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Photoionization of NaK molecule with a double-well potential in femtosecond pump–probe pulse laser fields*

Yu Jie(于 杰), Wang Sen-Ming(王森铭), Yuan Kai-Jun(元凯军), and Cong Shu-Lin(丛书林)†

Department of Physics, Dalian University of Technology, Dalian 116024, *China*

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The method of time-dependent quantum wave packet dynamics is used to calculate the femtosecond pump–probe photoelectron spectra and study the wave packet dynamic processes of the double-minimum potential state $6\,^1\Sigma^+$ of NaK in intense laser fields. The evolutions of the wave packet and the photoelectron energy spectra with time and internuclear distance are described in detail. The wave packet dynamic information of the $6\,^1\Sigma^+$ state can be extracted from the photoelectron energy spectra.

Keywords: femtosecond laser, quantum wave packet, photoelectron spectra, NaK molecule
PACC: 3380, 3365, 8240J

1. Introduction

In recent years, with the development of ultrashort and ultrastrong laser pulse technology, more and more theoretical and experimental researches have focused on the control of atomic and molecular dynamics in real time.[1−16] Many interesting phenomena have been observed, such as above-threshold ionization,[1,2] bond-softening and bond-hardening,[3,4] ac-Stark shift,[5,6] Rabi oscillation,[7] laser-induced continuum structure (LICS),[8,9] etc. Alkali metal dimers, such as Li_2, Na_2, K_2, NaLi, NaK and KLi, are typical molecules with two valence electrons. The excited state dynamics of these dimers has been studied by using the femtosecond pump–probe technique.[17−21] Many alkali metal dimers have double-minimum potential states, such as $2\,^1\Sigma^+$ state of Na_2,[21] $7\,^1\Sigma^+$ state of K_2,[22] $6\,^1\Sigma^+$ state of NaK, and so on. Magnier and Millié predicted theoretically the existence of double-minimum potential $6\,^1\Sigma^+$ state of NaK molecule.[22] Poshov *et al* calculated the double-minimum potential of the $6\,^1\Sigma^+$ state of NaK.[23]

In this paper, we study the wave packet dynamics of $6\,^1\Sigma^+$ state of NaK and calculate the pump–probe photoelectron spectra in femtosecond pulse laser fields. A model of the three electronic states, the ground state $X(1)\,^1\Sigma^+$ and the double-minimum state $6\,^1\Sigma^+$ of the neutral NaK,[23,24] and the ionic ground state $X(1)\,^2\Sigma^+$[25] of NaK^+, is employed in calculation (see Fig.1). The ionization of NaK is a three-photon process. A pump laser prepares an initial vibrational wave packet in the $6\,^1\Sigma^+$ state, which is a two-photon process. After a delay time, a probe pulse ionizes the NaK molecule in the ground state $X(1)\,^2\Sigma^+$ of the NaK^+, which is a single photon process. Our aim is to study the wave packet dynamics of the $6\,^1\Sigma^+$ state and the ionization process of NaK by varying the laser parameters.

2. Theoretical treatment

The potential energy curves and the transition pathways of the NaK molecule in the two-colour laser pulses are depicted in Fig.1. The data of the molecular potentials are gathered from Refs.[23–25]. For simplicity the ground state $X(1)\,^1\Sigma^+$ and the double-minimum state $A(6)\,^1\Sigma^+$ of NaK are abbreviated to X and A, respectively, and the ionic ground state $X(1)\,^2\Sigma^+$ of NaK^+ to I.

