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飞秒泵浦-探测激光场中NaI解离和电离的场依赖

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摘 要:利用含时波包方法计算了NaI的基态、激发态和NaI^+离子基态的态布居数,全面研究且定量分析了泵浦和探测激光参数对非绝热NaI分子激发、解离和电离几率的影响。结果表明:泵浦激光是分子激发和解离的唯一影响因素,而电离则受泵浦激光和探测激光的共同影响。解离和电离过程相互竞争和共存。弱场强、短波长、窄脉宽和长延时的激光场有利于解离,反之则有利于电离。通过调整激光脉冲的形式,可以控制激发、解离和电离选择。研究结果对分子光谱学具有重要价值,也有助于在实验上实现光学分子控制。

关键词:飞秒泵浦-探测激光场;解离几率;电离几率;态布居;含时波包法
中图分类号:O431.2 **文献标识码**:A **doi**:10.3788/gzxb20225112.1214003

0 Introduction

With the advances in ultra-strong and ultra-short laser pulses, many research works have concentrated on the real-time control of molecular dynamics. Apart from plotting the wave packet dynamics data of electronic state, the state population is also capable of reflecting the excitation, dissociation and ionization of molecules. By controlling the wave packet evolution, the state population can be manipulated, thereby facilitating the optical control over the molecular processes experimentally.

NaI molecule is a typical molecule with an avoided crossing between two nonadiabatically coupled electronic states at the internuclear separation R_x=0.693 nm, and has been studied for monitoring wave packet evolution experimentally and theoretically. Some studies have considered photoelectron spectra. For instance, BRAUN M et al[1] introduced that for the NaI molecule, periodical motion of the wave packets on the electronic state potentials is possible, which results in the periodic fluctuation in the spectral of photoelectrons ARASAKI Y et al[2,3], TAKATUKA K et al[4], YAO H B et al[5] and LIU Y F et al[6] explored how the pump-probe pulse delay duration affects the photoelectron spectra of NaI. They proposed that the photoelectron spectrum can be used to map the bifurcation of the wave packets via the crossing region. Although the photoelectron spectrum offers the significant plotting of the exited state movement of wave packets and ionization yields, it is not enough to reflect the excitation, dissociation as well as ionization processes of molecules.

Some studies have presented some additional data. JOUVET C et al[7], CHARRON E et al[8] and MIAO X Y et al[9] explored the femtosecond dynamics of NaI photoionization and dissociative photoionization experimentally or theoretically. ROSE T S et al[10] experimentally studied the predissociation dynamics of NaI

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molecules with the use of Femtosecond Transition-state Spectroscopy (FTS) and examined the impact of laser wavelength and intensity on the dynamics of the dissociation. Moreover, the findings with classical and quantum mechanical calculations were compared in detail. ENGEL V et al [11-13] studied the predissociation dynamics of NaI molecules using LIF (laser-induced fluorescence) technique, and examined the LIF signal dependence on the pump and probe pulses properties (laser wavelength and pulse width). LIU Y X et al[14, 15], HAN Y C et al[16] and SUN Z P et al[17] proposed that NaI predissociation at the laser-induced crossing can be regulated using a controlled laser pulse (in addition to pump and probe pulses). Besides, the influences of the control pulse′s delay time, intensity, frequency, carrier-envelope phase, and chirping on the predissociation dynamics were discussed. YAO H B et al[18] and GUO X Q et al[19, 20] investigated the impact of pump wavelength, pulse width, and pulse profile on the dissociation probabilities following the initial passage through the crossing zone when the pump and probe pulse widths were varied at the same time. According to MA X G et al[21], several wavelength regions can efficiently trigger the excitation and photoionization.

The aforementioned literature mainly includes the photoelectron spectrum, the competitive ionization channel and the predissociation dynamics of the first passage through the crossing region. Herein, this work focuses on the study of the respective parameter effects of pump and probe pulses on the probabilities of excitation and ionization, and the total probability of dissociation of NaI molecules. By appropriately changing the laser parameters, the population in each state can be controlled, and so can the excitation, dissociation and ionization probabilities, which will benefit the molecular spectroscopy and light manipulation of molecular processes. This paper presents new and complete data on the influence of the laser parameters on the excitation, dissociation, and ionization by pump-probe pulses of NaI molecular by using time-dependent quantum wave packet method.

1 Computation details

The computational details, described elsewhere[2,14-16], are outlined here. Fig. 1 depicts the potential energy graphs for the NaI molecule in our quantum calculation[11,13]. A femtosecond pump laser pulse prepares a wave packet on the covalent excited state (A), nonadiabatically coupling the ionic ground state (X) at R_x=0.693 nm. Besides, the production from the covalent/ionic channel is ionized by a time-delayed probe pulse, and can derive emitted photoelectron from the ionic ground state (I). Additionally, the ionic channel describes a process of nonadiabatic transition, whereas the covalent channel depicts a process of dissociation, i.e., predissociation.

