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Effect of the Delay Time on Photoelectron Spectra and State Populations of Nonadiabatic Coupling Molecule

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Abstract: The influence of the delay time on the wave packet motion of NaI molecule was studied by intense femtosecond pump-probe pulses via time-dependent wave packet approach. The delay time dependence of state populations was studied firstly. Wave packet moves periodically with oscillation period 1000 fs. The wave packet reaches the crossing point at 200 fs firstly and at 800 fs secondly, and bifurcates. The periodical motion of the wave packet induces the periodical variation of photoelectron spectra. The wave packet bifurcation affects state populations. The results show the wave packet motion and selective distribution of state populations can be achieved by adjusting pump-probe delay time. The results can provide some important basis for realizing the optical control of molecules experimentally.

AMS subject classifications: 70F05, 65M22

Keywords: Intense femtosecond pump-probe pulse, State populations, Wave packet motion, Photoelectron spectra

Introducation

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. The photoelectron spectra and state populations map the wave packet dynamic information of the electronic state, are found to be sensitive to the parameters of

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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. Zhu et al. [14] suggested that the delay time affects state populations of CsI molecule.

The Photoelectron spectra reflect the excited state dynamics; however, the effect of the delay time on state populations of NaI molecule has not been reported. This paper presents new data on the influence of delay time on the photoelectron spectra and state populations driven by pump-probe pulses via time-dependence quantum wave packet method.

Formalism

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 **Figure 1**. The molecule initially populated in ground state *X* is resonantly excited to the excited state *A* by pump laser pulse with a central wavelength of $\lambda_1 = 328$ nm, then the excited molecule is ionized by probe laser pulse with a central wavelength of $\lambda_2 = 228$ nm after the time delay, and the emitted photoelectron is detected from *I*.

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

$$\boldsymbol{\Psi} = (\psi_X, \psi_A, \boldsymbol{\psi}_I)^{\mathrm{T}}, \tag{1}$$

Where ψ_X, ψ_A and $\boldsymbol{\psi}_I$ are the wave functions for the states *X*, *A*, and *I*, respectively. The ion ground state *I* is a continuum state and can be discretized into a band of quasicontinuum states. The ψ_I can be further expressed as

$$\boldsymbol{\psi}_I = (\psi_1, \psi_2, ..., \psi_N)^{\mathrm{T}}, \tag{2}$$

where *N* represents the number of discrete states of NaI ion. The wavefunctions $\boldsymbol{\psi}_I$ within

the Born-Oppenheimer approximation can be obtained by solving the time-dependent Schrödinger equation

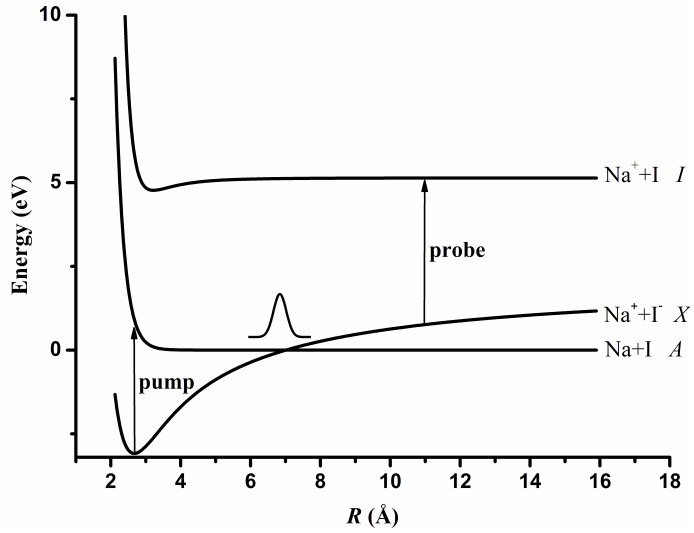

Figure 1: Potential energy curves of NaI molecule. The arrows indicate indicate the excitation energy of 3.780 eV (328 nm) and 5.438 eV (228 nm), respectively.

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

Where μ the reduced mass and R is is the internuclear distance, while the potential matrix $\boldsymbol{V}(R,\mathrm{t})$ can be explicitly written as

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

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. $E_{I,i}=(i-1)\Delta E_I\ (i=1,2,...,N)$ is the emitted photoelectron energy. Other nonzero off-diagonal matrix elements are given by

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

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

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

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

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

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]

$$P_i(t)=\int|\psi_i(R,t)|^2 dR,\ (i=X,A,I), \tag{9}$$

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

$$P(E_{I,i})=\lim_{t\to\infty}\int dR\left|\psi_i(R,t,E_{I,i})\right|^2,\ (i=1,2,...,N), \tag{10}$$

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

Results and Discussions

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 X and the excited state A. 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 (**Figure 2a**), only a small part still moves toward large internuclear distance on the excited state (**Figure 2b**), which dissociates into Na and I atoms ultimately. 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 in Refs. [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].