The rotational degree of freedom is neglected in our treatment because of the ultrashort interaction time between the NaK molecule and the femtosecond laser pulses. Within the Born–Oppenheimer approx-

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†Corresponding author. E-mail: shlcong@dlut.edu.cn

imation, the wavefunctions of bound and continuum states can be found by solving numerically the time-dependent Schrödinger equation. The Hamiltonian of the molecule with two bound states and one ionization continuum state in external laser fields can be written as

$$\hat{H} = \sum_b |\Phi_b\rangle \hat{H}_b \langle\Phi_b| + \int \mathrm{d}E_k |\Phi_k\rangle (\hat{H}_I^0 + E_k) \langle\Phi_k| + \hat{W}(t), \quad (1)$$

where $|\Phi_b\rangle (b = X, A)$ denote the two bound electronic states of NaK molecule, $|\Phi_k\rangle$ denotes the orthonormal scattering state of the photoelectron with kinetic energy E_k. The $\hat{H}_b$ and $\hat{H}_I^0$ represent the Hamiltonians for the nuclear motions in the two bound states of NaK and the ground state of NaK^+, respectively. $\hat{W}(t)$ denotes the interaction between the molecule and laser fields.

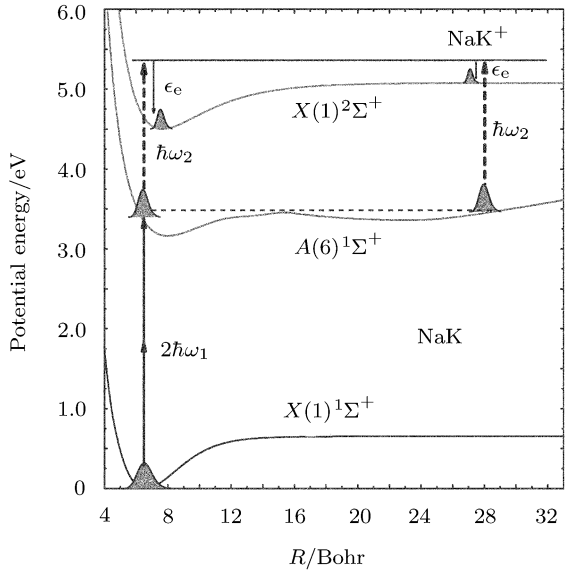


Fig.1. The transition pathways and the potential energy curves for the $X(1)\,^1\Sigma^+$ and $6\,^1\Sigma^+$ states of NaK and the $X(1)\,^2\Sigma^+$ state of NaK^+.

The molecular wavefunction is expressed as[26−30]

$$\begin{aligned}\Psi(r,R,t) &= \sum_b \chi_b(R,t)\,\Phi_b(r;R) + \int \mathrm{d}E_k \chi_{E_k}(R,t)\,\Phi_k(r;R) \\ &= \sum_b \chi_b(R,t)\,\Phi_b(r;R) + \sum_{k=0}^{N-1} \chi_{k\delta\epsilon}(R,t)\,\Phi_k(r;R)\delta\epsilon\,, \end{aligned} \quad (2)$$

where R is the internuclear separation. $\chi_b(R,t)$ and $\chi_{k\delta\epsilon}(R,t)$ are the nuclear wavefunctions corresponding to the Φ_b and Φ_k respectively. For the convenience of numerical calculation, the continuum state has been expressed in a series of discrete states (quasi-continuum states) with the photoelectron kinetic energies

$$\begin{aligned} E_k &= k\delta\epsilon = V_k(R) - V_I(R)\,, \\ k &= 0, 1, \ldots, N-1\,, \end{aligned} \quad (3)$$

where $V_I(R)$ is the potential energy for ground state of NaK^+, $V_k(R)$ the potential energy for the kth discrete state. And $\delta\epsilon$ is the energy interval between the adjacent two discrete states. In Eq.(3), $V_k(R) > V_I(R)$ for $k > 0$ and $V_0(R) = V_I(R)$ for $k = 0$.

The Hamiltonian in Eq.(1) can be rewritten in the matrix representation as $\hat{H} = (H_{ij})$. The diagonal elements can be expressed as

$$H_{ii} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}R^2} + V_i(R)\,, \quad i = b, k\,, \quad (4)$$

where m is the reduced mass of NaK, and $V_i(R)$ including the bound and quasi-continuum states are the potential matrix elements of the molecule in the absence of laser fields.

