The effect of field modulation on the vibrational population of the photoassociated NaK and its dynamics*

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This paper presents calculation results for the photoassociation of a NaK molecule with a two-color modulated laser and gives a detailed analysis about them. For the two-step photoassociation process in intense fields, the effect of two-color modulated laser parameters, such as relative phase, envelope period, and laser intensity, on the population of the molecular electronic state can be obtained by solving the time-dependent Schrödinger equation through the quantum wave packet method. The numerical simulation shows not only that the influence of laser parameters on the vibrational distribution presents some regularity, but also that a higher population in the ground electronic state can be realized through adjusting these laser parameters.

Keywords: photoassociation, time-dependent wave packet method, light-matter interaction, NaK

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1. Introduction

Recent advances in the techniques of atomic manipulation with laser fields stimulate scientists to study the manipulation of some neutral molecules, even the cooling and trapping of polar molecules.[1] Among them, ultracold molecules have received considerable attention from researchers[2–4] due to their promising applications in such new platforms as quantum computing,[5] novel quantum phase transitions,[6] ultracold chemistry,[7–9] etc. According to the ways they are obtained through associating ultracold atoms using an external optical or magnetic field, the scheme can be classified correspondingly into two kinds, i.e., photoassociation (PA)[1,10] and magneto-association.[11,12] In particular, the formation of ultracold molecules can be achieved via PA in the long-range potential area. In the usually applied scheme, PA includes a laser-induced transition from the colliding cold atoms to a molecule in an electronic excited state. This step is followed by a transition to the molecular electronic ground state through either spontaneous or induced emission.[13] In general, the ultrashort laser pulse for PA with a broad frequency width will reduce the yield of associated molecules.

With the rapid development of laser techniques, well shaped lasers have been achieved[14,15] and widely used in the coherent PA process of the cold or ultracold molecular systems in recent years.[16] In 2006, Koch *et al.* investigated the PA process with chirped laser pulses in theory.[17,18] In 2008, Sugawara *et al.* proposed a strategy to achieve laser-field-free molecular orientation with the combination of an electrostatic field and an intense, nonresonant laser field with rapid turn-off.[19] In the same year, Salzmann *et al.* experimentally investigated various processes presented in the photoassociative interaction of an ultracold atomic sample with shaped femtosecond laser pulses.[20] In 2010, in order to obtain more associated molecules, Zhang *et al.* used a slowly-turned-on and rapidly-turned-off laser pulse to prevent the associated molecule from returning to the initial scattering state.[21] Subsequently, an efficient population accumulation in the PA process was implemented via a train of asymmetric laser pulses.[22] In the above works, the modulation of the PA process is by changing the laser parameters, which involves only the transition from a continuum state to an electronic excited state of the molecule. What we expect, however, is to produce the ultracold molecule efficiently in lower vibrational levels of the electronic ground state.

In this paper, we present a theoretical study on the formation of ultracold molecule NaK through a two-step PA process in lower vibrational levels of the electronic ground state, which is driven by a two-color modulated laser pulse. Here, we will first write out the Hamiltonian of the system in intense laser fields. Then by solving the time-dependent Schrödinger equation with time-dependent wave packet method,[23] we will obtain the wave packet evolving with time in each state. We know that the PA effect can be represented via the popula-

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tion of the ultracold molecule, so by analyzing the population changing with the field parameters, we can get the influence of laser parameters on the PA dynamic process.

The remainder of this paper is organized as follows: Section 2 provides the time-dependent wave packet method which has been proved to be an effective and accurate one to study the interaction between molecules and an external field[24–26] in the PA process. As an example, the numerical simulation results and the related discussions about the PA process of NaK molecule are presented in Section 3. In Section 4, we summarize the results and give conclusions.

2. Review of the theoretical treatment

2.1. Time-dependent Schrödinger equation for the two-step PA

In the content of the following, we mainly investigate the two-step PA process of NaK using a time-dependent wave packet method. Employing the similar method, one can study other alkali-metal atoms.[27,28]

Figure 1(a) shows the schematic representation of the two-step PA process. The potential curves are taken from Ref. [29]. In the first step, two colliding atoms in the ground state are driven to the first excited state $A^1\Sigma^+$ by a laser pulse to form a long-range molecule which is usually at high vibrational levels. In the second step, the long-range molecule is further excited to the second excited state $F^1\Sigma^+$ to form a molecule at lower vibrational levels. Because the second step is a bound-bound transition, efficient excitation is possible with moderate laser powers even if the Frank–Condon factors are small.[30] Finally, by the process of spontaneous emission, we can get photoassociated molecules in lower vibrational levels of the $X^1\Sigma^+$ state.

