

Theoretical study of the femtosecond photoionization of the NaI molecule

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The time-resolved photoelectron spectra of the NaI molecule, as well as the populations of the Na⁺ ion and the NaI⁺ ion have been calculated in this paper by using the time-dependent wave packet method. The results agree well with the experimental ones [J. Phys. Chem. A **101**, 2555 (1997)]. It is found that exchange of the wave packets in the crossing area plays a prominent role in the process of photoionization. Two conclusions can be derived from the calculation: First, the population of the Na⁺ ion is approximately seven times that of the NaI⁺ ion when the pump and probe delay is 150 fs and, second, the vibrational period is about 700 fs and has an increasing trend with the increase of time.

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I. INTRODUCTION

During the past two decades, femtochemistry has made remarkable progress, and more and more scientists have paid attention to the dynamical research on a femtosecond time scale [1–16]. Since the first dynamical study [1,2] about NaI molecule in 1988 by Zewail *et al.*, numerous experimental and theoretical researches [3–13] on the same system have been performed. For example, a femtosecond ionization experiment [12] on NaI was performed by Juvet *et al.* in 1997, and all of the experimental results, including time-resolved photoelectron spectra, molecular and atomic ion kinetic energy distributions, as well as ion and electron total yields, were displayed in Ref. [12]. One year later, quantum mechanical simulation invoking the rotating wave approximation (RWA) [13] was carried out by Charron *et al.* in 1998, and the branching ratio between three fragmentation channels was investigated. In this paper, the femtosecond pulse time-resolved photoelectron spectroscopy (TRPES) of NaI is simulated by using the time-dependent wave packet method and the results accord well with the experimental ones [12].

In the experimental paper [12], Juvet *et al.* included their own classical calculations, albeit the classical simulations considered that ionization occurred only when the wave packet is in the ionic region of the excited state of the NaI molecule. In subsequent theoretical work [13], Charron *et al.* invoked the rotating wave approximation (RWA) to simulate the experimental results. Obviously, parts of their calculated results did not agreed well with the experimental results. In their opinions, the discrepancy (Fig. 6 and Fig. 9 in Ref. [13]) between the experimental and their theoretical results was due to the autoionization process, partial dissociation by the static field, as well as the vibrational distribution of the NaI⁺ ion, and so on. Compared with the earlier simulations, in our paper, both the pump and the probe pulses were considered using the accurate quantum mechanics method without invoking the RWA, and then the dynamics of all states of the NaI dealt with the wave packet explicitly. Hence more intuitional images of the dynamical process were presented in our work.

II. THEORETICAL TREATMENT

In the experiment of Juvet *et al.* [12], two femtosecond pulses, namely a pump pulse and a probe pulse, were employed. The first pump pulse electronically excites the NaI molecule from its ground state (X) to the excited state (A). The second probe pulse has enough energy to access the ionic states of the NaI molecule and photodetaches the dissociating molecule to form a photoelectron and either an NaI⁺ ion or an I atom and an Na⁺ ion, where a competition between dissociative and nondissociative ionization may occur [13]. To describe these behaviors conveniently, we can also display the overall process using the time-resolved wave packet method in Fig. 1. Initially, the wave packet resides on the potential energy surface of the NaI molecule ground state (X) and can be detached by the pump pulse and form a new wave packet on the potential energy surface of the NaI molecule excited state (A). During the delay time, the new wave packet propagates on the potential energy surface of the NaI excited state (A). After that, the new wave packet is excited to the ionic potential energy surfaces of NaI electronic states by the probe pulse. In Fig. 1, the potential curves of the NaI molecule and the NaI⁺ ion have also been shown.

To calculate the TRPES of the NaI molecule, we performed the three-state (the ground state of the NaI molecule, the excited state of the NaI molecule, and the ionic state of the NaI molecule) quantum mechanical calculations. The rotational degree of freedom in our treatment is frozen because of the ultrashort interaction time between the NaI molecule and the femtosecond laser pulses. Invoking the Born-Oppenheimer approximation and neglecting the coupling between the core and photoelectron, we write the Hamiltonian for the vibration motion of the molecule as

$$H = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} I + V(R, t), \quad (1)$$

where I is the identity matrix, R is the internuclear separation, and μ is the reduced mass of the molecule, while the potential matrix $V(R, t)$ can be explicitly written as [17–23]

