Field dependence of state populations in pump-probe pulses

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ABSTRACT

The effects of pulse width, laser wavelength and laser intensity on the state populations of NaI molecule driven by a pump-probe pulse were studied via employing the time-dependent wave packet approach. Wave packet moves periodically with roundtrip time 1000 fs. That the wave packet bifurcates in the crossing region affects state populations. The excitation probability increases and dissociation probability decreases with increasing pulse width. The excitation probability approaches the maximum at the resonance pump wavelength 318 nm, and the dissociation probability decreases with increasing pump wavelength. The excitation probability increases with increasing pump intensity while the dissociation probability does not vary. The probe wavelength and probe intensity have no effect on state populations. The wave packet motion and selective distribution of state populations, excitation and dissociation of molecule can be achieved by adjusting laser parameters. The results can provide some important basis for realizing quantum manipulation of molecules experimentally.

Keywords:

Intense femtosecond pump-probe pulse; Nonadiabatic effect; Time-dependent wave packet approach; Population transfer; Dissociation probability

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1. Introduction

With the development of ultrashort and ultrastrong laser pulse technology, more and more researches have focused on the control of molecular dynamics in real time. Controlling the evolution of wave packet will be a benefit for light manipulation of molecular processes experimentally. State populations map the wave packet dynamic information of the electronic state, are found to be sensitive to the parameters of the laser fields, and have been studied in multi-level molecular systems [1-14].

NaI molecule is a typical molecule with a avoided crossing between two nonadiabatically coupled electronic states at internuclear distance 7 Å, and has been studied experimentally and theoretically. Braun et al. [1] and Charron and Suzor-Weiner [2] presented that the wave packet moves periodically on the electronic state potentials of NaI molecule, which induces the periodical variation of photoelectron spectra. Yao et al. [3,4] suggested that the first dissociation probability decreases with increasing pump wavelength. The photoelectron spectra are dependent on the delay time. Arasaki et al. [5-7] indicated that the total ion signal oscillates periodically with increasing delay time. Miao *et al.* [8,9] and Liu et al. [10] suggested that the delay time affects state populations and photoelectron spectra. Ma et al. [11] presented that the pump wavelength affects state populations. Zhao et al. [12] studied the influence of field-free orientation on the predissociation dynamics of the NaI molecule. Xiong et al. [13] presented that the wavelength affects state populations of CsI molecule, the populations of excited state approaches the maximum with the resonance excitation wavelength. Zhu *et al.* [14] suggested the delay time affects state populations of CsI molecule.

The studies on the nonadiabatic effects on state populations of NaI molecule above mostly focused on the influence of pump-probe delay time. The effects of the pulse width and laser intensity on state populations of NaI molecule have not been reported. This paper presents new data on the influence of pulse width, laser wavelength and intensity on state populations of NaI molecule driven by pump-probe pulses via time-dependence quantum wave packet method.

2. Computation details

Three states (the ground state *X*, the excited state *A* and the ion ground state *I*) are involved in the multiphoton ionization of NaI molecule [1-3], as shown in Fig.1. The transition from *X* to *A* is

induced by resonant one-photon absorption, then the excited molecule is ionized through single-photon absorption after the delay time, and the emitted photoelectron is detected from I .

Fig. 1. Potential energy curves of NaI molecule.

The wave function for the three-state model can be written as

$$\Psi = (\Psi_X, \Psi_A, \Psi_I)^T, \quad (1)$$

Where Ψ_X, Ψ_A and Ψ_I are the wave functions for the states X, A, and I, respectively. The ion ground state is a continuum state and can be discretized into a band of quasicontinuum states.

The Ψ_I can be further expressed as

$$\Psi_I = (\psi_1, \psi_2, \dots, \psi_N)^T, \quad (2)$$

where N represents the number of discrete states of NaI ion. The wavefunctions Ψ_I , within the Born-Oppenheimer approximation can be obtained by solving the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \Psi_X \\ \Psi_A \\ \psi_1 \\ \psi_2 \\ \vdots \\ \psi_N \end{pmatrix} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} \begin{pmatrix} \Psi_X \\ \Psi_A \\ \psi_1 \\ \psi_2 \\ \vdots \\ \psi_N \end{pmatrix} + V(R, t) \begin{pmatrix} \Psi_X \\ \Psi_A \\ \psi_1 \\ \psi_2 \\ \vdots \\ \psi_N \end{pmatrix}, \quad (3)$$

where μ is the reduced mass and R is the internuclear distance, while the potential matrix

$V(R, t)$ can be explicitly written as

$$V(R, t) = \begin{pmatrix} V_{XX} & W_{XA} & 0 & 0 & \cdots & 0 \\ W_{AX} & V_{AA} & W_{AI} & \cdots & \cdots & W_{AI} \\ 0 & W_{IA} & V_{II} + E_{I,1} & 0 & \cdots & 0 \\ \vdots & \vdots & 0 & \ddots & \cdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & W_{IA} & 0 & 0 & \cdots & V_{II} + E_{I,N} \end{pmatrix}, \quad (4)$$

where V_{XX} , V_{AA} , and V_{II} refer to the potential matrix elements of states X , A , and I in the absence of laser fields. $E_{I,k} = (k-1)\Delta E_I$ ($k=1,2,\dots,N$) is the emitted photoelectron energy.