In the electronic dipole approximation, the matrix elements of the interaction between the molecule and the pump pulse can be written as[30,31]

$$\begin{aligned} W_{XA}(t) &= W_{AX}(t) \\ &= [\mu_{XA} E_1 f(t-t_1)]^2 \cos[2\omega_1(t-t_1)]\,, \end{aligned} \quad (5)$$

where μ_{XA} is the projection of the transition dipole moment between the states X and A on the polarization vector of the laser of frequency ω_1. The pulse envelope

$$f(t-t_1) = \exp[-(4\ln 2.0)(t-t_1)^2/\tau_1^2]$$

is a Gaussian function with the centre time t_1 and the full-width at half-maximum (FWHM) τ_1. E_1 is the electric field amplitude of the pump pulse. In the same manner the states A and I are coupled by the probe pulse of frequency ω_2 with the centre time t_2 and the FWHM τ_2. The coupling between the NaK molecule and the probe pulse is given by

$$\begin{aligned} W_{AI}(t) &= W_{IA}(t) \\ &= \mu_{AI} E_2 f(t-t_2) \cos[\omega_2(t-t_2)]\,, \end{aligned} \quad (6)$$

where E_2 is the electric field amplitude of the probe pulse. $\Delta t = t_2 - t_1$ is the delay time between the pump and probe pulses.

The evolutions of wave packets with time are found by the time-dependent coupled matrix equation

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\begin{pmatrix}\chi_X\\ \chi_A\\ \chi_I^0\\ \chi_I^1\\ \vdots\\ \chi_I^{N-1}\end{pmatrix}=\begin{pmatrix}H_{XX} & W_{XA} & 0 & 0 & \cdots & 0\\ W_{AX} & H_{AA} & W_{AI} & W_{AI} & \cdots & W_{AI}\\ 0 & W_{IA} & H_{II}^0 & 0 & \cdots & 0\\ 0 & W_{IA} & 0 & H_{II}^1 & \cdots & 0\\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots\\ 0 & W_{IA} & 0 & 0 & \cdots & H_{II}^{N-1}\end{pmatrix}\begin{pmatrix}\chi_X\\ \chi_A\\ \chi_I^0\\ \chi_I^1\\ \vdots\\ \chi_I^{N-1}\end{pmatrix}, \tag{7}$$

where

$$H_{II}^k = H_{II} + k\delta\epsilon\,, \qquad \chi_I^k = \chi_{k\delta\epsilon}\,.$$

This matrix equation can be solved by using the split-operator Fourier transform method.[32,33] The initial wavefunction of the ground electronic state is computed by employing the Fourier grid Hamiltonian method.[34]

Within the Condon approximation, the intensity of the photoelectron energy spectrum (PEES) signal with the kinetic energy E_k is directly related to the population of the $\chi_{Ik\delta\epsilon}$ state. The PEES is given by

$$P^I(k\delta\epsilon, \Delta t) = \lim_{t\to\infty}\int \mathrm{d}R|\chi_{k\delta\epsilon}(R,t)|^2\,, \tag{8}$$

where $k\delta\epsilon$ ($k = 0, 1, \ldots, N-1$) is the photoelectron kinetic energy. $\chi_{k\delta\epsilon}(R,t)$ are numerically calculated by resolving Eq.(7). The kinetic energy of photoelectron is determined by

$$E_k = \hbar\omega_2 - D_{IA}(R)\,, \tag{9}$$

where

$$D_{IA}(R) = V_I(R) - V_A(R)$$

is the difference in potential energy between the $6\,^1\Sigma^+$and $X^2\Sigma^+$ states.