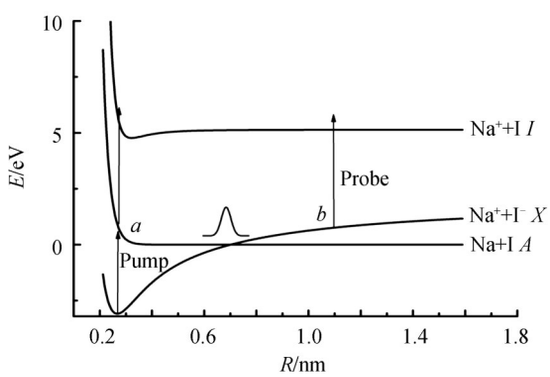

Fig.1 Potential energy graphs

The core of the time-dependent quantum wave packet method is to solve the time-dependent Schrödinger equation. The time-dependent wave packet method has many advantages. In addition to the efficient numerical calculation, this method provides definite physical meanings and intuitive image for the dynamic. And it has the intuition of classical mechanics and no lack of accuracy of quantum mechanics. Besides, the time-dependent wave packet method is especially suitable for the study of molecular evolution after excitation by femosecond laser pulse, thus it becomes a powerful tool for the research of molecular photoionization problems [2,14-16].

Solving the three-state-coupled time-dependent Schrödinger equation yields the nuclear wave functions.

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\begin{pmatrix}\boldsymbol{\Psi}_X\\ \boldsymbol{\Psi}_A\\ \boldsymbol{\Psi}_I\end{pmatrix}=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial R^2}\begin{pmatrix}\boldsymbol{\Psi}_X\\ \boldsymbol{\Psi}_A\\ \boldsymbol{\Psi}_I\end{pmatrix}+V(R,t)\begin{pmatrix}\boldsymbol{\Psi}_X\\ \boldsymbol{\Psi}_A\\ \boldsymbol{\Psi}_I\end{pmatrix} \tag{1}$$

where $\boldsymbol{\Psi}_X$, $\boldsymbol{\Psi}_A$ and $\boldsymbol{\Psi}_I$ represent the wave functions for three states (X, A, and I), respectively. R is the internuclear separation and m is the reduced mass.

We can discretize the state of ionization continuum state into multiple levels of quasi-continuum. Accordingly, the wave function $\boldsymbol{\Psi}_I$ can be written as

$$\boldsymbol{\Psi}_I=\sum_{l=1}^{n}\psi_l\left|E_{I,l}\right\rangle \tag{2}$$

where $E_{I,l}=(l-1)\Delta E_I$ $(l=1,2,...,n)$ is the emitted photoelectron energy, n denotes the discrete state counts of the NaI ion. Apparently, the value range of $E_{I,l}$ is 0~1.2 eV, while the value of n is assigned as 120.

In the dimensions of $(n+2)\times(n+2)$, where the number of discrete states is n and the number of bound states is 2, the potential matrix $\boldsymbol{V}(R,t)$.

$$V(R,t)=\begin{pmatrix}V_X & W_{XA}+V_{XA} & W_{XI} & W_{XI} & \cdots & W_{XI}\\ W_{XA}+V_{XA} & V_A & W_{AI} & W_{AI} & \cdots & W_{AI}\\ W_{XI} & W_{AI} & V_I+E_{I,1} & 0 & \cdots & 0\\ W_{XI} & W_{AI} & 0 & V_I+E_{I,2} & \cdots & \vdots\\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots\\ W_{XI} & W_{AI} & 0 & 0 & \cdots & V_I+E_{I,l}\end{pmatrix} \tag{3}$$

where V_X, V_A and V_I are the potential matrix elements of three states in the scenario without laser field. V_{XA} is the nonadiabatic coupling element. The nonzero elements for off-diagonal matrix are the coupling between two states via external laser field, are given as follows

$$W_{XA}=\mu_{XA}e_1f_1(t)\cos\omega_1 t \tag{4}$$

$$W_{AI}=\mu_{AI}e_2f_2(t)\cos\omega_2(t-\Delta t),\ (R\leqslant 0.693\ \mathrm{nm}) \tag{5}$$

$$W_{XI}=\mu_{XI}e_2f_2(t)\cos\omega_2(t-\Delta t),\ (R>0.693\ \mathrm{nm}) \tag{6}$$

where μ are the transition dipole moments, e_1 and e_2 are the pulse amplitudes, ω_1 and ω_2 are the angular frequencies. $f_1(t)$ and $f_2(t)$ are the pulse profiles and take the Gaussian form

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

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

where τ refers to the FWHM (full width at half maximum) of pulse and Δt indicates the pump-probe delay time.

Split-operator fast-Fourier methods are used for solving the time-dependent Schrödinger equation[2,14-16], wherein the state population can be determined following the earlier studies [6,8-9,16,18-20,22]

$$P_i(t)=\int\left|\boldsymbol{\Psi}_i(R,t)\right|^2\mathrm{d}R,\ (i=X,A,I) \tag{9}$$

We take the transition dipole moments from Ref. [8]. The nonadiabatic coupling element is taken from Refs. [19,11]. The pump wavelength is taken 268-368 nm around the resonance wavelength 328 nm (3.78 eV [1]). The wave packet moves between the internal (R=0.27 nm, marked a in Fig. 1) and the external turning points (R=1.1 nm, marked b in Fig. 1). The ionization occurs when the probe photon energy is greater than the ionization energy at the internuclear distance R between a and b. The probe wavelength is taken 190~270 nm around 240 nm (corresponding to the maximum potential energy difference 5.14 eV between the potentials of states X/A and I[13]) to guarantee ionization. Laser intensities and pulse widths are 1.0×10^{11}~1.0×10^{15} W/cm^2 and 10~200 fs, respectively. A complete motion period of the wave packet is about 1 000 fs (see Fig. 2 below), and the time delay of 3 000 fs is taken for completely observing more periods.