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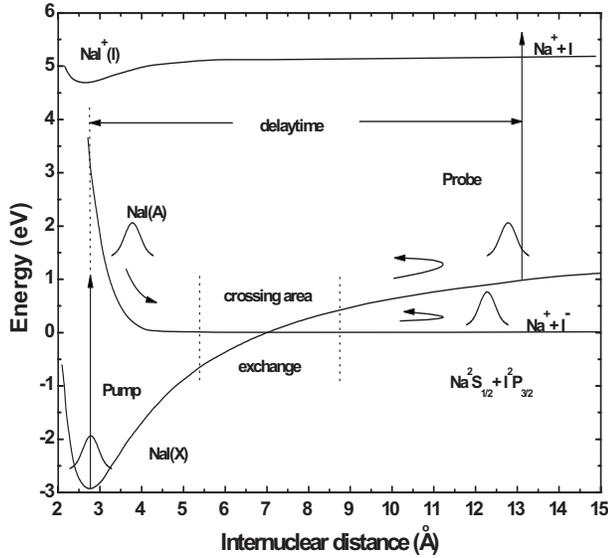


FIG. 1. Potential energy curves for the NaI molecule are taken from Refs. [7,28–30] and the movement of the wave packet on the potential energy curves are also shown.

$$V(R,t) = \begin{pmatrix} V_{XX} & V_{XA} & 0 & 0 & \cdots & 0 \\ V_{AX} & V_{AA} & V_{AI} & \cdots & \cdots & V_{AI} \\ 0 & V_{IA} & V_{II} + E_{I,1} & 0 & \cdots & 0 \\ \vdots & \vdots & 0 & \ddots & \cdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & V_{IA} & 0 & 0 & \cdots & V_{II} + E_{I,n} \end{pmatrix} \quad (2)$$

where X , A , and I stand for the ground state of the NaI molecule, the excited state of the NaI molecule, and the ground state of the NaI^+ ion, respectively, and V_{ii} ($i = X, A, I$) refers to the potential matrix element of the molecule in the absence of any laser field. For the continuum state of the NaI^+ ion, the free electron-ion pair states are detached by 50 discrete states. $V_{II} + E_{I,n}$ ($n = 0, 2, \dots, 50$) denote the total energies of the discrete set of continuum states in the part of the free electron-molecule pair states, and $E_{I,n}$ are the electron kinetic energies of the ground state of the NaI^+ ion.

The energies $E_{I,n}$ of the quasicontinuum states can be written as $E_{I,n} = (E_{\max} - E_{\min})/n$, where E_{\max} (E_{\min}) is the maximum (minimum) of the kinetic energy (photoelectron) which is detected in the experiment [12]. The discretization of the continuum is not arbitrary. To get accurate dynamic results, it is necessary to validate the astringency of our results. In the paper, $n = 50$ was found suitable to get the stable results in our calculation. Actually, we have calculated the photoelectron spectrum when n is equal to 40, 50, 60, and 70, respectively. After calculation, it was found that the results were different when n is equal to 40 and 50, whereas the same results were obtained when n is equal to 50, 60, and 70, respectively. That is to say, the results are stable when n is equal to 50. Therefore, it is enough to get the accurate dynamical results when n is equal to 50.

V_{ij} denotes the coupling between the ground state of the NaI molecule or the excited state of the NaI molecule and the ground state of the NaI^+ ion, and it can be written as

$$V_{ij} = V_{ji} = \mu_{ij}E(t), \quad i = X, A, I, \quad (3)$$

where μ_{ij} and $E(t)$ are the dipole matrix elements and the external field, respectively. The dipole matrix elements μ_{ij} are the same as those in Ref. [13]. The shape of the laser pulses is chosen as

$$E(t) = \{E_1 f(t_1) \cos(\omega_1 t) + E_2 f(t_2 - \Delta t) \cos(\omega_2 t)\} \hat{e}, \quad (4)$$

where E_1 and E_2 are the electric field amplitudes of the pump and probe pulses with the linearly polarized direction \hat{e} , respectively. ω_1 and ω_2 are the corresponding angular frequencies. Δt is the delay time between the two Gaussian pulses. The envelopes $f(t_1)$ and $f(t_2 - \Delta t)$ of the pulses are expressed as

$$f(t_1) = \exp\left[-\left(\frac{t}{\tau_1}\right)^2\right],$$

$$f(t_2 - \Delta t) = \exp\left[-\left(\frac{t - \Delta t}{\tau_2}\right)^2\right], \quad (5)$$

where τ_1 and τ_2 denotes a full width at half maximum (FWHM) of pump and probe pulse, respectively.