3. Results and discussions

The potential energy curve of the $6\,^1\Sigma^+$ state of NaK possesses a double-minimum structure, in which the minimum of the inner potential well lies at $R = 8.01$ Bohr and the corresponding potential energy $U(R) = 3.16$ eV, and the minimum of the outer well is at $R = 22.77$ Bohr and $U(R) = 3.36$ eV. There exists a barrier at $R = 15.27$ Bohr between the two potential wells. The height E_b of the barrier is 3.46 eV which is 0.1 eV higher than the lowest point of the outer potential well. The lowest point of the ground state of the NaK^+ is at $R = 7.65$ Bohr and its energy is equal to 4.50 eV. The eigenenergy of the vibrational ground state is $E_{g0} = 0.118$ eV. The intensities of the pump and probe pulses are taken as 1.6×10^{13} W/cm^2 and 8.0×10^{12} W/cm^2, respectively. The FWHMs of laser pulses are $\tau_1 = \tau_2 = 85$ fs. The photon energies of pump laser are chosen as 1.63, 1.73 and 1.77 eV which are below the barrier, at the top of the barrier, and above the barrier, respectively.

The NaK molecule is firstly excited to the $6^1\Sigma^+$ state by the pump pulse. After a delay time Δt, the probe pulse ionizes the NaK molecule in the ground state $X(1)\,^2\Sigma^+$ of NaK^+. The evolutions of wave packet on the $6\,^1\Sigma^+$ state are shown in Fig.2. Panels (a), (b) and (c) in Fig.2 correspond to the cases $E_{g0} + 2\hbar\omega_1 = E_\alpha < E_b$ ($\hbar\omega_1 = 1.63$ eV and $\hbar\omega_2 = 2.00$ eV), $E_\alpha \approx E_b$ ($\hbar\omega_1 = 1.73$ eV and $\hbar\omega_2 = 1.90$ eV), and $E_\alpha > E_b$ ($\hbar\omega_1 = 1.77$ eV and $\hbar\omega_2 = 1.90$ eV). From Fig.2(a) we can see that when $E_\alpha < E_b$ almost all the wave packet is trapped and oscillates in the inner well. The oscillating period is about 480 fs. When $E_\alpha \approx E_b$ as shown in Fig.2(b), the wave packet splits into two parts in the barrier region: one moves to the outer well and the other is restricted in the inner well. The part that moves outward is reflected at the outer tuning point (at about 30 Bohr) and then moves back inwards. The oscillating periods of the wave packet in the outer and inner wells are about 2300 fs and 1100 fs, respectively. When $E_\alpha > E_b$, we can see from Fig.2(c) that nearly all the wave packet passes over the barrier region and moves into the outer well. In this case, the wave packet can reach the internuclear distance $R \approx 32$ Bohr.