2 Results and discussions

Fig. 2 shows the evolutions of wave packet motions ((a) and (b)) and state populations ((c) and (f)) when the laser parameters are as follows: pump intensity $I_1=5.0\times10^{12}$ W/cm$^2=5I_0$ ($I_0=1.0\times10^{12}$ W/cm^2),

probe intensity $I_2=5I_0$, pump wavelength $\lambda_1=328$ nm, probe wavelength $\lambda_2=228$ nm, pump and probe pulse widths $\tau_1=\tau_2=30$ fs, and time delay $\Delta t=3\,000$ fs. The wave packet moves periodically between the internal and external turning points with an oscillation period of 1 000 fs. The excited state population following excitation from the ground state is P_A (peak1 in Fig. 2(d)). On the excited state, the outward motion of wave packets hit the crossing point ($R_x=0.693$ nm) at 180 fs and bifurcates due to the nonadiabatic coupling V_{XA}. Although the majority (population P_X) of the wave packets pass to the ground state (Fig. 2(a)), a slight portion (population P_A-P_X) exhibits irreversible motion towards a long internuclear distance in the excited state (Fig. 2(b)). This leads to dissociate into Na and I atoms, ultimately elevating the ground state population to $1-P_A+P_X$ (Fig. 2(c)), and diminishing the excited state population to P_A-P_X, which can eventually reach 0 because of the dissociation (Fig. 2(d)). Moreover, the sum of populations of three states declines to $1-P_A+P_X$ (Fig. 2(f)). As defined and discussed in previous reports, $(P_A-P_X)/P_A$ reflects the predissociation probability following the initial passage through the crossing zone [14-20]. On the ground state, the wave packets hit the external turning point ($R=1.24$ nm) at 500 fs, which split again after returning to the crossing point at 800 fs. At this point, most (population P'_A) shift to the excited state, while a slight portion (population $P_X-P'_A$, peak2 in Fig. 2(d)) remains on the ground state. On the excited state, the wave packets hit the internal turning point ($R=0.27$ nm) at 1 000 fs, finishing one periodic movement. Thereafter, the second period commences, and the wave packets repeat the identical process continually. Apart from that, the wave packet passes the ionic-covalent crossing point twice per cycle. The predissociation mechanism occurs at the crossing point due to the nonadiabatic coupling. The heights of the four successive peaks decrease successively, i.e., $P'_A<P_A$, indicating the dissociation in each passage via the crossing zone as the delay duration is prolonged, which agrees with the ion signal-based results [2,13].

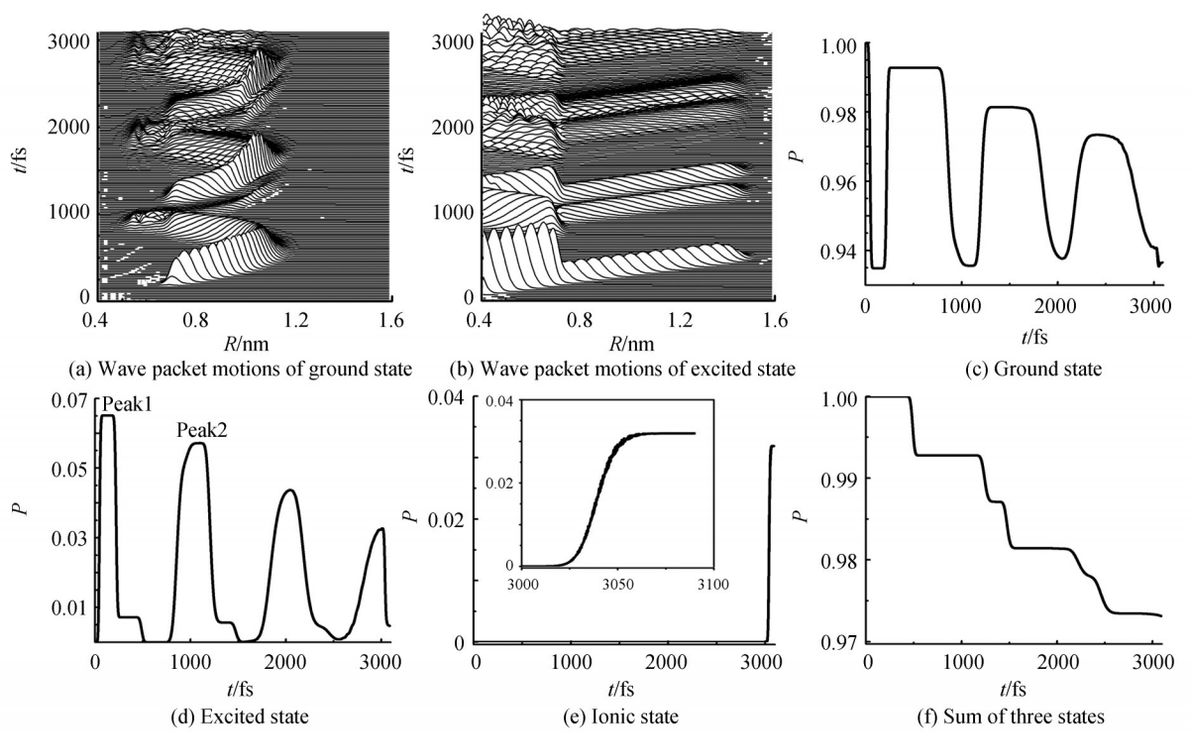

Fig. 2 The evolutions of wave packet motions and state populations

After about three periodical motions (3 000 fs), the probe laser is present, and the population of the ionization state enhances to P_I (Fig. 2(e)), while the sum of populations of three states decreases to P_S (Fig. 2(f)). The total dissociation probability after three back and forth crossings is $(1-P_S)/P_A$. The femtosecond laser conditions for controlling the excitation, dissociation and ionization can be obtained by analyzing the effects of femtosecond laser parameters on excitation population P_A, total dissociation probability $(1-P_S)/P_A$, and ionization probability P_I/P_A of NaI.