The time-dependent *Schrödinger* matrix equation can be written as

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \Psi_X \\ \Psi_A \\ \Psi_{I1} \\ \vdots \\ \vdots \\ \Psi_{In} \end{pmatrix} = \begin{pmatrix} H_{XX} & H_{XA} & 0 & \cdots & \cdots & 0 \\ H_{AX} & H_{AA} & H_{AI} & \cdots & \cdots & H_{AI} \\ 0 & H_{IA} & H_{II} + E_{I,1} & 0 & \cdots & 0 \\ \vdots & \vdots & 0 & \ddots & \cdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & H_{IA} & 0 & \cdots & \cdots & H_{II} + E_{I,n} \end{pmatrix} \begin{pmatrix} \Psi_X \\ \Psi_A \\ \Psi_{I1} \\ \vdots \\ \vdots \\ \Psi_{In} \end{pmatrix}, \quad (6)$$

where Ψ_i ($i=X,A$) and Ψ_{In} ($n=0, \dots, 50$) denote the wave function of the bound states and quasicontinuum states (discrete states). The diagonal element can be expressed as

$$H_{ii} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R^2} + V_{ii}(R,t). \quad (7)$$

The off-diagonal element can be expressed as

$$H_{ij} = H_{ji} = V_{ij} = \mu_{ij}E(t). \quad (8)$$

The above matrix equation can be solved by using the ‘‘split-operator Fourier’’ method [17–27]. The evolution of the wave packets with time can be expressed as

$$\Psi(R,t + \Delta t) \approx U_T^{1/2}(R,t)U_V U_T^{1/2}(R,t)\Psi(R,t), \quad (9)$$

where U_T and U_V denote the kinetic and potential energy evolution operators, respectively. The kinetic energy operator is given by

$$U_T = \exp\left[-\frac{i\Delta t}{\hbar}T_R\right] = F^{-1}\exp\left[-\frac{i\hbar k^2\Delta t}{2m}\right]F, \quad (10)$$

where F denotes the Fourier transform

$$F[f] = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dR' e^{ikR'} f(R'), \quad (11)$$

The potential operator is calculated by [18,19]

$$U_V = \exp\left[-\frac{i}{\hbar}V\Delta t\right] = M \exp\left[-\frac{i}{\hbar}M^T V M \Delta t\right] M^T = M \begin{pmatrix} \exp(-i\lambda_1\Delta t/\hbar) & 0 & \cdots & 0 \\ 0 & \exp(-i\lambda_2\Delta t/\hbar) & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \exp(-i\lambda_n\Delta t/\hbar) \end{pmatrix} M^T, \quad (12)$$

where M denotes the matrix that diagonalizes the potential matrix V from Eq. (2), the superscript T represents the transpose of the matrix, and $\lambda_1, \lambda_2, \dots, \lambda_n$ are the eigenvalues of the matrix V .

Therefore, Eq. (9) can be rewritten as

$$\Psi(R,t + n\Delta t) \approx \left[\prod_{k=0}^{n-1} U_T^{1/2}(R,t + k\Delta t) U_V U_T^{1/2}(R,t + k\Delta t) \right] \Psi(R,t). \quad (13)$$

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

$$P_i(t) = \int dR |\Psi_i(R,t)|^2, \quad i = X, A, I+1, \dots, I+n \quad (14)$$

and the photoelectron spectrum can be expressed as follows:

$$P(E) = \lim_{t \rightarrow \infty} \int dR \sum_i |\Psi_{Ii}(R,t)|^2, \quad i = 1, 2, \dots, n. \quad (15)$$