The two-step PA process can be described by the time-dependent Schrödinger equation

$$\mathrm{i}\hbar\frac{\partial\Psi(R,t)}{\partial t}=[\boldsymbol{T}+\boldsymbol{V}]\Psi(R,t), \tag{1}$$

where $\boldsymbol{T}$ is the kinetic matrix, $\boldsymbol{V}$ is the potential matrix, and

$$\Psi(R,t)=\begin{pmatrix}\psi_1\\ \psi_2\\ \psi_3\end{pmatrix}, \tag{2}$$

$$\boldsymbol{T}=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial R^2}\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix},$$

$$\boldsymbol{V}=\begin{pmatrix}V_1&W_{12}&0\\W_{21}&V_2&W_{23}\\0&W_{32}&V_3\end{pmatrix}, \tag{3}$$

where ψ_1, ψ_2, and ψ_3 denote the nuclear wave functions of the $X^1\Sigma^+$, $A^1\Sigma^+$, and $F^1\Sigma^+$ states, respectively. m is the reduced mass, V_i $(i=1,2,3)$ represent the potential functions for the three neutral electronic states $X^1\Sigma^+$, $A^1\Sigma^+$, and $F^1\Sigma^+$ states, respectively. $W_{ij}=\mu_{ij}E(t)$ $(i,j=1,2,3)$ refer to the coupling between the involved electronic states with dipole matrix elements μ_{ij} and external field $E(t)$. The electric field is modulated by two Gaussian carrier-wave pulses[31]

$$\begin{aligned}E(t)&=E_1f_1(t)\cos(\omega_1(t-t_k)+\phi_1)\\&\quad+E_2f_2(t)\cos(\omega_2(t-t_k)+\phi_2),\end{aligned} \tag{4}$$

where $f_1(t)=f_2(t)=f(t)$, as the Gaussian envelope, can be expressed as

$$f(t)=\exp\left(-2\ln 2(t-t_k)^2/\sigma^2\right), \tag{5}$$

with t_k denoting the centre of the envelope and σ the full width at half maximum (FWHM) of the laser pulse. For convenience of calculation, we define a new carrier frequency ω_{L} and a new period T_{P} as

$$\omega_{\mathrm{L}}=\frac{1}{2}(\omega_1+\omega_2),\quad\frac{2\pi}{T_{\mathrm{P}}}=\frac{1}{2}(\omega_1-\omega_2), \tag{6}$$

with $\omega_1>\omega_2$. Then the time-dependent electric field can be rewritten as

$$E(t)=E_0S(t)\cos(\omega_{\mathrm{L}}(t-t_k)), \tag{7}$$

where $E_0=2E_1=2E_2$,

$$S(t)=f(t)\cos(2\pi(t-t_k)/T_{\mathrm{P}}-\phi)$$

is the new total envelope function of the modulated laser pulse and $\phi=-\phi_1=\phi_2$. Here, we define $A(t)=E_0S(t)$ as a new amplitude, which is modulated by ϕ, T_{P}, and E_0. Thus the interaction can be rewritten as

$$W_{ij}=\mu_{ij}A(t)\cos(\omega_{\mathrm{L}}(t-t_k)),\quad(i,j=1,2,3). \tag{8}$$

2.2. Preparation and propagation of wave packet

In the long-range region where the pump laser induces the photoassociation, the interaction of two colliding atoms at their ground states can be described by the long-range portion of the potential. So in theory here we can regard the wave function of the molecule near the dissociation limit as the initial wave function of two colliding atoms. Through solving the one-dimension time-independent Schrödinger equation by the Fourier grid Hamiltonian method,[32] the obtained initial wave packet on the electronic ground state is well represented by the wave function of the highest vibrational level $v=73$ for the NaK system shown in Fig. 1(b). Certainly, $\exp(-\mathrm{i}k_{\mathrm{e}}R)$ can be multiplied to express the propagating direction and the relative momentum $\hbar k_{\mathrm{e}}$ of the initial wave packet. For the NaK system, k_{e} is taken as 0.004 a.u., the unit a.u. is short for atomic unit, which corresponds to a temperature of about 95 μK.