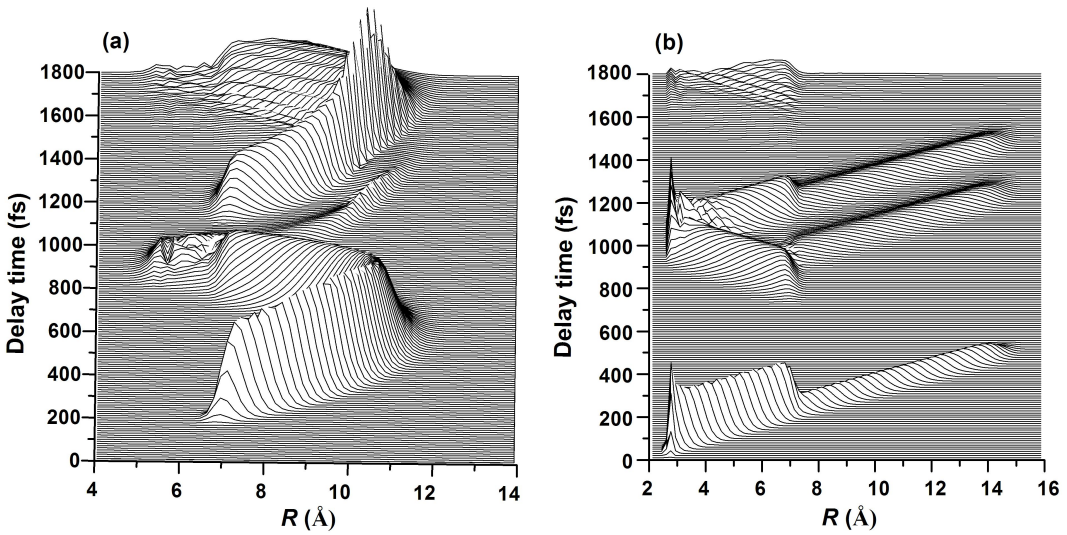

Figure 2: The evolution of wave packet on ground state *X* (a) and excited state *A* (b) with time and internuclear distance. Laser parameters are pump wavelength $\lambda_1 = 328$ nm, probe wavelength $\lambda_2 = 228$ nm, pump and probe intensity $I_1 = I_2 = 5.0\times10^{11}$ W/cm^2, and pulse width τ=30 fs.

The effect of the delay time on photoelectron spectra is considered. **Figure 3** shows the evolution of photoelectron spectra. The periodical motion of the wave packet results in the periodical variation of photoelectron spectra. The peaks move toward low energy within 0-200 fs. As the delay time increases from 0 fs to 200 fs (i.e. 2.66 Å ≤ R ≤ 7 Å in **Figure 1**), the difference between the potentials of ground state *I* and excited state *A* increases with increasing internuclear distance, accordingly the photoelectron energy decreases with increasing internuclear distance. The peaks move toward high energy within 200-500 fs while the peaks move toward low energy within 500-800 fs. The wave packet reaches the crossing point firstly at 200 fs and bifurcates, most of the wave packet transfers to the ground state. The difference between the potentials of ion ground state *I* and ground state *X* decreases with increasing internuclear distance (R>7Å), accordingly the photoelectron energy increases with increasing internuclear distance. The same procedure may be easily adapted to explain the decrease of photoelectron energy with decreasing internuclear distance within 500-800 fs. The wave packet passes the crossing point secondly at 800 fs and bifurcates, most of the wave packet on the excited state moves toward small internuclear

distance within 800-1000 fs, which is opposite to the process within 0-200 fs. The wave packet motion and photoelectron spectra variation complete a periodical oscillation at 1000 fs. The similar periodical variation of photoelectron spectra has been referred in Refs. [1,2,5,7]. The wave packet repeats almost the same process within the second period (1000-2000 fs).