The total ion signal P_{ion} is then given by the sum of $P(E)$ over all possible kinetic energies for the ejected electron

$$P_{\text{ion}} = \int dE P(E). \quad (16)$$

For the NaI^+ ion, the probability in a given vibrational state can be written as

$$P_\nu = \int dE \left| \int dR \Psi_\nu^*(R) \Psi(R,t) \right|^2, \quad (17)$$

where $\Psi_\nu(R)$ is the field-free vibrational states of the NaI^+ ion, and the total signal of the NaI^+ ion P_{NaI^+} is the sum of the P_ν over the complete set of ion vibrational states [13]

$$P_{\text{NaI}^+} = \sum_\nu P_\nu \quad (18)$$

whereas the population of the Na^+ ion with a relative nuclear kinetic energy ε is written as [13]

$$P_{\text{Na}^+}(\varepsilon) = \int dE \left| \int dR \Psi_\varepsilon^*(R) \Psi(R,t) \right|^2, \quad (19)$$

where $\Psi_\varepsilon(R)$ is the field-free continuum states of the Na^+ ion and the total signal of the Na^+ ion P_{Na^+} is the sum of the $P_{\text{Na}^+}(E)$ over all possible energies

$$P_{\text{Na}^+} = \int d\varepsilon P_{\text{Na}^+}(\varepsilon). \quad (20)$$

In the experiment [12], the slow electron and the fast electron are described as $0 \text{ eV} < \varepsilon_{\text{slow}} < 0.06 \text{ eV}$ and $0.25 \text{ eV} < \varepsilon_{\text{fast}} < 0.5 \text{ eV}$, respectively. So the population of the slow electron can be written as [13]

$$P_{\text{slow}} = \int_0^{0.06 \text{ eV}} dE \int_0^\infty \Psi^*(R,t) \Psi(R,t) dR \quad (21)$$

and the population of the fast electron can be written as

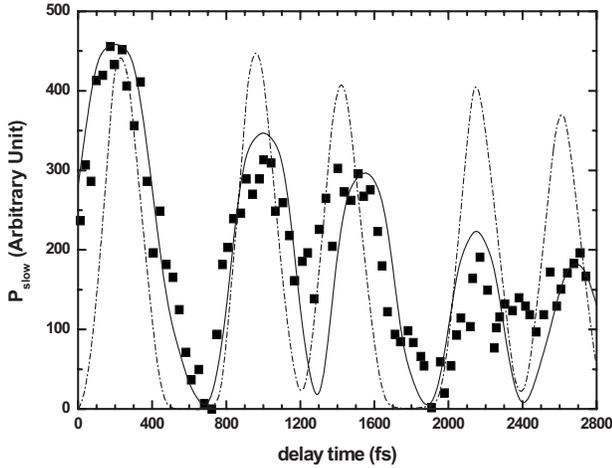


FIG. 2. The comparison of the slow electron population between our calculated result (solid line) and experimentally obtained result (solid square), as well as the result of the theoretical study [13] (dashed line). The 312 pump radiation and the 263 nm probe pulse are used in the calculation.

$$P_{\text{fast}} = \int_{0.25 \text{ eV}}^{0.5 \text{ eV}} dE \int_0^{\infty} \Psi^*(R,t) \Psi(R,t) dR, \quad (22)$$

where the $\Psi(R,t)$ is the wave function of the electron.

In this paper, the internal time $\Delta t=0.2$ fs is found to be suitable for the converged results. Except for the dipole matrix elements, other parameters, such as laser wavelengths and width, are the same as those of the experiment [12].

III. RESULTS AND DISCUSSIONS

In experiment [12], signals of slow ($0 \text{ eV} < \varepsilon < 0.06 \text{ eV}$) and fast ($0.25 \text{ eV} < \varepsilon < 0.5 \text{ eV}$) electrons as well as populations of Na^+ ion and NaI^+ ion have been measured, respectively. Subsequently, invoking the rotating wave approximation (RWA), Charron *et al.* simulated the experimental results [13]. Here, the electron spectra and the ion spectra have been calculated by using the accurate quantum mechanics method. The parameters of the pump (312 nm) and the probe (263 nm) pulse, such as intensity, full width at half maximum, frequency *et al.*, are the same as those of the theoretical simulation by Charron *et al.* [13].