Fig. 3 demonstrates state populations P_A, $1-P_S$, and P_I, the probabilities P_I/P_A and $(1-P_S)/P_A$, and the pathway ratio $(1-P_S)/P_I$ at different delay times (0～3 000 fs) when other laser parameters as in Fig. 2. It can be observed that in the excited state, the population is not affected by the delay time. As the delay time is prolonged, the dissociation becomes more possible, whereas the ionization turns more impossible. The longer the delay time, the longer the duration of wave packet movement prior to the ionization. Accordingly, the crossing point is reached multiple times by the wave packet, so that more wave packets are dissociated into the Na and I atoms. Besides, the onset time for photodissociation is 300 fs and the photodissociation enhances with the enhancement of delay time. The obtained findings are in consistence with those of MIAO X Y et al[22]. The pump-probe delay time evolution of the total dissociation probability reveals a series of increasing stair-stepped plateaus, which are indicative of the individual parts of the wave packet reaching the asymptotic region i.e., discontinuous dissociation process. The asymptotic zone (R=1.06 nm) can be arrived at by the first portion of wave packet around 300 fs due to the bifurcation at its initial passage through the crossing point, and till 1 200 fs, the asymptotic region is occupied by this portion of wave packet only. At around 1 300 fs, the asymptotic region is arrived at by a second wave packet, and till 2 300 fs, and the presence of 2 well-branched wave packets is noted inside the asymptotic zone. As a result, the regular steps reflect these well-branched wave packets that are dissociating[23].

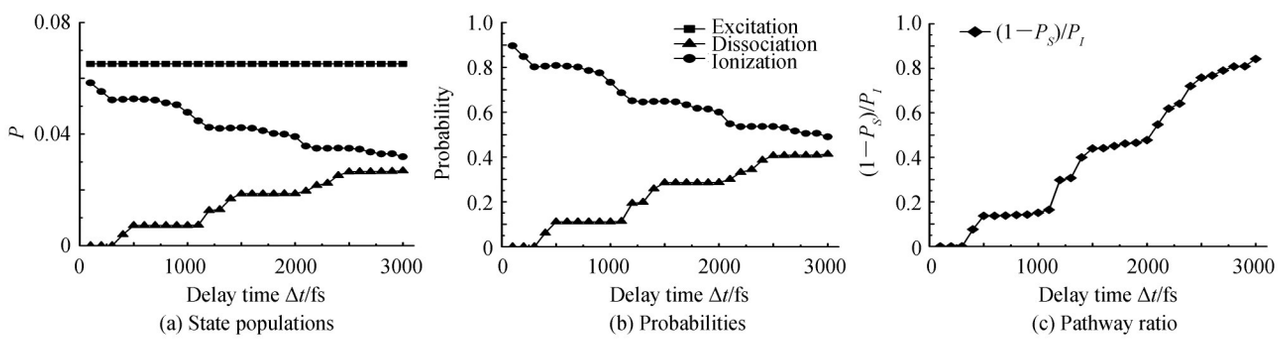

Fig.3 The state populations, the probabilities and the pathway ratio at different delay times

The effects of the laser intensity on excitation, dissociation and ionization are investigated. Figs. 4(a)～4(c) show state population P_A, $1-P_S$, and P_I, probabilities P_I/P_A and $(1-P_S)/P_A$, and pathway ratio $(1-P_S)/P_I$ vs. pump laser intensity I_1. Other laser parameters are: $I_2=5I_0$, λ_1=328 nm, λ_2=228 nm, $\tau_1=\tau_2$=30 fs. The results reveal an increase in the excitation, marginally decrease in dissociation probability, and marginally increase in ionization probability with the increase of pump laser intensities. The FTS signal intensity is linear with the pump pulse intensities (over a reasonable range) and the off-resonant FTS transient shape is independent of the pump intensity, which indicates the invariance of the dissociation probability to pump intensity[10, 24]. SUN et al suggested that the dissociation probability after the first passage of the curve crossing is nearly independent of the pump intensity[17]. However, our result appears to be different with the result of SUN et al, which can be due to the examination of a wide range (10^{11}～10^{15} W/cm^2) of pump intensities that is far wider than those in previous reports. It can be observed from the Fig. 4(c) that the pathway ratio decreases with the increase of the pump laser intensity.

Figs. 4(d)～4(f) show the P_A, $1-P_S$, P_I, P_I/P_A, $(1-P_S)/P_A$, and $(1-P_S)/P_I$ vs. probe laser intensity I_2. Other laser parameters are: $I_1=5I_0$, λ_1=328 nm, λ_2=228 nm, $\tau_1=\tau_2$=30 fs. It is observed that the probe laser intensity has not affected excitation and dissociation. The intensity of FTS transients is linear with the probe pulse intensities (over a reasonable range) and the off-resonant FTS transient shape is independent of the probe intensity, which indicates the invariance of the dissociation probability with the probe intensity[10]. Our result is consistent with previous reports. The ionization probability increases as the probe laser intensity enhances, when $I_2<10I_0$, and it does not change when $I_2\geqslant 10I_0$, i.e., ionization saturation. The ionization is lower than the dissociation, when $I_2<3I_0$, but is larger than the dissociation when $I_2\geqslant 3I_0$. It can be observed from Fig. 4(f) that the pathway ratio decreases with increasing pump laser intensities. The ratio, however, has no change when the intensity is above 1.0×10^{13} W/cm^2.

