Control of reaction channels of CsI molecule by ultra-short laser pulse*

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(Received 10 March 2010; revised manuscript received 8 April 2010)

The influence of the ultra-short pulse wavelength on the populations in the three electronic states of CsI molecule is investigated using the time-dependent wave packet method. The calculated results show that the populations in the two excited states approach to the maxima at the wavelengths of 369 nm and 297 nm, respectively. The photodissociation reaction channels of the CsI molecule can be chosen by controlling the pump pulse wavelength.

Keywords: pump pulse wavelength, time-dependent wave packet method, reaction channel, CsI molecule
PACC: 3380, 3390, 8240J

1. Introduction

With the rapid development of the ultra-short laser pulse technique, the femtosecond laser pulse serves as not only an observation tool,[1−5] but also an efficient way to control the molecular dynamics.[6,7] The effect of external field on molecular potential, which is often called field-matter interaction (FMI),[8] always becomes an interesting topic of many dynamical calculations.[9−12] When molecules are subjected to an intense laser field, some interesting phenomena, such as Rabi oscillation,[13] ac-Stark shift,[14] etc. may appear. In order to investigate the interaction conveniently, the concept of light-induced potential[15] is introduced and applied to the study of the distribution of molecules. For CsI molecule, Ruhman and Kosloff[16] used a chirped ultra-short pulse to control the population in the vibrational state of the ground state. And later, Stibbe *et al.*[17] investigated the dissociative ionization of CsI aggregated with CH_3CN, and observed an oscillatory ionized signal. Kurosaki *et al.*[18] invoked spin–orbit (SO) coupling and calculated thirteen states of CsI molecule with the molecular symmetries 0^+, 0^-, 1, and 2, respectively. Moreover, Alekseyev *et al.*[19] used the three 0^+-state potential energy curves to well describe the photodissociation dynamics of NaI, so the three 0^+ states of CsI molecule are chosen for dynamics calculations, which may be acceptable as a first step of understanding the photochemical nature. The three states with the symmetry $\Omega = 0^+$ are ground state $X0^+$ ($Cs^+(^1S_0) + I^-(^1S_0)$), excited state $A0^+$ ($Cs(^2S_{1/2}) + I(^2P_{3/2})$), and excited state $B0^+$ ($Cs(^2S_{1/2}) + I(^2P_{1/2})$). (Hereafter, we use X, A, and B to denote an ionic state and two covalent states, respectively).

It is known that the ultra-short pulse wavelength plays an important role in the light-matter interaction.[20] To the best of our knowledge, the theoretical study that the ultra-short pulse manipulates the photodissociation reaction[21] of the CsI molecule has not been reported yet. Therefore, in this paper, the effect of the pump pulse wavelength on the populations in each electronic state is investigated using the time-dependent wave packet method. The results may provide some significant information for further investigation on experiment.

2. Theoretical treatment

The three potential energy curves of diabatic states of CsI molecule with symmetry $\Omega = 0^+$ are shown in Fig. 1. To describe the dynamics of CsI in intense field, a pump pulse is used to prepare a

*Project supported by the National Natural Science Foundation of China (Grant Nos. 10674114 and 10604045).
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wave packet on the potential energy curves of the excited states A and B. After that, the prepared wave packet will propagate on the potential energy curves of the CsI molecular states. The ionic and the covalent potential energy curves cross at $R_x = 12$ Å (1 Å = 0.1 nm).[18] The diabatic coupling between the two states is given by[22]

$$\mathrm{Coup_{XA}} = A_{12} \exp[-\beta(R - R_x)^2], \tag{1}$$

where R is the internuclear distance, and A_{12} denotes the effective coupling value given in Ref. [23] as

$$|E_1 - E_2| = 2\,|V_{\mathrm{if}}| = 2\,|A_{12}|\,. \tag{2}$$

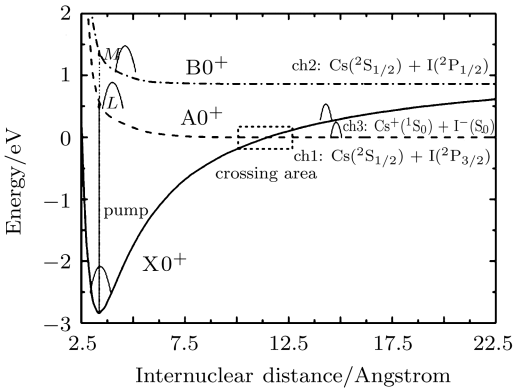


Fig. 1. Schematic representation of the pump and probe scheme with ground and two excited potential energy curves of CaI molecule, cited from Ref. [18].