For the slow electron and Na^+ ion, Fig. 2 and Fig. 3 compare our calculated result (solid line) with the experimentally obtained result (solid square) as well as the result of the theoretical study [13] (dashed line), respectively. In Fig. 2, the double peaks (the first peak and the second peak, or the third peak and the fourth peak) structure (dashed line) calculated by Charron *et al.* [13] can be seen clearly. The double peak structure was explained by Charron *et al.* in Ref. [13] as follows: The first peak appears when the wave packet is moving toward large internuclear distances, while the second occurs when it is located at the same place but moving in the opposite direction during the squeezing of the molecular bond [13]. Similarly, double peak structure (dashed line) calculated by Charron *et al.* [13] appears again in Fig. 3 about

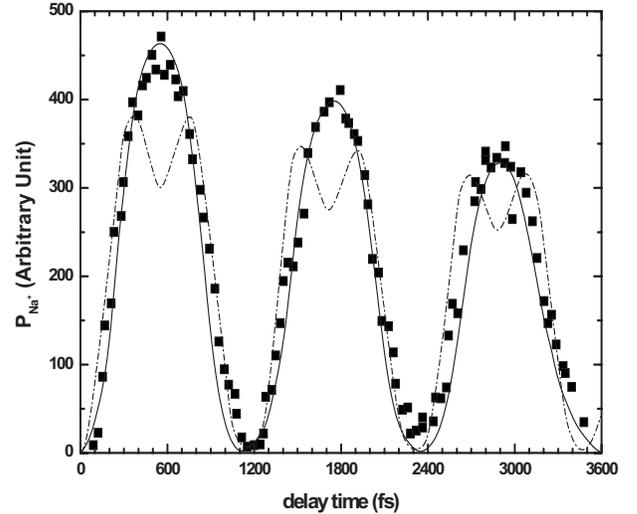


FIG. 3. The comparison of the Na^+ population between our calculated result (solid line) and experimentally obtained result (solid square), as well as the result of the theoretical study [13] (dashed line). The 312 pump radiation and the 263 nm probe pulse are used in the calculation.

the Na^+ ion. In their opinions, the double peak structure was due to the autoionization process, partial dissociation by the static field, as well as the vibrational distribution of the NaI^+ ion. However, we do not think that their explanations are reasonable.

Obviously, prominent differences can be seen in Fig. 2 and Fig. 3 between our calculated results (solid line) with the results calculated by Charron *et al.* In Fig. 2 and Fig. 3, instead of the double peaks structure, the peaks are degressive one by one in our calculations, and our results agree well with the experimental ones. By using the time-resolved wave packet theory, a conclusion can be obtained that the degressive peaks of our calculations in Fig. 2 and Fig. 3 are mainly due to the exchange of the wave packets in the crossing area. Obviously, there is a potential crossing between the ground state (X) and the excited state (A) in Fig. 1. Excited by the pump pulse, the initial wave packet is pumped into the excited state (A). After that, the wave packet transmits on the excited state (A). When the wave packet reaches the crossing, the wave packet is divided into two parts. One part of the wave packet remains in the potential of the excited state (A), whereas the other part of the wave packet runs out of the excited state (A) and leaks to the ground state (X). After a vibrational period, the wave packet that moved along the ground state (X) returns partly to the excited state (A) and overlaps with the next wave packet entering into the crossing area, which will impact the populations of the slow electron and the Na^+ ion after exciting by the probe pulse.

With regard to the fast electron and NaI^+ ion, our calculated results (solid line) with the experimentally obtained results (solid square) as well as the results of the theoretical study [13] (dashed line) are displayed in Fig. 4 and Fig. 5, respectively. Except for the height of each peak in Fig. 4 and Fig. 5, there are few differences between our results and those calculated by Charron *et al.* Similarly, in our opinions, the differences are due to the wave packet counteracting with

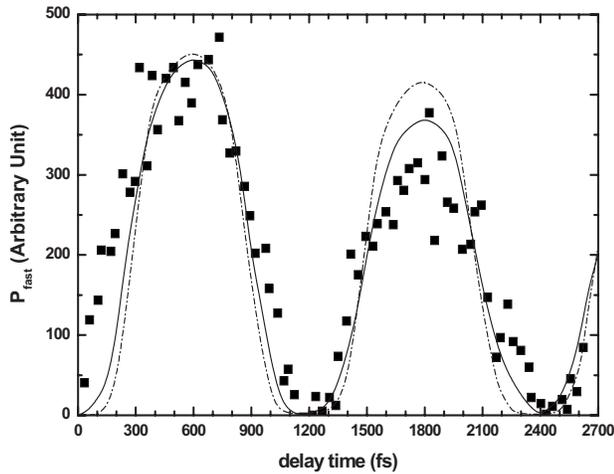


FIG. 4. The comparison of the fast electron population between our calculated result (solid line) and experimentally obtained result (solid square), as well as the result of the theoretical study [13] (dashed line). The 312 pump radiation and the 263 nm probe pulse are used in the calculation.

the returned wave packet. The other characters have been illuminated explicitly in Ref. [12] and Ref. [13].