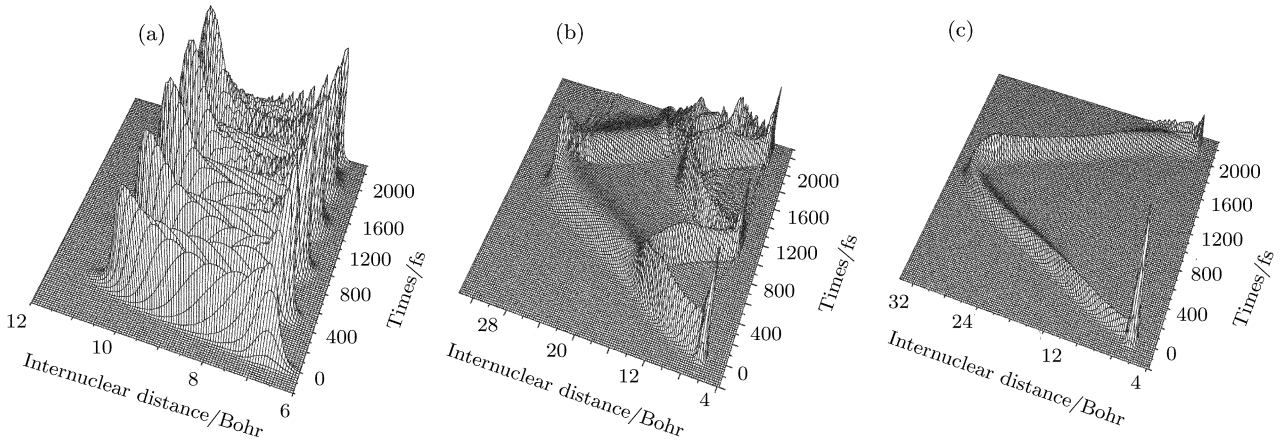


Fig.2. The evolutions of wave packets in the $6\,^1\Sigma^+$ state with time and internuclear distance for (a) $E_\alpha < E_b$ ($\hbar\omega_1 = 1.63$ eV and $\hbar\omega_2 = 2.00$ eV), (b)$E_\beta \approx E_b$ ($\hbar\omega_1 = 1.73$ eV and $\hbar\omega_2 = 1.90$ eV) and (c) $E_\gamma > E_b$ ($\hbar\omega_1 = 1.77$ eV and $\hbar\omega_2 = 1.90$ eV).

Figure 3 shows the femtosecond time- and energy-resolved photoelectron energy spectra (PEESs) for three different delay times ($\Delta t = 625$, 1250 and 1875 fs) and three different energies ($E_\alpha < E_b$, $E_\alpha \approx E_b$ and $E_\alpha > E_b$). When

$$\Delta t = 625 \text{ fs},$$

the evolutions of the PEESs with time t and internuclear distance R for the cases of $E_\alpha < E_b$, $E_\alpha \approx E_b$ and $E_\alpha > E_b$ are shown in Figs.3(a), 3(b) and 3(c), respectively. Each of these PEESs has one peak because the wave packet only moves in the inner well. When

$$\Delta t = 1250 \text{ fs},$$

the PEESs are shown in Figs.3(d–f) for the three different energies. The PEESs in Figs.3(d) and 3(f) have one peak. And the PEES in Fig.3(e) has two peaks because the wave packet splits into two parts in the barrier region. Figs.3(g–i) show the PEESs for the three different energies when Δt =1875 fs. We see from Fig.3 that the PEESs can clearly reflect the evolutions of wave packets on the $6\,^1\Sigma^+$ potential energy curve.

The evolutions of PEESs with the delay time Δt and the photoelectron kinetic energy E_k are plotted in Fig.4. When $E_\alpha < E_b$, as shown in Fig.4(a), the peak position of the PEES changes periodically with the delay time. The energy region of photoelectron is $0.45 \sim 0.67$ eV. When $E_\alpha \approx E_b$, the photoelectron energy lies in a range from 0.20 to 0.68 eV. Because the split of wave packet takes place in the barrier region, the PEES in Fig.4(b) displays a complex structure. The PEES when $E_\alpha > E_b$, is shown in Fig.4(c). The kinetic energy of photoelectron changes in a range of $0.20 - 0.67$ eV.

Moreover, the PEES of the NaK molecule in strong two-colour laser fields can be used to determine the value of the barrier of the double minimum potential. We can gradually enhance the pump energy ($\hbar\omega_1$) in a range of delay time from 800 to 2100 fs until the PEES splits into two peaks. The height of the barrier is approximately equal to $2\hbar\omega_1$.

In addition, in the practical experiment the potential energy curves of the molecule shifts because of the ponderomotive energy of the electron in intense laser fields.[35,36] In general the light shift should be considered to describe accurately the experimental phenomena. However, our work here is just an exploratory study to show theoretically that the evolutions of wave packet and the photoelectron energy spectra can be controlled by varying the laser parameters, the frequency ω_1 of the pump pulse and the delay time Δt between pump and probe laser pulses. The additional effects caused by the intense laser pulses are ignored. In fact, the parameters of the used pulses can be optimized further to control the dynamics and the intensities of the pump and probe pulses should be lowered. Thus the conclusions drawn above are of certain practical signification.