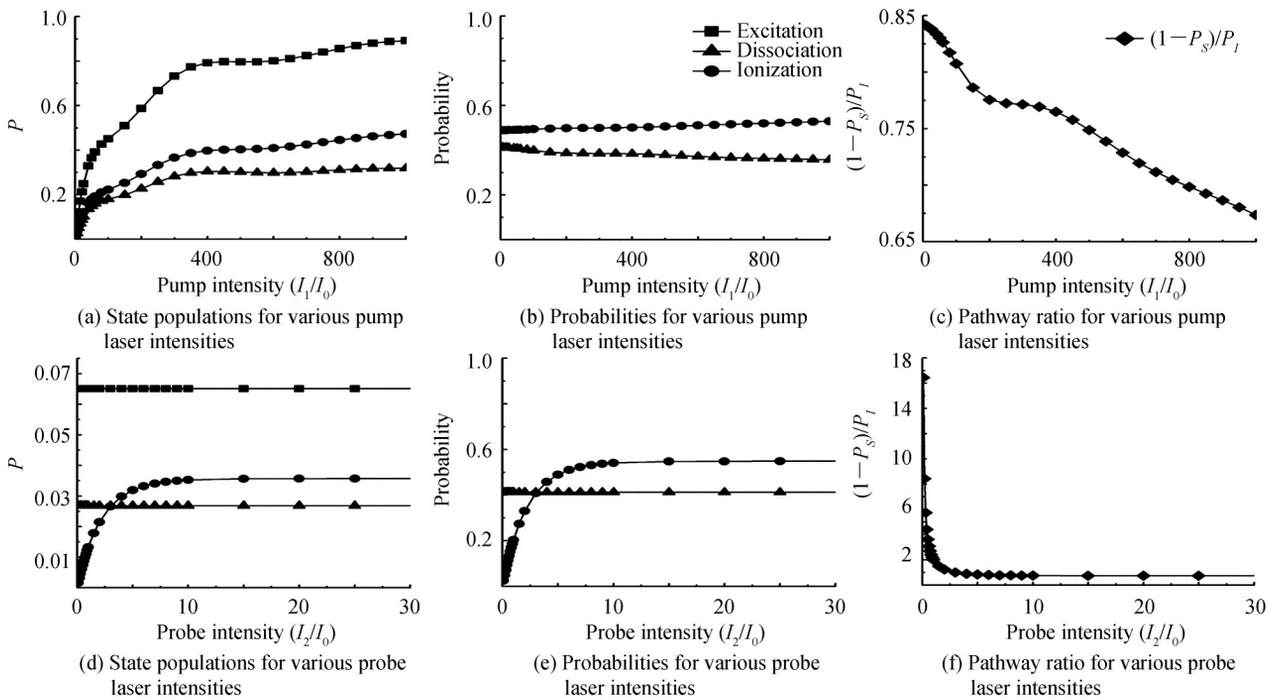

Fig.4 State populations, the probabilities and the pathway ratio for various pump/probe laser intensities

The dependence of excitation, dissociation and ionization on the laser wavelength is examined. Figs. 5(a)～5(c) show P_A, $1-P_S$, P_I, P_I/P_A, $(1-P_S)/P_A$, and $(1-P_S)/P_I$ vs. pump laser wavelength λ_1 (278～368 nm). Other laser parameters are: $I_1=I_2=5I_0$, $\lambda_2=228$ nm, $\tau_1=\tau_2=30$ fs. With the increase in pump wavelength, the excited state population increases initially and then decreases, reflecting the resonant region of 313～328 nm. An increase in the wavelength (278～368 nm) monotonically drops the dissociation probability, which is consistent with the result obtained from the FTS measurements and the dissociation probability associates with the wave packet propagation velocity[10]. This is because a pulse with shorter wavelength, i.e., the higher