Other nonzero off-diagonal matrix elements are given by

$$W_{XA} = W_{AX} = \mu_{XA} \{ \varepsilon_1 f_1(t) \cos \omega_1 t + \varepsilon_2 f_2(t) \cos \omega_2 (t - \Delta t) \}, \quad (5)$$

$$W_{AI} = W_{IA} = \mu_{AI} \{ \varepsilon_1 f_1(t) \cos \omega_1 t + \varepsilon_2 f_2(t) \cos \omega_2 (t - \Delta t) \}, \quad (6)$$

where μ_{XA} and μ_{AI} are the transition dipole matrix elements, ε_1 and ε_2 are the amplitudes of the pump and probe pulses, ω_1 and ω_2 are the angular frequencies. The envelopes of the pulses $f_1(t)$ and $f_2(t)$ take Gaussian form

$$f_1(t) = \exp \left[-4 \ln 2 (t/\tau)^2 \right], \quad (7)$$

$$f_2(t) = \exp \left[-4 \ln 2 ((t - \Delta t)/\tau)^2 \right], \quad (8)$$

τ is the full width at half maximum (FWHM) of pulse and Δt is the delay time between the pump and probe pulses.

The time-dependent Schrödinger equation is solved by split-operator Fourier methods rigorously [15,16], once the wave function $\Psi_i(R, t)$ is determined, the population on each electronic state can be written as [2,3,5,8-10,12,13]

$$P_i(t) = \int |\Psi_i(R, t)|^2 dR, (i = X, A, I), \quad (9)$$

The photoelectron spectrum can be obtained via [1,2,4-6,10]

$$P(E_{I,k}) = \lim_{t \rightarrow \infty} \int dR |\psi_k(R, t, E_{I,k})|^2, (k = 1, 2, \dots, N), \quad (10)$$

In the calculation, $E_{I,k}$ span over 0-1.2 eV and N equals 120.

3. Results and Discussion

The effect of the delay time on the wave packet motion is considered. Figure 2 shows the evolution of wave packet on the ground state and the excited state. The wave packet moves periodically with oscillation period 1000 fs. The wave packet moves on the excited state potential within 0-200 fs, reaches the crossing point ($R=7$ Å) for the first time at 200 fs and bifurcates: most of the wave packet transfers to the ground state [Fig. 2(a)], only a small part still moves toward large internuclear distance on the excited state [Fig. 2(b)], which eventually dissociates into Na and I atoms. The wave packet on the ground state is reflected at the outer turning point ($R=11$ Å) at 500 fs, returns to the crossing point at 800 fs and splits again, where most of the wave packet transfers to the excited state and a small component remains on the ground state. The similar periodical motion and bifurcation of wave packet have been referred to [1-8,10-12]. The wave packet propagates at different velocity on the ground state and on excited state after the second bifurcation, and returns to the crossing point at 1100 fs and 1200 fs, respectively, which results that the wave packet is composed of two envelopes, and is no longer a good-localization envelope, i.e. the nonadiabatic effect of NaI molecule becomes more and more obvious with increasing delay time. The wave packet on the ground state returns to the crossing point earlier than that on the excited state is referred to in Refs. [3,4,6].

Fig. 2. The evolution of wave packet on (a) ground state X and (b) excited state A.

The effect of the pulse width on state populations is considered. Figure 3 demonstrates the evolution of state populations at different pulse width. All molecules are on the ground state initially until the pump laser excites them to the excited state, which makes the population of