Based on the above preparations, we can write approximately the wave function using the 'split-operator' scheme of wave packet propagation[33,34] as follows:

$$\Psi(R,t_0+\Delta t) \cong \boldsymbol{U}_{\mathrm{T}}^{1/2}\boldsymbol{U}_{\mathrm{V}}\boldsymbol{U}_{\mathrm{T}}^{1/2}\Psi(R,t_0), \tag{9}$$

where Δt is a short time step, and $\Psi(R,t_0)$ is the initial wave function when $t=t_0$. The two new operators $\boldsymbol{U}_{\mathrm{T}}$ and $\boldsymbol{U}_{\mathrm{V}}$ represent the time evolution of kinetic energy and potential energy, respectively, and can be written as

$$\boldsymbol{U}_{\mathrm{T}} = \exp\left[-\frac{\mathrm{i}\Delta t}{\hbar}\boldsymbol{T}\right], \quad \boldsymbol{U}_{\mathrm{V}} = \exp\left[-\frac{\mathrm{i}\Delta t}{\hbar}\boldsymbol{V}(R,t_0)\right]. \tag{10}$$

The wave function after propagating n steps is given as

$$\Psi(R,t_0+n\Delta t) \cong \left[\prod_{k=0}^{n-1}\boldsymbol{U}_{\mathrm{T}}\boldsymbol{U}_{\mathrm{V}}(R,t_0+k\Delta t)\right]\Psi(R,t_0). \tag{11}$$

It is worth noting that the kinetic energy operator and the potential energy operator can be diagonalized in momentum and coordinate representations, respectively. In the propagation, when meeting the operator $\boldsymbol{U}_{\mathrm{T}}$, the wave function should be changed into one in momentum space; when meeting the operator $\boldsymbol{U}_{\mathrm{V}}$, the wave function should be changed back to one in coordinate space. In fact we perform the transformation between momentum space and coordinate space with the fast Fourier transform technique.[35]

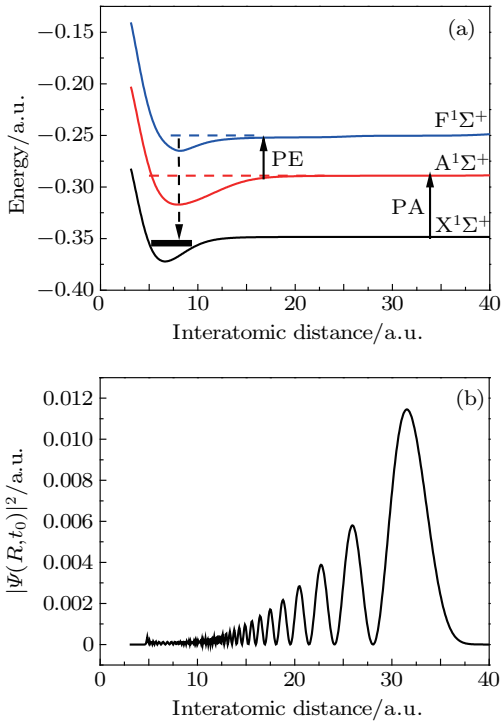


Fig. 1. (color online) The scheme of two-step PA and initial wave packet of the NaK molecule. (a) The potential energy curves and two-step PA process. (b) The norm square of the initial wave packet.

Once the wave packet at time t is obtained, the time-dependent population distribution in each state can be extracted from the norm of the wave packet $\psi_i(R,t)$ $(i=1,2,3)$,[26] i.e.

$$P_i(t) = \int \mathrm{d}R\psi_i^*(R,t)\psi_i(R,t). \tag{12}$$

The population of each vibrational state in the electronic state $\mathrm{X}^1\Sigma^+$ is computed by

$$P = |\langle\varphi_v(R,t)|\ \psi_i(R,t)\rangle|^2, \tag{13}$$

where $\varphi_v(R,t)$ $(v=1,2,3,\ldots)$ is the corresponding vibrational wave function in electronic state $\mathrm{X}^1\Sigma^+$. It is worth mentioning that the wave function $\varphi_v(R,t)$ $(v=1,2,3,\ldots)$ is obtained through solving the one-dimensional time-independent Schrödinger equation in each electronic state by the Fourier grid Hamiltonian method.