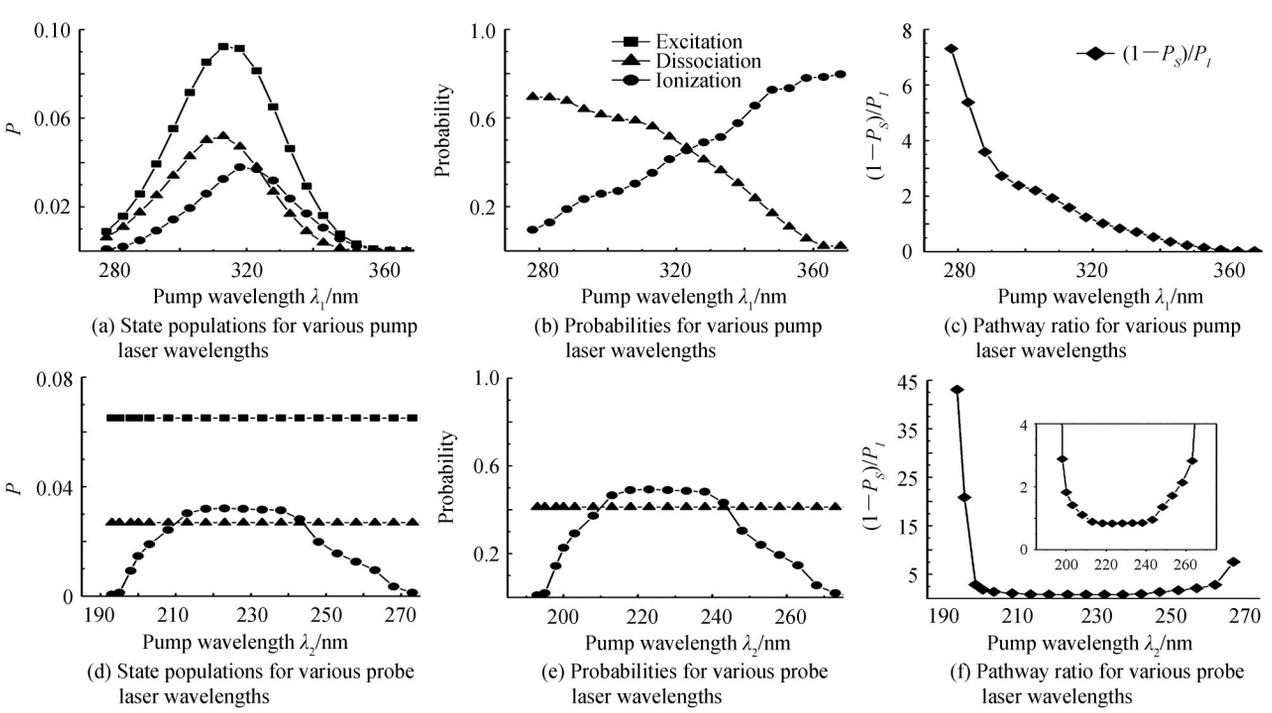

Fig. 5 State populations, the probabilities and the pathway ratio for various pump/probe laser wavelengths

energy, causes a wave packet with a higher velocity at the crossing point, increasing the predissociation. The tendency of the increasing ionization probability with the increasing pump wavelengths is consistent with the conclusion obtained from the NaI^+ signal[8]. The dissociation is higher than the ionization when $\lambda_1 \leqslant 323$ nm, while it is lower than the ionization when $\lambda_1 > 323$ nm. It can be observed from Fig. 5(c) that the pathway ratio decreases when pump wavelengths increase. Figs. 5(d)~(f) exhibit the P_A, $1-P_S$, P_I, P_I/P_A, $(1-P_S)/P_A$ and $(1-P_S)/P_I$ vs. probe wavelength λ_2. Other laser parameters are: $I_1=I_2=5I_0$, $\lambda_1=328$ nm, $\tau_1=\tau_2=30$ fs. The probe laser wavelength has no effect on excitation and dissociation. This is manifested by that the shape of the FTS transient is essentially independent of the probe wavelength experimentally[10]. The ionization probability initially increases, later remains constant, and finally decreases with the increase of probe laser wavelength. The peaks corresponding to a longer probe wavelength decay faster than those corresponding to a shorter probe wavelength in the Na^+ signal, indicating the decrease in ionization with the increasing probe wavelengths (248~302 nm)[13]. The ionization is lower than the dissociation when $\lambda_2 < 210$ nm/$\lambda_2 > 244$ nm, while it is larger than the dissociation when 210 nm$\leqslant \lambda_2 \leqslant$244 nm. This indicates that the region of the probe wavelength 210~244 nm efficiently triggered the photoionization process, which is an expected wavelength region for triggering ionization indicated in Ref. [21]. It can be confirmed that in the region of 210~244 nm, NaI molecules are promoted to some ionic continuum states (0~1.2 eV).

The impact of the laser pulse width on excitation, dissociation, and ionization is also examined. Figs. 6(a)~(c) show P_A, $1-P_S$, P_I, P_I/P_A, $(1-P_S)/P_A$, and $(1-P_S)/P_I$ vs. pump pulse width τ_1(10~200 fs). Other laser parameters are: $I_1=I_2=5I_0$, $\lambda_1=328$ nm, $\lambda_2=228$ nm, $\tau_2=30$ fs. The population of excitation, dissociation, and ionization all increase with the increase of the pump pulse width, because the increase of the pulse width means the increase of the laser on time, which will increase the population[11]. The dissociation probability decreases slightly and the ionization probability enhances slightly with enhancing pump pulse width for $\tau_1 < 100$ fs. This is in consistence with the result acquired from the LIF signal[11, 12, 25]. The dissociation probability increases slightly and the ionization probability reduces slightly with rising pump pulse width for 100 fs$\leqslant \tau_1 \leqslant$180 fs. The dissociation probability associates with the propagation velocity[10] and time taken for passing through the crossing zone[11]. The larger the propagation velocity[10] or the longer the time spends in the crossing region[11], the higher the dissociation probability. These two processes coexist and compete. If propagate velocity dominates, a lower dissociation probability for longer pulse width is anticipated, owing to longer pulses indicative of lower laser energy, which can cause a wave packet with low velocity at the crossing point, decreasing the predissociation. It is clearly the case in our results for shorter pulse widths ($\tau_1 < 100$ fs). If the propagated time dominates, this should result in a larger dissociation probability for longer pulse width, because a longer pulse causes a wider wave packet in spatial terms, and accordingly, longer time is consumed through the crossing zone, leading to a relative larger dissociation probability. It is the case in our results for longer pulse widths (100 fs$\leqslant \tau_1 \leqslant$180 fs). When $\tau_1 > 180$ fs, the sum of the dissociation probability and the ionization probability is more than 1 (Fig. 6(b)). In other words, the sum of the dissociation population and the ionization population is more than the excited state population. The reason is that multi-time excitation of the molecules is probable when the pulse width is broad. According to Fig. 6(c) that the pathway ratio exhibits a decline when the pump pulse widens for $\tau_1 < 100$ fs, and it increases with the increase of the pump pulse width for 100 fs$\leqslant \tau_1 \leqslant$180 fs. Figs. 6(d)~(f) show the P_A, $1-P_S$, P_I, P_I/P_A, $(1-P_S)/P_A$, and $(1-P_S)/P_I$ vs. probe pulse width τ_2. Other laser parameters are: $I_1=I_2=5I_0$, $\lambda_1=328$ nm, $\lambda_2=228$ nm, $\tau_1=30$ fs. The population of ionization increases as the probe pulse width enhances due that the increase of the pulse width means the increase of the laser on time, which will increase the population[11]. The ionization probability increases with the rise of the probe pulse width when $\tau_2 < 100$ fs, and it shows no significant change when $\tau_2 \geqslant 100$ fs, i.e., ionization saturation. The ionization is lower than the dissociation when $\tau_2 < 20$ fs, while is larger than the dissociation when $\tau_2 \geqslant 20$ fs. It can be observed from Fig. 6(f) that the pathway ratio initially decreases and then does not change with the increase of the pump pulse width.