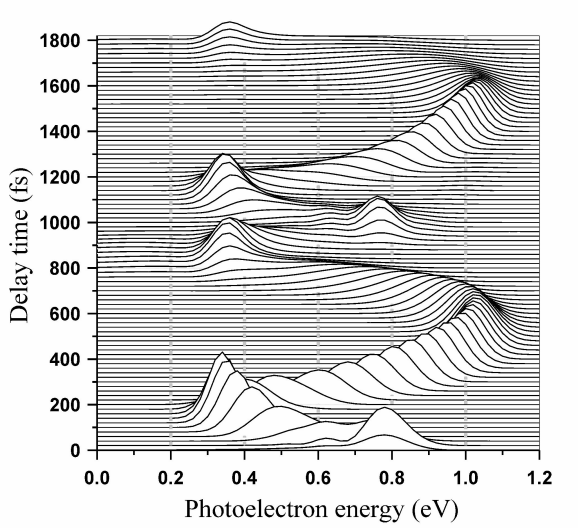

Figure 3: The evolution of photoelectron spectra of NaI molecule for different delay time.

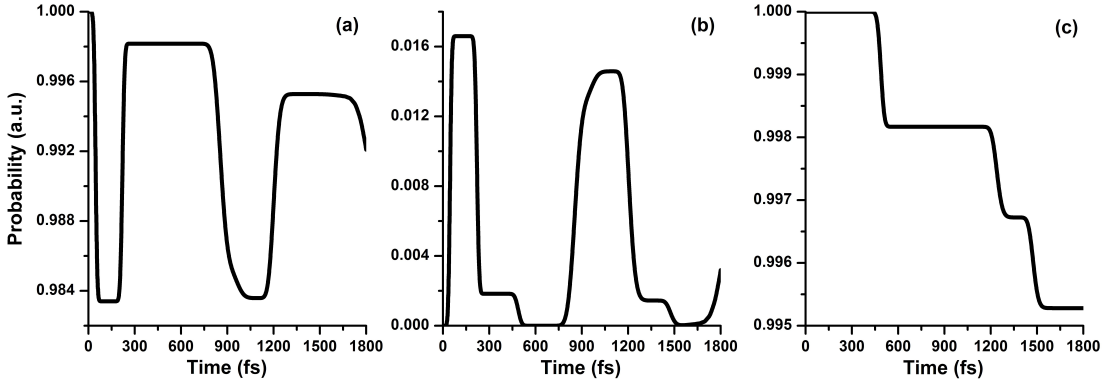

Figure 4: State populations for different delay time. (a), (b), (c) represent ground state *X*, excited state *A*, and sum of the three states.

The effect of the delay time on state populations is considered. **Figure 4** demonstrates the evolution of state populations. 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 from 1.000 to 0.983 (**Figure 4a**), the corresponding population of excited state

increases from 0.000 to 0.017 (**Figure 4b**), i.e., the excitation probability 1.7%, the sum population of three states is 1.000 (**Figure 4c**). At 200 fs the wave packet of excited state reaches the crossing point firstly, most of the wave packet is on the ground state, therefore the population of ground state increases from 0.983 to 0.998, the population of excited state declines from 0.017 to 0.002. i.e., the first dissociation probability 11.8%, the sum of three states remains 1.000. 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. At 500 fs the small part of the wave packet on the excited state after the first bifurcation undergoes dissociation, therefore the population of excited state declines from 0.002 to 0.000, the sum of three states declines from 1.000 to 0.998. Miao et al. [16] presented the onset time of photodissociation of NaI is 300 fs, more and more NaI molecules photodissociate with increasing delay time. At 800 fs, the wave packet of ground state returns to the crossing point secondly and splits again; most of the wave packet crosses to the excited state, therefore the population of ground state decreases while the population of excited state increases. 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 0.000, similar to the process at 500 fs, the small part of wave packet on the excited state dissociates ultimately, and the sum of three state declines again. The effect of the delay time on the state populations, excitation and dissociation of NaI molecule has not studied before.

Conclusions

The effect of delay time on photoelectron spectra and state populations of NaI molecule by pump-probe pulses was investigated via time-dependent wave packet approach. Wave packet moves periodically with roundtrip time 1000 fs between the inner turning point (2.66 Å) and outer turning point (11 Å). The wave packet reaches the crossing point for the first time at 200 fs and splits into two parts: most of the wave packet transfers to the ground state; a small part of the wave packet is still on the excited state, which dissociates into Na and I atoms ultimately. The wave packet is reflected at the outer turning point at 500 fs, returns to the crossing point at 800 fs and bifurcates again. The wave packet passes the crossing point thirdly at 1200 fs. The periodical motion of the wave packet results in the periodical variation of photoelectron spectra. The peaks move toward high energy within 200-500 fs while the peaks move toward low energy within 500-800 fs. Delay time affects wave packet motion, thus affects the distribution of state populations. It is found that the wave packet motion and selective distribution of state populations can be achieved by adjusting

pump-probe delay time. The results can provide some important basis for realizing the optical control of molecules experimentally.

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