A more detailed picture about the exchange of the wave packet in the crossing area is presented in Fig. 6. The evolutive populations of the Na^+ ion (solid line) and the NaI^+ ion (dashed line) have been shown in Fig. 6 when the delay time is 150 fs. It can be seen that the population of the Na^+ ion is approximately seven times greater than the population of the NaI^+ ion, and the populations of the Na^+ ion and the NaI^+ ion have prominent oscillation with the propagation of time. Obviously, it is the exchange of the wave packets in the crossing area that leads to the vibration of the populations. We can also find in Fig. 6 that the vibrational period is approximately equal to 700 fs and the period becomes longer and longer

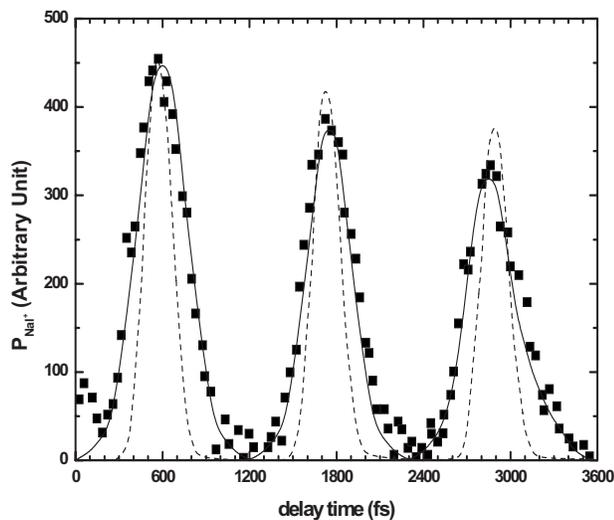


FIG. 5. The comparison of the NaI^+ population between our calculated result (solid line) and experimentally obtained result (solid square), as well as the result of the theoretical study [13] (dashed line). The 312 pump radiation and the 263 nm probe pulse are used in the calculation.

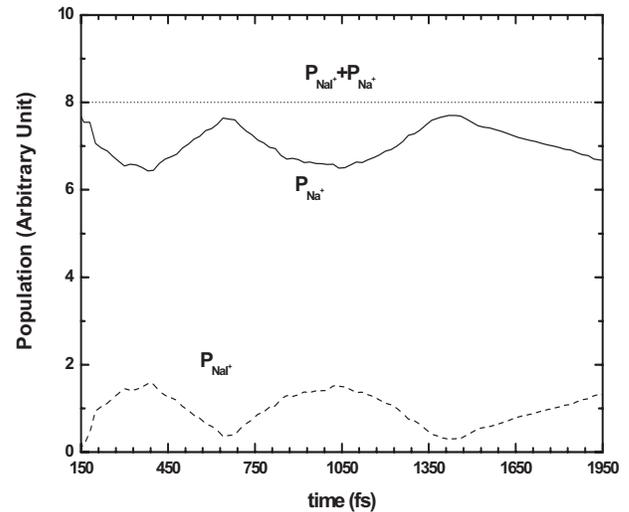


FIG. 6. The solid line and the dashed line present the populations of the Na^+ ion and the NaI^+ ion, respectively. The dotted line presents the total population of the Na^+ ion and the NaI^+ ion. The delay time is equal to 150 fs.

with the increase of time, which is mainly due to the wave packets' interacting many times. Noticeably, the total population $P_{\text{Na}^+} + P_{\text{NaI}^+}$ (dotted line in Fig. 6) of the two competitive photoionization processes (Na^+ and NaI^+) should be equally constant according to the “split operator-Fourier transform” scheme.