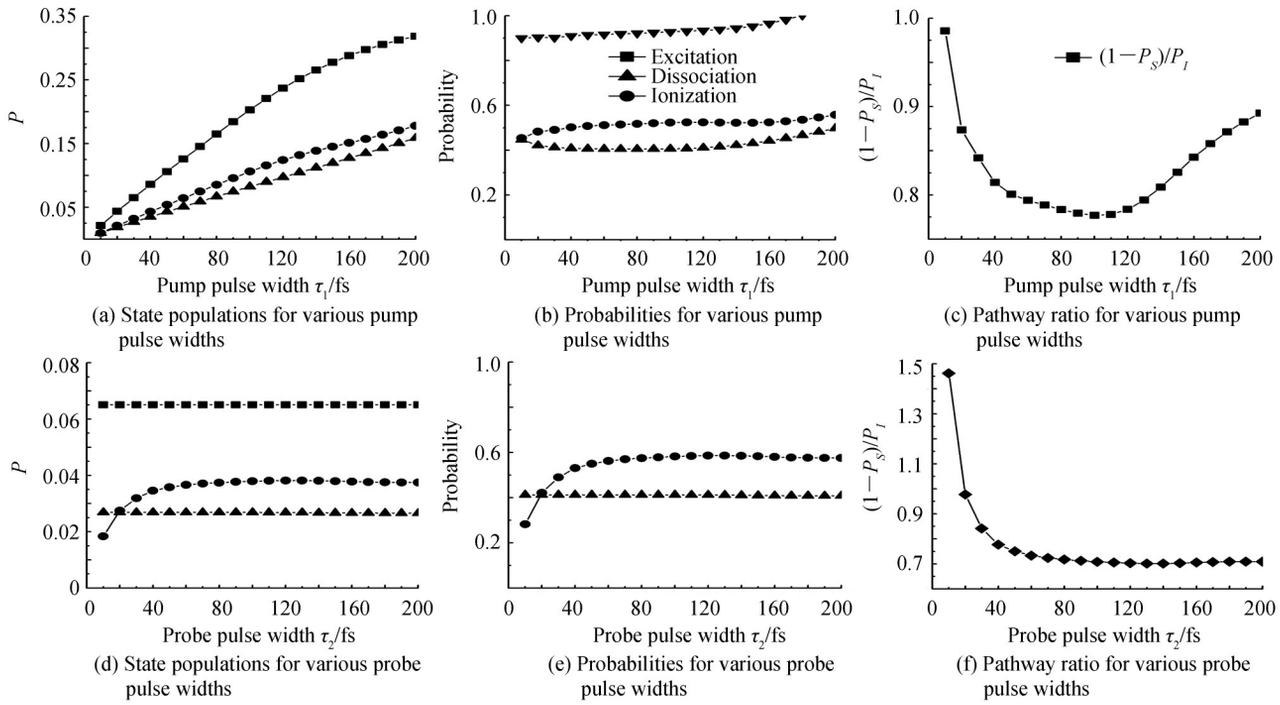

Fig. 6 State populations, the probabilities and the pathway ratio for various pump/probe pulse widths

3 Conclusion

The wave packet dynamics of nonadiabatic coupling NaI molecule driven by a pump-probe pulse is investigated via a time-dependent wave packet approach. The impacts of pump and probe laser parameters on the excitation, dissociation and ionization are studied in detail and are analyzed quantitatively. The excitation and dissociation are affected only by the pump laser, while the ionization is affected by both the pump and the probe lasers. Combined the discussion above, the seemingly counterintuitive understanding: the pump pulse affects the ionization probability, can be clarified. The pump laser parameters affect the dissociation of the wave packets moving between the internal and external points before the probe pulse appears. Then ionization may occur when the probe pulse appears at 3 000 fs. The ionization follows the general understanding of photoionization: ionization occurs when the photon energy is greater than the ionization energy, and the ionization probability is determined by the ionization dipole moment at the internuclear distance R for the delay time of 3 000 fs. In other words, due to the competition of dissociation and ionization, the pump pulse affects the wave packets before ionization through affecting the dissociation, thus affects the ionization. This provides an additional control means for controlling ionization, and even in a very effective way. For example, the pump laser wavelength can effectively control the ionization.