3. Results and discussion

It is known that for a molecule exposed to a laser field, laser parameters, such as intensity, pulse width, delay time, and center frequency, etc., play important roles in light–matter interaction.[36] In this calculation, the relative phase ϕ, envelope period T_{P}, and intensity E_0 of modulated laser pulses are regarded as the controllable parameters. The wavelength of the first laser pulse is set to be 900 nm, which is a small red detuning. To facilitate calculation, the Gaussian-type pulse is chosen as the second pulse, which has a central frequency (corresponding wavelength is 1000 nm) resonant with the vibrational level $v=35$ for electronic state $\mathrm{F}^1\Sigma^+$.

Figures 2(a) and 2(b) illustrate the modulated pulse envelopes with $T_{\mathrm{P}}=150$ fs, $\sigma=17.4$ fs for $\phi=0$, $\pi/6$, $\pi/3$, $\pi/2$, and $\phi=2\pi/3$, $5\pi/6$, π, respectively. It is clear that the shape of envelope is sensitive to the phase ϕ. Figures 2(c) and 2(d) describe the total population in the $\mathrm{A}^1\Sigma^+$ state of NaK varying with the corresponding laser. It shows that when the pulse is present, the total population in the $\mathrm{A}^1\Sigma^+$ state will take the form of oscillation, which is often called Rabi oscillation.[25] Besides, with the increasing of the phase, the population is decreasing when $0<\phi<\pi/2$, and increasing when $\pi/2<\phi<\pi$. These phenomena are due to the properties of the modulated laser pulses, the repeat cycle of which is π.

Figures 3(a) and 3(b) illustrate the population of associated molecules varying with relative phase ϕ and evolution time t. From this figure, we can see that because of both the positive and negative of laser-matter interaction $W(t)$ having no effect on the PA dynamics process, the period of PA is π, half of one modulated electric field. Obviously, the maximum of the time-dependent population occurs in the vicinity of central time $t=75$ fs and phase $\phi=0$, π or 2π. So we can obtain a higher population by cutting off the laser at $t=75$ fs or excite the molecule in the $\mathrm{A}^1\Sigma^+$ state with another pulse at the moment.

