Influence of laser fields on the vibrational population of molecules and its wave-packet dynamical investigation*

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The time-dependent wave packet method is used to investigate the influence of laser-fields on the vibrational population of molecules. For a two-state system in laser fields, the populations on different vibrational levels of the upper and lower electronic states are given by wavefunctions obtained by solving the Schrödinger equation with the split-operator method. The calculation shows that the field parameters, such as intensity, wavelength, duration, and delay time etc. can have different influences on the vibrational population. By varying the laser parameters appropriately one can control the evolution of wave packet and so the vibrational population in each state, which will benefit the light manipulation of atomic and molecular processes.

Keywords: intense laser field, time-dependent wave packet method, light-matter interaction, vibrational population

PACC: 3310G, 3380

1. Introduction

With the rapid development of ultra-short laser pulse technique, the investigations on the light–matter interaction (LMI) have been made in a brand new perspective both experimentally and theoretically recently. An excellent review on the LMI is given in Ref. [1] and the references therein. When molecules are subjected to an intense laser field, many interesting phenomena, such as saturation, above-threshold dissociation,[2−4] AC Stark effect,[5,6] Rabi oscillation,[7] etc., can be observed. These side effects induced by LMI have received much attention from many researchers in the past decade.[8−12] In order to facilitate the discussion, we concentrate thereafter only on the theoretical treatment of a two-state system in strong laser fields.

Traditionally, the method to deal with a two-state system is by solving the so-called semiclassical coupled Maxwell–Bloch equations, which can provide a foundation for analysing the nonlinear interaction of a few-cycle pulsed laser with the system.[13] In the study of photodetachment properties of high Rydberg state of atoms in intense fields, the semiclassical closed-orbit theory can be served as an alternative.[14,15] Besides the above, other methods, such as PIC (particle-in-cell) method,[16] the tensor density matrix theory[17] etc., are also used to interpret LMI. As a powerful tool to investigate the atomic and molecular scattering, the time-dependent wave-packet method has also been successfully transplanted to deal with LMI.[18−20] In recent years Han *et al.* have generalized the method to the electronically nonadiabatic processes in chemical reactions.[21] Its advantages in both the time-saving and the flexibility to use have been illustrated in the simulation of the multi-photon process of some diatomic molecules, such as NaRb, RbI, NaI, etc.[22−27] Most of the above works, however, concentrated mainly on the discussion of electronic state distribution, few attention was paid to the influence of external fields on the vibrational population. Since, as we know, the vibrational distribution is very significant in some cases, such as the resonant phenomenon, the energy redistribution, etc. and what is more, through affecting the molecular states, LMI can also influence the population in each vibrational state, in the present work, we will use the time-

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dependent wave-packet method to study the influence of the intense laser field on the vibrational distribution of a two-state system. By analysing the motion of wave-packet on each vibrational level, we can obtain the information of intense field effects.

This paper is arranged as follows. In Section 2, by reviewing the time-dependent wave packet dynamical theory briefly, the Hamiltonian of the two-state system in the laser fields and the relevant Schrödinger equation are presented. The formulations of some dynamical information, such as the population in each vibrational state, are also given. In Section 3, taking NO molecules in intense laser fields as an example, the results of the influence of laser parameters on vibrational population and the related discussion are displayed. In the last section, the main conclusions are summarized.

2. Theoretical treatment

2.1. Hamiltonian and Schrödinger equation

Consider a two-state system which is coupled by the laser pulses chosen as

$$E(t) = E_1 f(t)\cos(\omega_1 t) + E_2 f(t-\Delta t)\cos(\omega_2 t), \quad (1)$$

where E_1 and E_2 are the electric field amplitudes, with ω_1 and ω_2 the corresponding angular frequencies; Δt is the delay time between the two Gaussian pulses. The envelopes $f(t)$ and $f(t-\Delta t)$ of the pulses are expressed as

$$\begin{aligned} f(t) &= \exp\left(-\left(\frac{t}{\tau_1}\right)^2\right), \\ f(t-\Delta t) &= \exp\left(-\left(\frac{t-\Delta t}{\tau_2}\right)^2\right), \end{aligned} \quad (2)$$

where τ_1 and τ_2 denote, respectively, the full-widths at half-maximum (FWHM) of the two Gaussian pulses. In our treatment the rotational motion is ignored because the heavy molecule does not rotate essentially on the femtosecond time scale.[28] Employing the Born–Oppenheimer approximation, the field-free Hamiltonian can be written as