It can be seen from Fig. 1 that there are two dissociation channels corresponding to the reaction: channel-1 CsI → Cs(^{2}S$_{1/2}$) + I(^{2}P$_{3/2}$) and channel-2 CsI → Cs(^{2}S$_{1/2}$) + I(^{2}P$_{1/2}$). When the excited wave packet passes through the diabatic coupling region, the reaction channel-3 corresponding to the reaction CsI → Cs$^+$ + I$^-$ is formed.

To calculate the population of CsI molecules, the time-dependent wave packet method is applied and the rotational degree of freedom in our treatment is frozen. Invoking the Born–Oppenheimer approximation, the time-dependent Schrödinger equation in the diabatic representation is written as

$$\mathrm{i}\hbar\frac{\partial \Psi(R,t)}{\partial t} = H\Psi(R,t), \tag{3}$$

where Ψ is the column vector of wave functions. The Hamiltonian for the vibrational motion of the molecule can be written as

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial R^2} I + U(R,t), \tag{4}$$

where R is the internuclear separation, m is the reduced mass of the CsI molecule, and the potential matrix $U(R,t)$ can be written explicitly as

$$U\,(R,t) = \begin{pmatrix} V_{\mathrm{X}} & W_{\mathrm{XA}} & W_{\mathrm{XB}} \\ W_{\mathrm{AX}} & V_{\mathrm{A}} & 0 \\ W_{\mathrm{BX}} & 0 & V_{\mathrm{B}} \end{pmatrix} + \begin{pmatrix} 0 & \mathrm{Coup_{XA}} & 0 \\ \mathrm{Coup_{AX}} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{5}$$

where V_i (i = X, A, B) refer to the potential energies of the electronic states X, A, and B; $W_{ij} = \mu_{ij}E(t)$ (i, j = X, A, B) denote the coupling between the electronic states involved with the dipole matrix elements μ_{ij} and the external field $E(t)$. Usually, the dipole approximation is employed, and the dipole moment transition matrix elements are obtained by fitting *ab initio* results.[18] The shape of the laser pulse is chosen as

$$E(t) = E_0 f(t)\cos(\omega t)\hat{e}, \tag{6}$$

where E_0 is the electric field amplitude of the pump pulse with the linearly polarized direction $\hat{e}$, ω is corresponding angular frequency, and the envelope $f(t)$ of the pulse is expressed as

$$f\,(t) = \exp\left[-2\ln 2\left(\frac{t}{\tau}\right)^2\right] \tag{7}$$

with τ denoting a full width at half maximum of pump pulse.

The time-dependent Schrödinger matrix equation can be written as

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\begin{pmatrix} \Psi_{\mathrm{X}} \\ \Psi_{\mathrm{A}} \\ \Psi_{\mathrm{B}} \end{pmatrix} = \begin{pmatrix} H_{\mathrm{XX}} & H_{\mathrm{XA}} & H_{\mathrm{XB}} \\ H_{\mathrm{AX}} & H_{\mathrm{AA}} & 0 \\ H_{\mathrm{BX}} & 0 & H_{\mathrm{BB}} \end{pmatrix}\begin{pmatrix} \Psi_{\mathrm{X}} \\ \Psi_{\mathrm{A}} \\ \Psi_{\mathrm{B}} \end{pmatrix}, \tag{8}$$

where Ψ_i (i = X, A, B) represent wave functions of the electronic states. The diagonal elements can be written as

$$H_{ii} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial R^2} + V_{ii}(R,t). \tag{9}$$

The off-diagonal elements can be expressed as

$$H_{\mathrm{XA}} = H_{\mathrm{AX}} = \mu_{\mathrm{XA}}E(t) + \mathrm{Coup_{XA}}, \tag{10a}$$

$$H_{\mathrm{XB}} = H_{\mathrm{BX}} = \mu_{\mathrm{XB}}E(t). \tag{10b}$$

The above matrix equation can be solved by using the "split-operator Fourier" method.[24−30] The evolution of the wave packet with time can be expressed as

$$\Psi(R,t+\Delta t) \approx U_{\rm T}^{1/2}(R,t)U_{\rm V}U_{\rm T}^{1/2}(R,t)\Psi(R,t), \quad (11)$$

where $U_{\rm T}$ and $U_{\rm V}$ denote the kinetic and the potential energy evolution operators, respectively. The kinetic energy operator is given by

$$U_{\rm T} = \exp\left[-\frac{{\rm i}\Delta t}{\hbar}T_R\right] = F^{-1}\exp\left[-\frac{{\rm i}\hbar k^2\Delta t}{2m}\right]F, \quad (12)$$

where F represents the Fourier transform

$$F[f] = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\exp({\rm i}kR')f(R'){\rm d}R'. \quad (13)$$