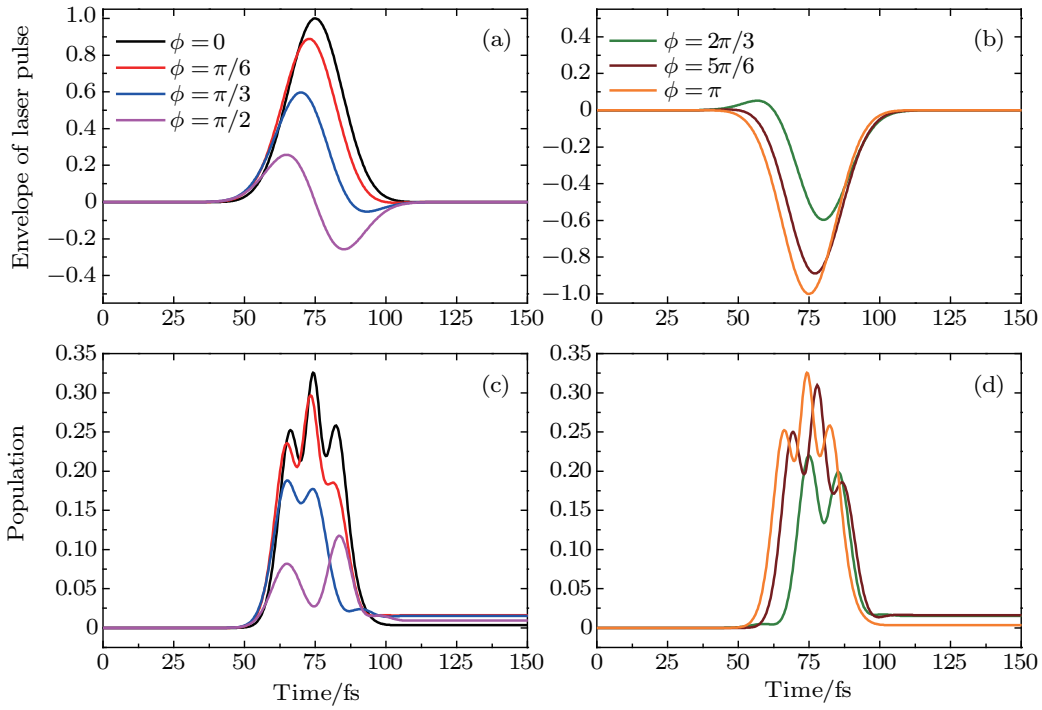


Fig. 2. (color online) (a) and (b) the envelopes of the laser pulse with different relative phases ϕ; (c) and (d) the corresponding total population of associated molecules in $A^1\Sigma^+$ state.

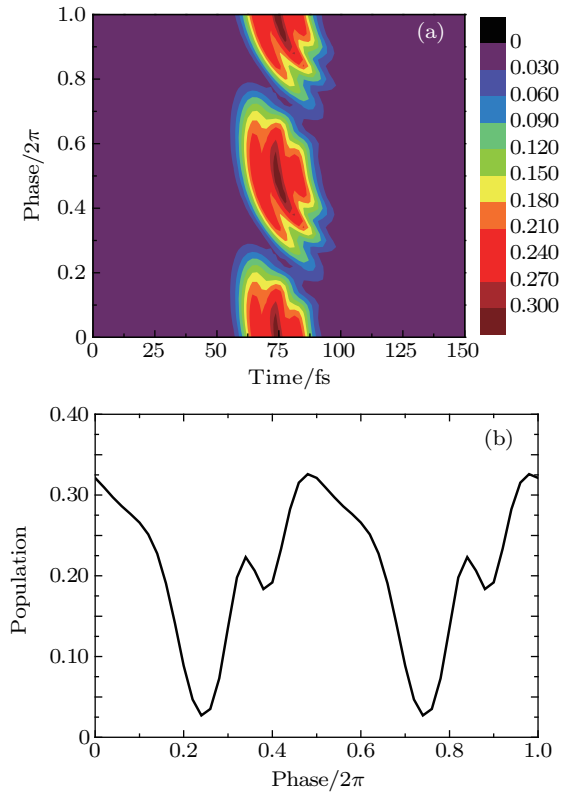


Fig. 3. (color online) (a) The time-dependent population in $A^1\Sigma^+$ state varying with ϕ. (b) The population varying with ϕ at $t = 75$ fs moment.

The envelope period T_P is another important modulation parameter of a pulse laser. To describe its influence, six different periods $T_P = 40$, 80, 140, 160, 200, 300 fs are taken as examples. In Fig. 4 both the relative envelope of the laser pulses (a) and (b) and the time-dependent population in $A^1\Sigma^+$ state (panels (c) and (d)) are shown when $\phi = 0$. In Figs. 4(c) and 4(d), we can see obvious oscillations due to the rapid change of laser pulse. Through numerical calculations, we find that the time-dependent population drops with the increase of T_P (less than 150 fs) which is illustrated in Fig. 4(c). However, once T_P reaches a specified threshold (150 fs), the population will remain approximately the same just as in Fig. 4(d).

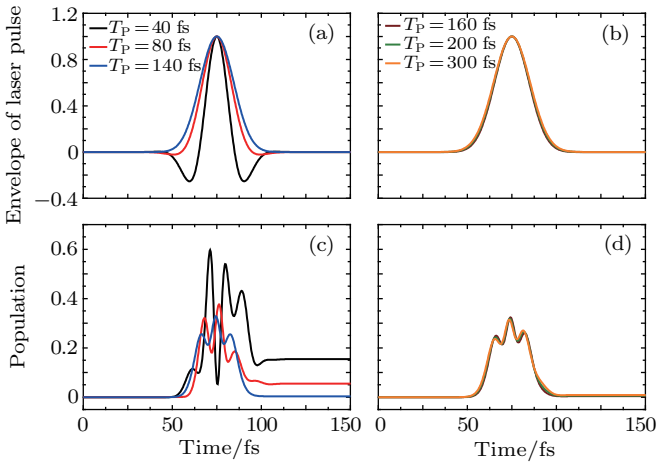


Fig. 4. (color online) The envelopes of the laser pulse with different periods T_P and the corresponding time-dependent population of associated molecules in $A^1\Sigma^+$ state.