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial R^2} I + \hat{V}(R,t), \quad (3)$$

where R is the internuclear separation, I the identity matrix, m the reduced mass of the molecule, and $\hat{V}(R,t)$ the potential matrix. The potential matrix can be written as

$$\hat{V}(R,t) = \begin{pmatrix} V_{\rm g} & \mu E(t) \\ \mu E(t) & V_{\rm e} \end{pmatrix}, \quad (4)$$

where μ is the transition dipole moment, $E(t)$ the laser field as described in Eq. (1), $V_{\rm g}$ and $V_{\rm e}$ are respectively the potential functions for lower and upper states, which are always chosen as Morse potentials for bound states. Consequently, the time-dependent Schrödinger equation can be written as

$$\mathrm{i}\,\hbar\frac{\partial}{\partial t}\psi(R,t) = \hat{H}(R,t)\psi(R,t) \quad (5)$$

with $\psi(R,t) = (\psi_{\rm g}(R,t),\ \psi_{\rm e}(R,t))^{\rm T}$, where $\Psi_{\rm g}(R,t)$ and $\Psi_{\rm e}(R,t)$ represent the time-dependent nuclear wavefunctions in lower and upper states respectively.

2.2. Solution of the Schrödinger equation

Once the Hamiltonian is given, the time-dependent Schrödinger equation can be solved through the split-operator technique of wave-packet method. For simplicity, we give here only the review of the method below. For more details, the reader is referred to the review articles and references therein.[29–32]

Denotes the small time interval Δt, the canonical solution of Eq. (5) can be written as

$$\psi(R,t+\Delta t) = \exp\left(-\frac{\mathrm{i}}{\hbar}\hat{H}\Delta t\right)\psi(R,t), \quad (6)$$

where $\exp[-(\mathrm{i}/\hbar)\hat{H}\Delta t]$ is the time evolution operator. According to the split-operator scheme, the wave packet can propagate as

$$\begin{aligned} \psi(R,t_0+\Delta t) \approx\ & [U_T^{1/2}(R,t_0)U_V(R,t_0)U_T^{1/2}(R,t_0)] \\ & \times \psi(R,t_0), \end{aligned} \quad (7)$$

where

$$\begin{aligned} U_T &= \exp\left[-\frac{\mathrm{i}\,\Delta t}{\hbar}T\right], \\ U_V &= \exp\left[-\frac{\mathrm{i}\,\Delta t}{\hbar}U(R,t_0)\right] \end{aligned} \quad (8)$$

with U_V and U_T being two evolution operators, which represent the evolutions of kinetic energy and potential energy, respectively; and $\Psi(R,t_0)$ the wave packet at initial time t_0, which is usually chosen as the wavefunction for the vibrational ground state of the lower

electronic state. After propagating n steps, the wavefunction has the following approximate form

$$\psi(R, t_0 + n\Delta t) = \left[\prod_{k=0}^{n-1} U_T U_V(R, t_0 + k\Delta t)\right] \times \psi(R, t_0). \quad (9)$$

Since U_T and U_V can be diagonalized in momentum and coordinate spaces, respectively, it is natural that, when meeting operator U_T in calculation, the wave function should be transformed into the one in the momentum representation; on the other hand, when meeting operator U_V, the wave function should be transformed back into the one in the coordinate representation. The transformation process is performed by the so-called Fourier transform. For example, if $F(k)$ is the wave function in momentum representation, the wave function in the coordinate representation can be written as

$$F(R) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} F(k) \exp(\mathrm{i}\, kR)\mathrm{d}k, \quad (10)$$

and the inverse transformation of the above equation is

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} F(R) \exp(-\mathrm{i}\, kR)\mathrm{d}R. \quad (11)$$

In the split-operator scheme, the general Fourier transform is replaced by the fast Fourier transform (FFT). In the present treatment of the basis functions, the discrete variable representation (DVR) approach is used.

2.3. The population in each vibrational state

In this work we only concentrate on the influence of the external fields on the population in vibrational states. Once the wave function of the molecule is determined, the wave packet at any time in each state will be easily obtained by Eq. (9). The population in each electronic state can be written as

$$P_i(t) = \int \mathrm{d}R \psi_i^*(R, t)\psi_i(R, t), \quad i = \mathrm{g},\ \mathrm{e}. \quad (12)$$

Since LMI can induce the redistribution of vibrational population in each electronic state, according to Han's idea,[33] the population in each electronic state can be written as the projection of the wave packet onto different vibrational states. For an electronic state k, the projection of the calculated wave packet ψ_k on each vibrational state ϕ_{k_i} can be given by

$$p_{ri} = \int \mathrm{d}R \phi_{k_i}^*(R, t)\psi_k(R, t) \quad (13)$$

with electronic state symbol $k = \mathrm{g},\ \mathrm{e}$ and the relevant vibrational quantum number $i = 0, 1, 2, \ldots$. So the population in each vibrational state i ($i = 0, 1, 2, \ldots$) can be expressed as

$$P_{ri} = |p_{ri}|^2 = \left| \int \mathrm{d}R \phi_{k_i}^*(R, t)\psi_k(R, t) \right|^2. \quad (14)$$

By analysing the variation of population in each vibrational state with the laser parameters, we can obtain the effect of external fields on vibrational distribution. In the next section, we will take NO in laser fields as an example to discuss the so-called strong field effect.