The potential operator is calculated by (in a.u.)[31]

$$U_{\rm V} = \exp[-{\rm i}V\Delta t] = M\exp[-{\rm i}M^{\rm T}VM\Delta t]M^{\rm T} = M\begin{pmatrix}\exp(-{\rm i}\lambda_1\Delta t) & 0 & 0\\ 0 & \exp(-{\rm i}\lambda_2\Delta t) & 0\\ 0 & 0 & \exp(-{\rm i}\lambda_3\Delta t)\end{pmatrix}M^{\rm T}, \quad (14)$$

where M denotes the matrix that diagonalizes the potential matrix V from Eq. (5), the superscript T represents the transpose of matrix, and λ_i $(i=1,2,3)$ are the eigenvalues of the matrix V. Therefore, equation (11) can be written as

$$\begin{aligned}&\Psi(R,t+n\Delta t)\\ \approx&\left[\prod_{k=0}^{n-1}U_{\rm T}^{1/2}(R,t+k\Delta t)U_{\rm V}U_{\rm T}^{1/2}(R,t+k\Delta t)\right]\\ &\times\Psi(R,t).\end{aligned} \quad (15)$$

Once the wave function $\Psi(R,t)$ is determined, the population in each electronic state can be written as

$$P_i(t) = \int {\rm d}R\,|\Psi_i(R,t)|^2, \quad i = {\rm X},\ {\rm A},\ {\rm B}. \quad (16)$$

3. Results and discussion

To describe the influence of the ultra-short laser pulse wavelength on the populations in the electronic states, we fix the laser intensity at 6.0×10^{12} W·cm^{-2}, the pulse duration at 60 fs and the evolution time at 200 fs. The results with two different laser wavelengths are displayed in Fig. 2. (In this period, the process of the FMI has finished, and the populations are unchanged before the wave packet reaches the cross area.) We can find that when the pulse presents the population in each electronic state will appear Rabi oscillation[32] as a result of the FMI and spontaneous emission. When the excitation wavelength is fixed at 366 nm in Fig. 2(a), the population in the excited state A is more than that in the ground state X, and the population in the excited state B nearly equals zero. However, when the wavelength of the pump pulse is set at 295 nm, in Fig. 2(b), in the ground state X, the population is less than the one in the excited state B. The population in the excited state A almost decreases to zero.

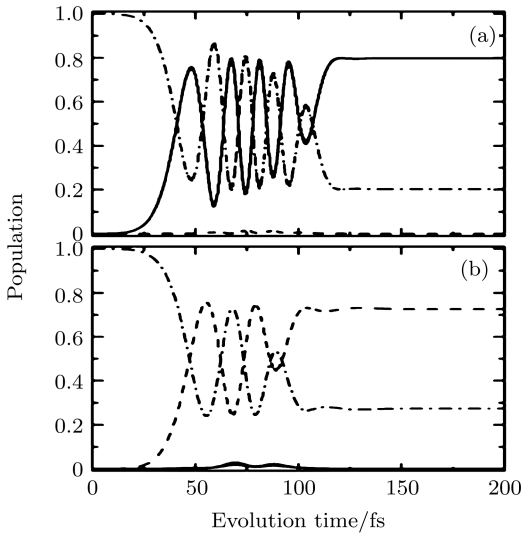


Fig. 2. Populations in the ground state X (dash-dot line) and two excited states A (solid line) and B (dash line) at laser wavelengths 366 nm (a) and 295 nm (b).

For further investigating the relationship between the wavelengths and the populations in the two excited states, we try to take into account more wavelengths in the calculations. The laser intensity and the pulse duration are still fixed at 6.0×10^{12} W·cm^{-2} and 60 fs, respectively. The results are shown in Fig. 3. As can be seen in the figure, the population of the excited state A has a peak at 369 nm and the one of the excited state B has a maximum at 297 nm. The ranges of the two peaks are from 350 nm to 390 nm and from 280 nm to 310 nm which are called long wave (LW) region and short wave (SW) region, respectively.

Moreover, the populations in both two excited states approach to zero when the wavelength is located in the special area (SA) which ranges from 310 nm to 350 nm.

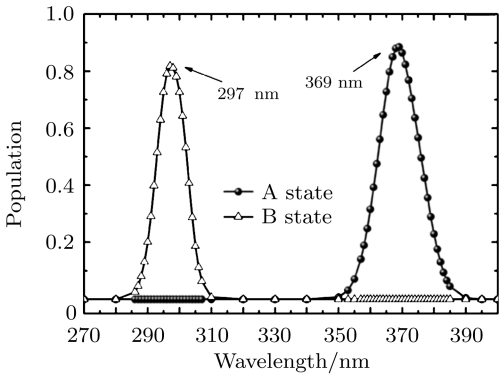


Fig. 3. Variations of populations in excited states A and B with the wavelength increasing from 270 nm to 400 nm, respectively.