In order to study the influence of laser intensity on the population in $X^1\Sigma^+$ and $A^1\Sigma^+$ states of NaK, we vary it from 1.287×10^{13} W/cm^2 to 9.653×10^{14} W/cm^2, and the calculation results are displayed in Fig. 5. It shows that when the laser intensity increases, the oscillation of the population in each state is more obvious. After the pulse is moved away, the oscillation will disappear, but each state is still occupied by populations until other influences are imposed.

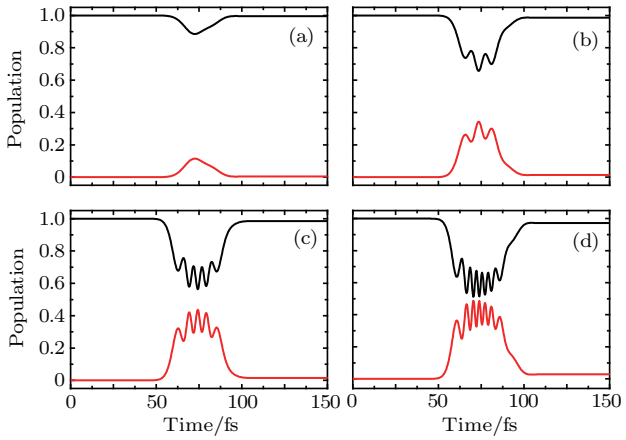


Fig. 5. (color online) The time evolution of the ground state (black) and the excited state (red) populations for different laser intensities: (a) 1.287×10^{13} W/cm^2, (b) 3.861×10^{13} W/cm^2, (c) 6.435×10^{14} W/cm^2, and (d) 9.653×10^{14} W/cm^2.

In general, the PA process tends to favor production of molecules in very high vibrational levels, and followed by a spontaneous transition back down to a ground-state continuum of hot free atoms. The phenomenon is explained by the Franck–Condon factors between the $X^1\Sigma^+$ state and the $A^1\Sigma^+$ state shown in Fig. 6(a). However, what we expect is to produce a larger number of ground-state molecules and have them be in lower vibrational levels. For this purpose, after a delay time of the PA pulse, we introduce a second laser pulse to drive an upward transition from bound levels of the $A^1\Sigma^+$ state to lower bound levels of the $F^1\Sigma^+$ state, and the delay time is defined as the difference between the start time of the second laser pulse and the first one. Taking into account the Franck–Condon factors between the $X^1\Sigma^+$ state and the $F^1\Sigma^+$ state which display a quasi-symmetrical character shown in Fig. 6(b), the molecule thus formed quickly decays by spontaneous emission to a bound-state molecule in lower vibrational levels of the $X^1\Sigma^+$ state.