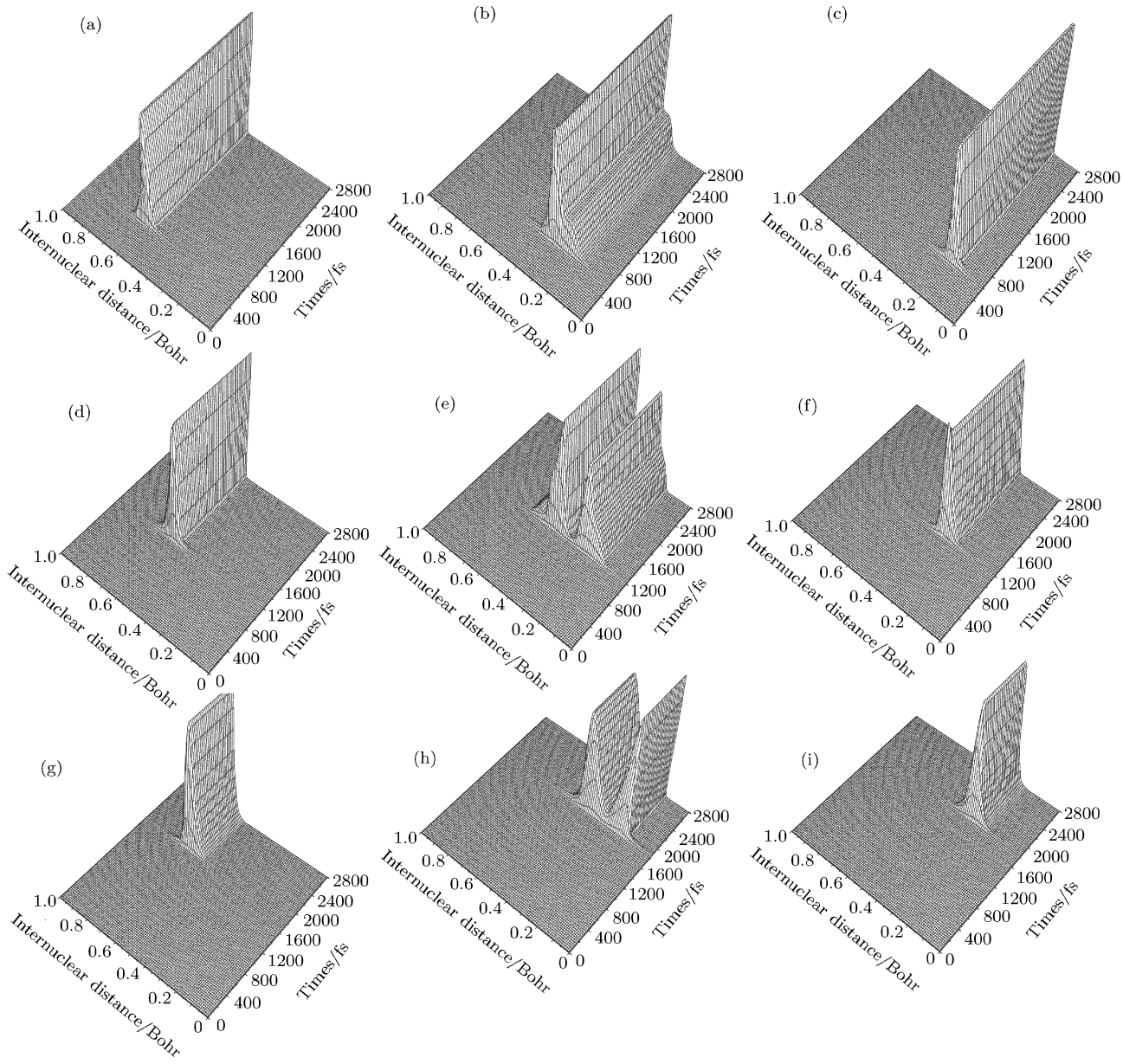


Fig.3. The time- and energy-resolved photoelectron spectra at three different delay times for three different energies. (a) $\Delta t = 625$ fs, $E_\alpha < E_b$; (b) $\Delta t = 625$ fs, $E_\alpha \approx E_b$; (c) $\Delta t = 625$ fs, $E_\alpha > E_b$; (d) $\Delta t = 1250$ fs, $E_\alpha < E_b$; (e) $\Delta t = 1250$ fs, $E_\alpha \approx E_b$; (f) $\Delta t = 1250$ fs, $E_\alpha > E_b$; (g) $\Delta t = 1875$ fs, $E_\alpha < E_b$; (h) $\Delta t = 1875$ fs, $E_\alpha \approx E_b$; (i) $\Delta t = 1875$ fs, $E_\alpha > E_b$.

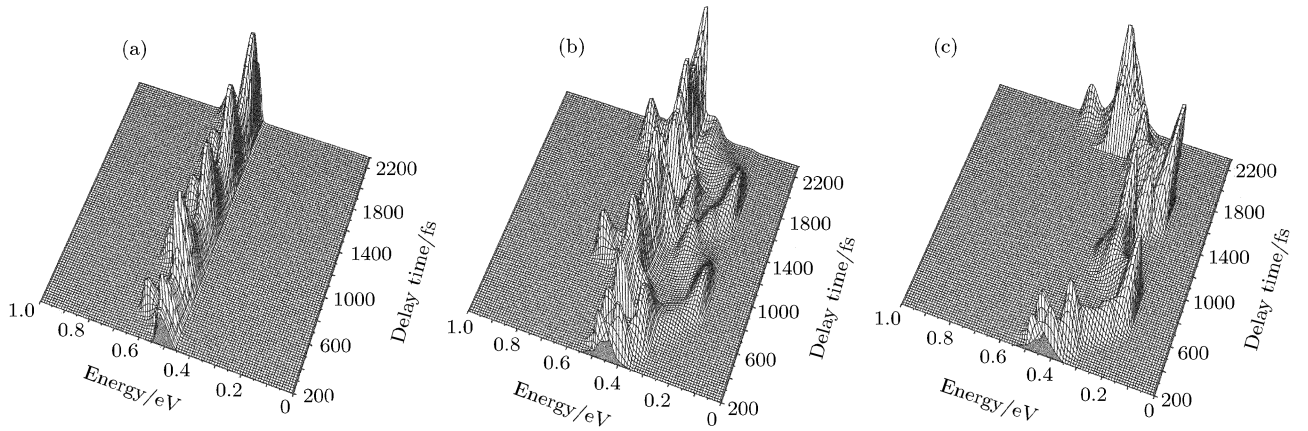


Fig.4. The evolutions of photoelectron energy spectra with the delay time and the photoelectron kinetic energy for (a) $E_\alpha < E_b$, (b) $E_\alpha \approx E_b$ and (c) $E_\alpha > E_b$.

4. Conclusions

We have studied the wave packet dynamics of the $6\,^1\Sigma^+$ state of NaK in intense femtosecond pump and probe laser fields and calculated the time- and energy-resolved photoelectron energy spectra. The evolutions of the wave packet and the photoelectron energy spectra with time and internuclear distance are described in detail. The calculated results indicate that we can control the evolutions of wave packet and the photoelectron energy spectra by varying the laser parameters, such as the frequency ω_1 of pump pulse and the delay time Δt between pump and probe laser pulses. The wave packet dynamic information of the $6\,^1\Sigma^+$ state can be extracted from the photoelectron energy spectra. The photoelectron energy spectra can also be used to determine the value of the barrier of the double minimum potential.

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