These phenomena can be explained by the potential coupling between the ground state X and the two excited states. Since the three electric states have $\Omega = 0^+$ molecular symmetry, when the pulse presents and the wavelength reaches a strong coupling area of the excitation wavelength between the two electronic states, the potential energy curves in the ultra-short laser field will be changed, and the phenomenon of coupling will appear. Then the electron in the ground state will be excited into different excited states of the CsI molecule with different excitation wavelengths. According to the Franck–Condon principle, both of the kinetic energies of nucleus at turning points L and M are kept zero in the process of FMI and the form of the excitation is vertical transition. So the electronic transition probabilities reach maxima corresponding to the transitions $\mathrm{A}(\nu_L) \leftarrow \mathrm{X}(\nu_0)$ and $\mathrm{B}(\nu_M) \leftarrow \mathrm{X}(\nu_0)$ with the vertical excitation wavelengths (VEWs) being 369 nm and 297 nm, respectively. Although the wavelengths near the VEWs can cause the two electronic states to transit, the coupling intensities are not so strong as those of the VEWs induced. These behaviours are reflected by the population in each excited state.

From Fig. 3, we can find that the width of the SW region is smaller than the one of the LW region. This is because the slope of the potential energy curve of the excited state A at the turning point L is smaller than the one of the excited state B at M. In addition, the two peaks with different heights are also induced by the coupling strength. The stronger the coupling strength is, the more the population in the excited state is. Therefore, the maximum of each electronic excited state can be obtained, and the strongest signal can be realized experimentally by adjusting the ultra-short pump pulse wavelengths at 297 nm and 369 nm corresponding to excited states A and B, respectively.

In the SA, the populations in both two excited states approach to zero, because the excitation wavelengths are beyond the two strong coupling regions. So in experiment, the signals of the two excited states can be easily distinguished from each other. When the laser wavelength is adjusted in the SW region, the single signal of the excited state B can be detected. Similarly, when the wavelength is fixed in the LW region, the single signal of the state A is observed. Therefore, the single reaction channel (either channel-1 or channel-2) of the CsI molecule can be chosen by adjusting the laser wavelength. And the strongest signals of the reaction channel-1 and channel-2 are obtained by fixing the laser wavelengths at 369 nm and 297 nm, respectively.

There is a crossing region between the ground state X and the excited state A, so the reaction channel-1 is chosen by fixing the excitation wavelength at 369 nm (here the laser intensity is fixed at 6.0×10^{11} W$\cdot$cm^{-2}) and the signal of the state B disappears, then only the ground state X and excited state A are considered. In Fig. 4, the populations in both two electronic states are changed again during the evolution time from 800 fs to 900 fs. It can be

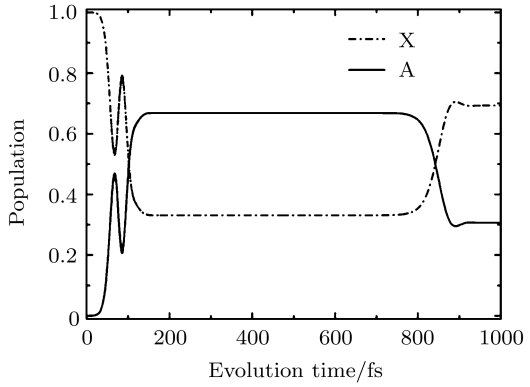


Fig. 4. Time evolutions of populations of the ground state (solid line) and the excited state (dash line) with the wavelength, the laser intensity, and the pulse duration fixed at 369 nm, 6.0×10^{11} W$\cdot$cm^{-2}, 60 fs, respectively.

explained by the fact that the wave packet on the excited state A is divided into two parts in the crossing area, which is prepared by an ultra-short pump pulse from ground state X. One part of the wave packet remains in the potential of the excited state A, while

the other part leaks to the ground state X corresponding to the reaction channel-3. Then the population in excited state A decreases, however, the one in the ground state X increases in this area. Thereby, it is another way to control the reaction channels of the CsI molecule by controlling the evolution time of the wave packet on the excited state A.

4. Conclusion

In this article, the time-dependent wave-packet dynamical method is used to investigate the influence of the ultra-short laser pulse wavelength on the populations in the three electronic states of the CsI molecule which have the same symmetry $\Omega = 0^+$. We find that the populations in the two excited states approach to the maxima at the excitation wavelengths of 369 nm and 297 nm, respectively. The reaction channel-1 and channel-2 can be chosen by adjusting the excitation wavelength. In addition, the nonadiabatic coupling has an important influence on the populations in the excited state A and the ground state X, so the reaction channel-1 and channel-3 can be controlled by determining the evolution time of wave packet on the excited state A.

Acknowledgement

The authors are indebted to Prof. Han Ke-Li for providing the code used in our calculation. All calculations for the present study were carried out at Shuguang 4000A Computer Centre of Ludong University.

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