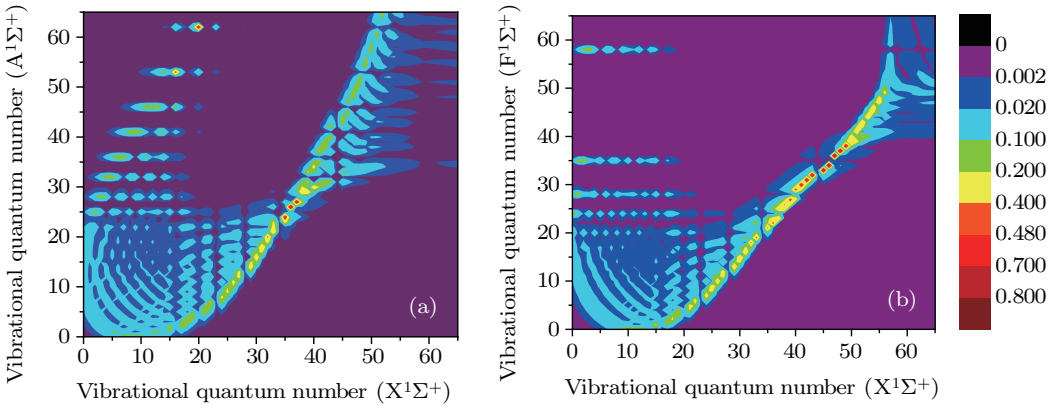


Fig. 6. (color online) FC factors between the $X^1\Sigma^+$ state and the $A^1\Sigma^+$ state (a), and between the $X^1\Sigma^+$ state and the $F^1\Sigma^+$ state (b).

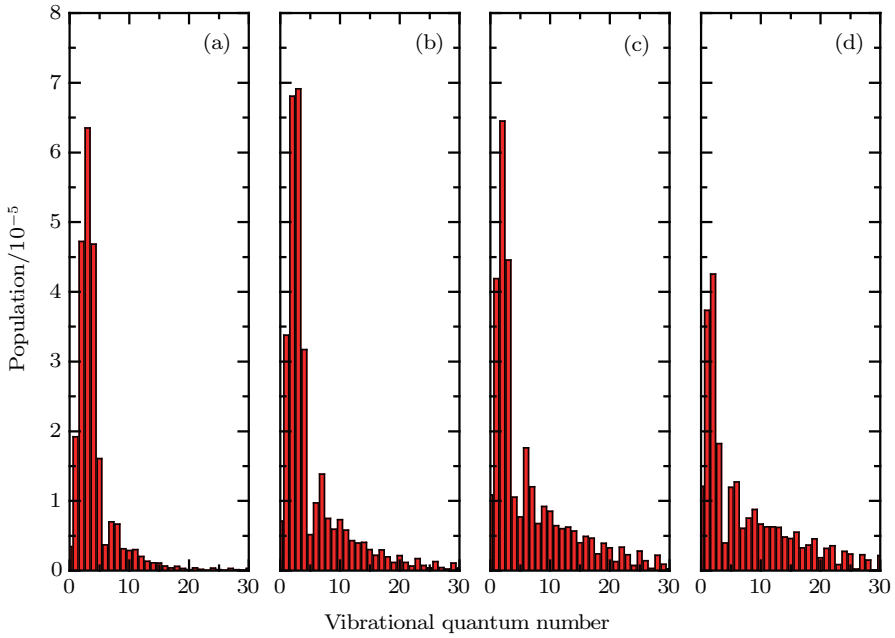


Fig. 7. (color online) The population distributions in the $X^1\Sigma^+$ state for the different delay times: (a) 0 fs, (b) 5 fs, (c) 10 fs, and (d) 15 fs.

Through numerical calculations, we can obtain the population of each vibrational state in the electronic ground state as shown in Fig. 7. We can see that the population is produced in lower vibrational levels, which is exactly what we expect. Besides, we also find that the amount of population is varying with the delay time. As the delay time is equal to 5 fs, the population is relatively good. This phenomenon can be illustrated by the evolution of the wave packet on the $A^1\Sigma^+$ state. Particularly for the two-step PA process, the first laser pumps the wave packet onto the $A^1\Sigma^+$ state. Then the wave packet in the $A^1\Sigma^+$ state moves to the short range of the potential and excited to lower vibrational levels of the $F^1\Sigma^+$ state after an appropriate delay time, which have larger Franck Condon overlaps with the vibrational wave functions in the ground electronic state for spontaneous emission.

4. Conclusions

In this paper, using the time-dependent wave packet dynamical approach to investigate the two-step PA process, we derive the changing tendency of population with relative phase, envelope period and laser intensity. The results reveal that the relative phase influences the population in each electronic excited state, which reaches the maximum as $\phi = \pi/2$. In order to obtain more population in the ground state of NaK, we can also regulate the envelope period and laser intensity. Besides, an appropriate delay time can also be helpful to improving the state distribution. Although in the present calculations we only consider three electronic states, the theoretical treatment can be easily extended to the case of multielectronic state and other alkali metal diatomic molecules. The present theoretical studies would also be helpful to providing a rough idea for the relevant experiments.

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