Series B), $P_2(t)$ (Series C), $P_3(t)$ (Series D), $P_D(t)$ (Series E) for the HF molecule. Laser pulse is assumed to be of the form $f(t) = e^{-(t-t_0)^2/2\tau^2}$ where $\tau = 6$ optical cycles in the pulse width, $t_0 = 48.32$ fs.
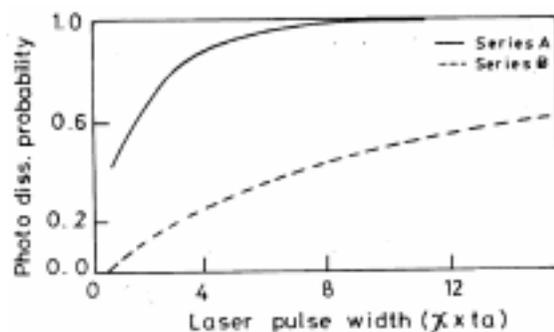
Figure 2. Variation of dissociation probability P_D with laser pulse for $I = 1.0 \times 10^{15}$ W/cm^2 (curve A) and $I = 0.5 \times 10^{14}$ W/cm^2 (curve B), pulse width $\tau = ta \times T, T = 1$ optical cycle.

state, and back. Each time population reaches the last state and ionization loss occurs. Indeed the modelling of ionization by the imaginary term $-i\Gamma/2$ in the Hamiltonian means that the ionization probability grows in direct proportion to the instantaneous population in the last state. Because the population reaches last state periodically, the ionization is not steady; it occurs in periodic spurts.

However, the population of level $\nu = 2$ and $\nu = 3$ increases first, have a maximum and then decreases finally. This is because $\omega = 3778$ cm^{-1} of the laser field is near the resonance frequency $\omega_{23} = 3778.24$ cm^{-1} between levels 2 and 3. The overall population loss from the last state is shown by the curve E, which clearly shows the steep increase initially with time and finally becomes almost constant beyond $T = 18$ optical cycles.

In figure 2, we have shown the effect of laser pulse width on the population loss. The results are presented after $T = 50$ optical cycles. Curve A corresponds to intensity $I = 10^{15}$ W/cm^2. As can be seen from figure, the population loss saturates for long pulses i.e. beyond $T = 10$ optical cycles. However, as the width of laser pulses decreases below $T = 10$ optical cycle the population decreases. Thus the population loss can be inhibited or stabilized against dissociation by using short laser pulses.

A similar effect is also found by decreasing the intensity of the laser pulse as shown by the curve B in this figure. Also as the curve B (at lower intensity) is below the curve A (at higher intensity), therefore there is population loss and increase of intensity is expected. The reason is, since the frequency is near resonance for $\nu = 2$ and $\nu = 3$, so possibility for excitation to various levels also get saturated for higher intensities, and population transfer to other levels remains at minimum. So dissociation probability which is $(1 - P_{\text{excitation}})$ gets saturated. In the case of low intensity, the interaction time for HF molecule and laser pulse is more and thus the ionization probability increases with laser pulse width.

In conclusion we have shown that one can suppress the dissociation by manipulating the width or shape of the pulse. This study will be helpful in studying molecules under ultra intense laser beam without being dissociated.

Acknowledgement

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