3. Results and discussion

3.1. Results

Since a diatomic molecule has only one vibrational freedom and the simplest Hamiltonian form, it is always chosen as the prototype of a two-state system. Specifically for the NO molecule, since its potential curves of all the dipole accessible electronic states have been characterized,[34–37] and its ground state and adjacent excited states are also bound states, we usually describe these curves in the form of Morse functions, i.e.

$$V_{\mathrm{g}} = D_{\mathrm{g}}[1 - \mathrm{e}^{-\alpha_{\mathrm{g}}(R-R_0)}]^2 + D_{0\mathrm{g}},$$
$$V_{\mathrm{e}} = D_{\mathrm{e}}[1 - \mathrm{e}^{-\alpha_{\mathrm{e}}(R-R_0)}]^2 + D_{0\mathrm{e}}, \quad (15)$$

where D_i, α_i, and D_{0i} ($i = \mathrm{g},\ \mathrm{e}$) are parameters for a Morse potential, as in Ref. [34]. In the calculation, the relevant dipole moment transition matrix elements are obtained by fitting to *ab initio* results.[36,37]

For a two-level system shown in Fig. 1, the laser field coupling the two states usually takes a form of Eq. (1), and the field parameters, such as intensity, pulse width, wavelength and delay time, etc. have been proved to be very significant for the strong field effect.[22,33,38] In the present work, we will investigate their influences on vibrational distribution in each electronic state.

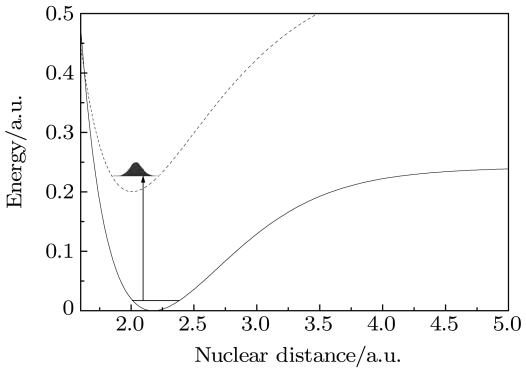


Fig. 1. Two-level system for NO molecule. A laser pulse induces a wave packet in the excited electronic state from the ground electronic state.

In Eq. (1), $E_i \propto \sqrt{I_i}$ with I_i $(i = 1, 2)$ representing the intensity of the laser pulses. In order to investigate the influence of the laser intensity on the population in each vibrational state, we first use only one pulse and vary its intensity from 1.0×10^{13} W/cm^2 to 1.0×10^{16} W/cm^2 while other laser parameters are fixed at some values. In this calculation, the pulse width $\tau = 50$ fs, the centre wavelength $\lambda = 380$ nm, and the calculation results for the lower and the upper states are shown in Figs. 2 and 3, respectively.

From Fig. 2, it is obvious that the vibrational distribution in lower state changes periodically with the increase of the laser intensity. Also shown in this figure is that the first vibrational energy level is always the one with the highest occupation probability no matter how high the laser intensity is. The variation of vibrational distribution in the upper electronic state with the increase of the laser intensity is displayed in Fig. 3. Except for the conserved distribution in both the lower and the upper state, also found in the figure is that there is more population in the fifth vibrational state than the others. Both figures 2 and 3 show that the increase of laser intensity does not imply the increase of population in each vibrational state, which is consistent with the conclusion given by Ref. [39].