ground state declines [Fig. 3(a)], the population of excited state increases [Fig. 3(b)], and the sum population of three states is 1.0 [Fig. 3(c)]. The increase of the population on excited state increases (i.e. the excitation probability increases) with increasing pulse width. At 200 fs the wave packet of excited state reaches the crossing point ($R=7 \text{ \AA}$) firstly and bifurcates: most of the wave packet transfers to the ground state with transfer probability P_X , while a small part remains on the excited state with transfer probability P_A , therefore the population of the ground state increases [Fig. 3(a)] and the population of the excited state declines [Fig. 3(b)], the sum of three states remains 1.0. [Fig. 3(c)]. The similar wave packet splitting induced by the nonadiabatic effects has been referred to [1-3,5-7,9-12]. Xiong et al. [13] and Zhu et al. [14] suggested that most of the wave packet of the excited state crosses to the ground state after the first bifurcation of CsI molecule. Figure 4 shows the first dissociation probability $P_A/(P_A+P_X)$ vs. pulse width. The dissociation probability decreases with increasing pulse width. The dissociation probability is related to the wave packet propagation velocity [3]. Due that the pulse width is inversely proportional to the range of energy, the propagation velocity of the molecule on the excited state decreases with increasing pulse width, which results in increasing time to reach the crossing region, leading to decreasing dissociation probability. At 500 fs the small part of the wave packet on the excited state dissociates, therefore the population of excited state declines to 0.0, and the sum of the three states declines [Fig. 3(c)]. The decrease of the sum of the three states increases with increasing pulse width. At 800 fs, the wave packet of ground state undergoes a second bifurcation as it moves inwards, most of the wave packet crosses to the excited state, only a small part wave packet is still on the ground state, therefore the population of ground state decreases [Fig. 3(a)] while the population of excited state increases [Fig. 3(b)]. At 1200 fs, the wave packet of excited state reaches the crossing point thirdly, similar to the process at 200 fs, most of the wave packet propagates on the ground state, thus the population of ground state increases while the population of excited state decreases. At 1500 fs, the population of excited state drapes to 0.0, similar to the process at 500 fs, the small part of wave packet on the excited state eventually dissociates, and the sum of three state declines again. The effect of the pulse width on the state populations and dissociation probability of NaI molecule have not studied before.

Fig. 3. The evolution of state populations at different pulse widths. (a), (b) and (c) denote ground state, excited state and the sum of the three states, respectively.

Fig. 4. The first dissociation probability vs. pulse width.

The effect of the laser wavelength on state populations is considered. Figure 5 demonstrates the evolution of state populations at different pump wavelengths (278-368 nm). After the pump laser excites the molecules to the excited state, the population on ground state achieves the minimum while that on the excited state achieves the maximum at the resonance pump wavelength 318 nm, which indicates the maximum excitation probability. This is consistent with the studies on the wavelength dependence of state populations of CsI/NaLi/NO molecule [13,17,18]. Figure 6 shows the first dissociation probability $P_A / (P_A + P_X)$ vs. pump wavelength. The dissociation probability decreases with increasing pump wavelength. Due that the laser wavelength is inversely proportional to the laser energy, the propagation velocity of the molecule on the excited state decreases with increasing laser wavelength, which results in increasing time to reach the crossing region, leading to decreasing dissociation probability. There are few studies

on the effect of the laser wavelength on the state populations and dissociation probability of NaI molecule before. Yao et al. [3] suggested that the longer the laser wavelength is (310-330 nm), the smaller the dissociation probability is. The effect of the probe wavelength (218-258 nm) on state populations is also studied, which shows the probe wavelength has no effect on state populations.

Fig. 5. The evolution of state populations at different pump wavelengths. (a), (b) and (c) denote ground state, excited state and the sum of the three states, respectively.

Fig. 6. The first dissociation probability vs. pump wavelength.

The effect of laser intensity on state populations is considered. Figure 7 demonstrates the evolution of state populations at different pump laser intensities. After the pump laser excites the molecules to the excited state, the decrease of the population on ground state increases while the increase of that on the excited state increases with increasing laser intensity, i.e., the excitation probability increases. The decrease of the sum of the three states increases with increasing pump laser intensities [Fig. 7(c)], but the dissociation probability does not change. The effect of the

probe laser intensities on state populations is also studied, which shows the probe laser intensity has no effect on state populations. The effect of the laser intensity on the state populations and dissociation probability of NaI molecule have not studied before.

Fig. 7. The evolution of state populations at different pump intensities. (a), (b) and (c) denote ground state, excited state and the sum of the three states, respectively.

4. Conclusion

The effect of the pulse width, laser wavelength and intensity on state populations of NaI molecule driven by a pump-probe pulse were studied via employing the time-dependent wave packet approach. Wave packet moves periodically with roundtrip time 1000 fs. The wave packet reaches the crossing point firstly at 200 fs and bifurcates: most of the wave packet transfers to the ground state, only a small part still on the excited state, which affects state populations. The excitation probability increases and dissociation probability decreases with increasing pulse width. The excitation probability approaches the maximum with the resonance pump wavelength 318 nm. The dissociation probability decreases with increasing pump wavelength. As the pump intensity increases, the excitation probability increases while the dissociation probability does not change. The probe laser wavelength and intensity do not affect the state populations. The wave packet motion, selective distribution of state populations, excitation and dissociation of molecule can be achieved by adjusting laser parameters. The results may be useful for realizing the optical control of molecule and the process of quantum manipulation of molecule experimentally, and provide some important basis for further theoretical research in this respect.

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