Additional information about the process of photoionization is calculated in our work and the results presented in Figs. 7(a)–7(c) are the simulated time-resolved photoelectron spectra responding to the delay time of 600 fs, 400 fs, and 200 fs, respectively. Two characters of the spectra can be observed clearly in Fig. 7. First, each spectrum has two peaks and the first peak decreases monotonically with the delay time, whereas the second one increases monotonically with the delay time. Secondly, as the pump-probe delay increases from 200 fs to 600 fs, the electron kinetic energies corresponding to the two peaks shift little by little toward the high electron kinetic energy.

The following is the detailed explanation for the first character. It has been described in Ref. [13] that the probe pulse has enough energy to access the photoionization ($\text{NaI}^* + \hbar\omega \rightarrow \text{NaI}^+ + e^-$) and the dissociative photoionization ($\text{NaI}^* + \hbar\omega \rightarrow \text{Na}^+ + \text{I} + e^-$). Obviously, the two competitive channels result in the decrease of the first peak and the increase of the second peak with the propagation of the delay time. Because of the existence of binding energy in the NaI^+ ion, the dissociative photoionization of the Na^+ ion needs more energy than the photoionization of the NaI^+ ion. Therefore, the conclusion can be acquired that the first peak corresponding to the lower electron kinetic energy in Fig. 7 is induced by the dissociative photoionization of the Na^+ ion, while the second one corresponding to the higher electron kinetic energy is induced by the photoionization of the NaI^+ ion.

With regard to the second character, time-resolved wave packet theory can be used to interpret the variety of spectra.

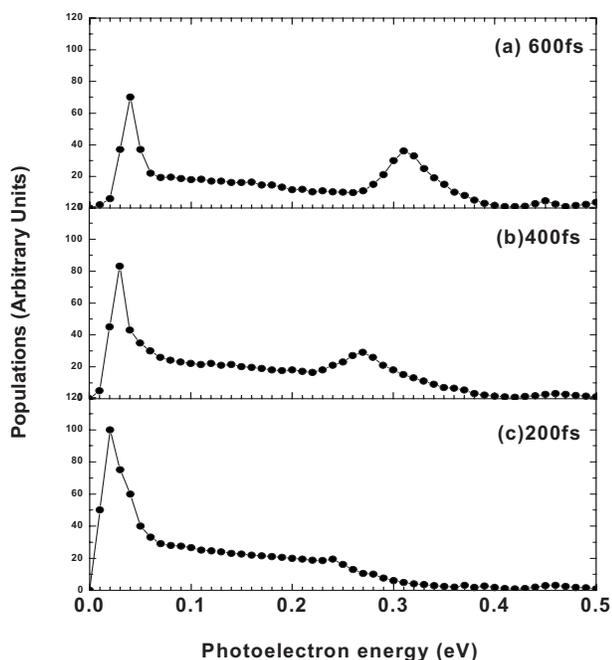


FIG. 7. The femtosecond time-resolved photoelectron kinetic energy spectra of the NaI molecule. The different delay times 600, 400, and 200 fs correspond to (a), (b), and (c), respectively. The 312 pump radiation and the 263 nm probe pulse are used in the calculation.

At short delay time, the wave packet on excited state (*A*) is mostly situated in a short internuclear area. With increasing of the delay time, the wave packet will move to an asymptotic area. Clearly, one can observe from Fig. 1 that

the potential energy curve of the excited state (*A*) is closer to that of the ionic state (*I*) in an asymptotic area than in a short internuclear area. That is to say, the vertical detachment energy is lower in an asymptotic area than in a short internuclear area, so the electron kinetic energy increases with the delay time increase from 200 fs to 600 fs. Hence the shift to higher electron kinetic energy with the delay time is due to the movement of the wave packet on the potential of the excited state (*A*).

IV. CONCLUSION

In this paper, the accurate quantum mechanics method was employed to calculate the photoelectron spectroscopy (PES) of the NaI molecule, as well as the populations of the Na⁺ ion and the NaI⁺ ion. By using the time-resolved wave packet theory, the PES was explained in reason. Through calculation, it has been found that not only is the population of the Na⁺ ion approximately seven times that of the NaI⁺ ion, but also the vibrational period is about 700 fs and has an increasing trend with the increase of time. We considered that exchange of the wave packets in the crossing area played a prominent role in the process of photoionization.

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