The excitation probability of molecules can be selected by adjusting pump laser parameters. For instance, in order to obtain a higher excitation probability, the pump laser field needs to work under a stronger laser intensity, longer pulse duration (<180 fs), and resonant region (303~328 nm).

The control of the dissociation probability of molecules can be possible by adjusting pump laser parameters. For example, with the purpose of acquiring a higher dissociation probability, the pump laser field needs to work under a stronger laser intensity, shorter pulse duration, near-resonant region (303~328 nm), and longer delay time.

The control of the ionization probability of molecules can be done by adjusting the pump and probe laser parameters. For example, in order to obtain a higher ionization probability, the pump laser field needs to work under a stronger laser intensity, longer pulse duration (<180 fs), and near-resonant region (303~328 nm). The probe laser field must operate with higher laser intensity, longer pulse duration, a wavelength range of 210~244 nm, and a shorter delay time.

The dissociation and ionization coexist and compete. The dissociation dominates when $I_2<3I_0$, $\lambda_1<323$ nm,

$\lambda_2<210$ nm/$\lambda_2>244$ nm, $\tau_2<20$ fs. The ionization dominates when $I_2\geqslant 3I_0$, $\lambda_1\geqslant 323$ nm, 210 nm$\leqslant\lambda_2\leqslant$244 nm, $\tau_2\geqslant 20$ fs.

Apart from being vital for the molecular spectroscopy, the obtained novel findings also contribute to attaining an optical molecular control in experimental settings, as well as providing some essential foundation for future theoretical research in this area.

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Field Dependence of Dissociation and Ionization of NaI in Femtosecond Pump-probe Laser Fields

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Abstract: With the advances in ultra-strong and ultra-short laser pulses, many research works have concentrated on the real-time control of molecular dynamics. Apart from plotting the wave packet dynamics data of the electronic state, the state population is also capable of reflecting the excitation, dissociation and ionization of molecules. By controlling the wave packet evolution, the state population can be manipulated, thereby facilitating the optical control over the molecular processes experimentally. NaI molecule is a reference molecule for monitoring wave packet evolution experimentally and theoretically because a crossing is present between two electronic states that are coupled in a nonadiabatic way. The wave packet moves periodically between the internal and external turning points, which induced the periodical change of the photoelectron spectrum. Many researches mainly investigated the photoelectron spectrum, the competitive ionization channel and the predissociation dynamics of the first passage through the crossing region. Although the photoelectron spectrum offers the significant plotting of the exited-state movement of wave packets and ionization yields, it is not enough to reflect the excitation, dissociation as well as ionization processes of molecules. Herein, this work focuses on the study of the respective parameter effects of pump and probe pulses on the probabilities of excitation and ionization, and the total probability of dissociation of NaI molecules, which are examined completely and quantitatively analyzed. State populations of the ground and excited states of NaI and the ionic ground state of NaI^+ are calculated by adopting a time-dependent wave packet method, because it has the intuition of classical mechanics, no lack of accuracy of quantum mechanics. By appropriately changing the laser parameters, the population on each state can be controlled, and so can the excitation, dissociation and ionization probabilities. The dissociation increases while the ionization decreases when the delay time is prolonged. The pump-probe delay time evolution of total dissociation probability reveals a series of increasing stair-stepped plateaus, which are indicative of the individual parts of the wave packet reaching the asymptotic region i.e., discontinuous dissociation process. The results reveal an increase in the excitation, marginal decrease in dissociation probability, and marginal increase in ionization probability with increasing pump laser intensities. With the increase in pump wavelength, the excited state population increases initially and then decreases, reflecting the resonant region of 313~328 nm. The ionization probability increases while the dissociation probability decreases with the increase of the pump wavelength. The dissociation probability associates with the wave packet propagation velocity and the time taken for passing through the crossing zone. A pulse with a shorter wavelength indicating the higher energy, causes a wave packet with a higher velocity at the crossing point, increasing the predissociation. The dissociation probability decreases slightly with enhancing pump pulse width for shorter pulse widths, in which the propagation velocity dominates. The dissociation probability increases slightly with rising pump pulse width for longer pulse widths, in which the propagation time dominates. As suggested by the derived results, pump laser is the sole influencing factor of molecular excitation and dissociation, while the ionization was affected by both pump and probe lasers. The seemingly counterintuitive understanding: the pump pulse affects the ionization probability, can be clarified. The pump laser parameters affect the dissociation of the wave packets moving between the internal and external points before the probe pulse appears. Then ionization may occur when the probe pulse appears at 3 000 fs. The ionization follows the general understanding of photoionization: ionization occurs when the photon energy is greater than the ionization energy, and the ionization probability is determined by the ionization

dipole moment at the internuclear distance for the delay time of 3 000 fs. In other words, The dissociation and ionization processes compete and coexist, the pump pulse affects the wave packets before ionization through affecting the dissociation, thus affects the ionization. This provides an additional control means for controlling ionization, and even a very effective way. The laser field with weak field intensity, short wavelength, narrow pulse width and long delay time is conducive to dissociation, on the contrary, it is conducive to ionization. The control of the excitation, dissociation, and ionization yields can be possible by adjusting the form of the laser pulse. The obtained findings are crucially valuable for the molecular spectroscopy, which can also contribute to attain optical molecular control experimentally.

Key words: Femtosecond pump-probe laser field; Dissociation probability; Ionization probability; State population; Time-dependent wave packet method

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