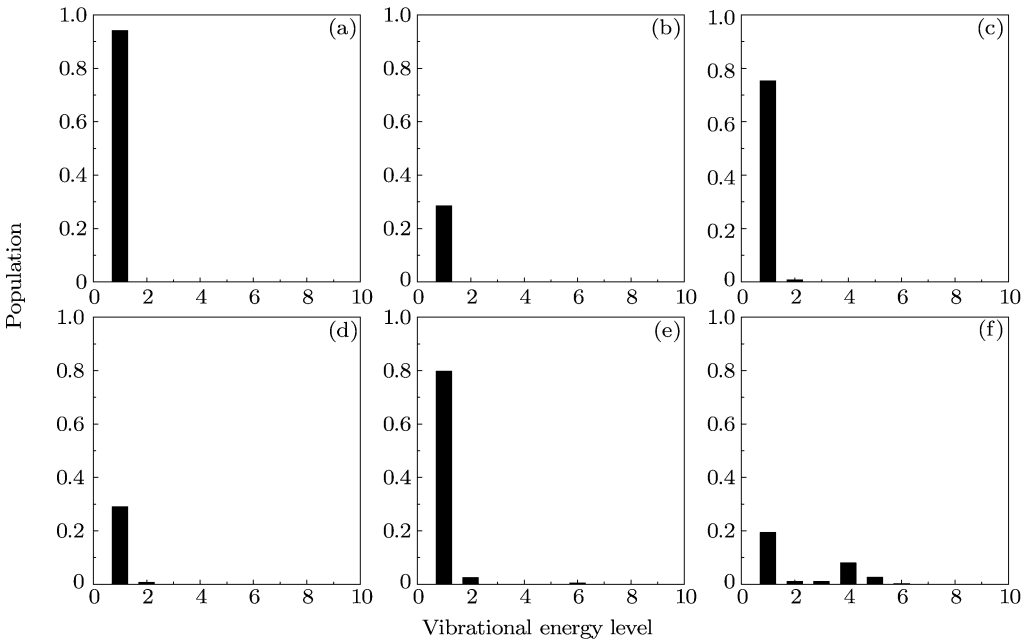


Fig. 2. Populations of different vibrational energy levels in lower electronic state with the change of laser intensity: (a) 1.0×10^{13} W/cm^2, (b) 1.5×10^{13} W/cm^2, (c) 1.5×10^{14} W/cm^2, (d) 0.9×10^{15} W/cm^2, (e) 1.5×10^{15} W/cm^2, and (f) 1.0×10^{16} W/cm^2.

Another important modulation parameter is the pulse width. In this calculation, it is varied from 35 fs to 60 fs, with the pulse intensity fixed at 1.0×10^{15} W/cm^2 and the centre wavelength at $\lambda = 380$ nm. The calculation results are shown in Figs. 4 and 5. From Fig. 4 we can see that the amount of population in lower state changes also periodically with the increase of the pulse width, and more particles occupy the first vibrational state. In Fig. 5, the complementary results are given and it is found that the fifth vibrational state is the most probable state occupied.

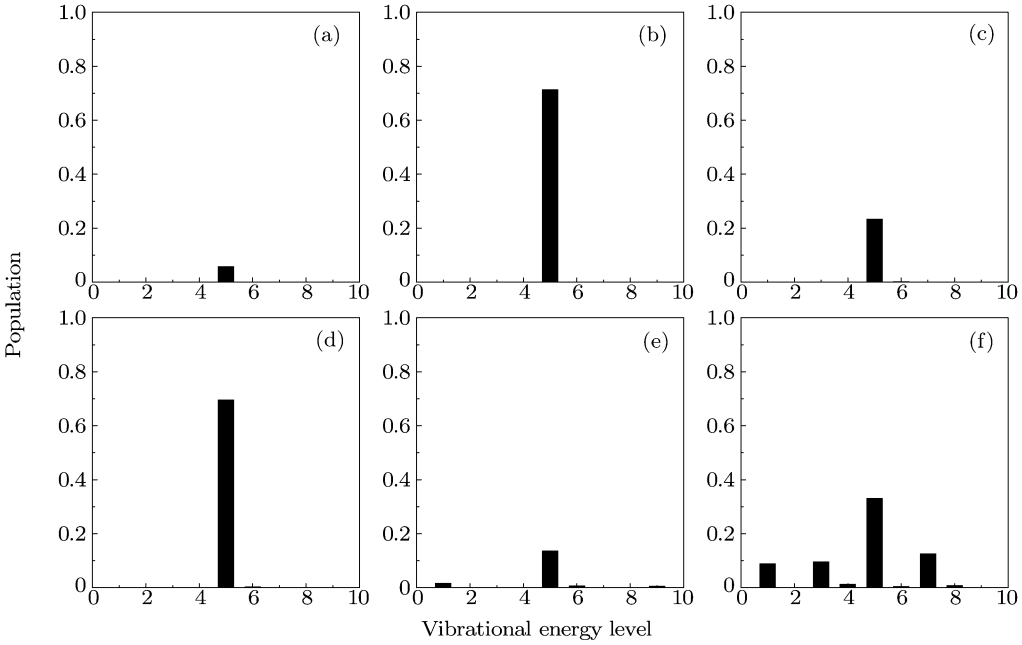


Fig. 3. Populations of different vibrational energy levels in upper electronic state with the change of laser intensity: (a) 1.0×10^{13} W/cm^2, (b) 1.5×10^{13} W/cm^2, (c) 1.5×10^{14} W/cm^2, (d) 0.9×10^{15} W/cm^2, (e) 1.5×10^{15} W/cm^2, and (f) 1.0×10^{16} W/cm^2.

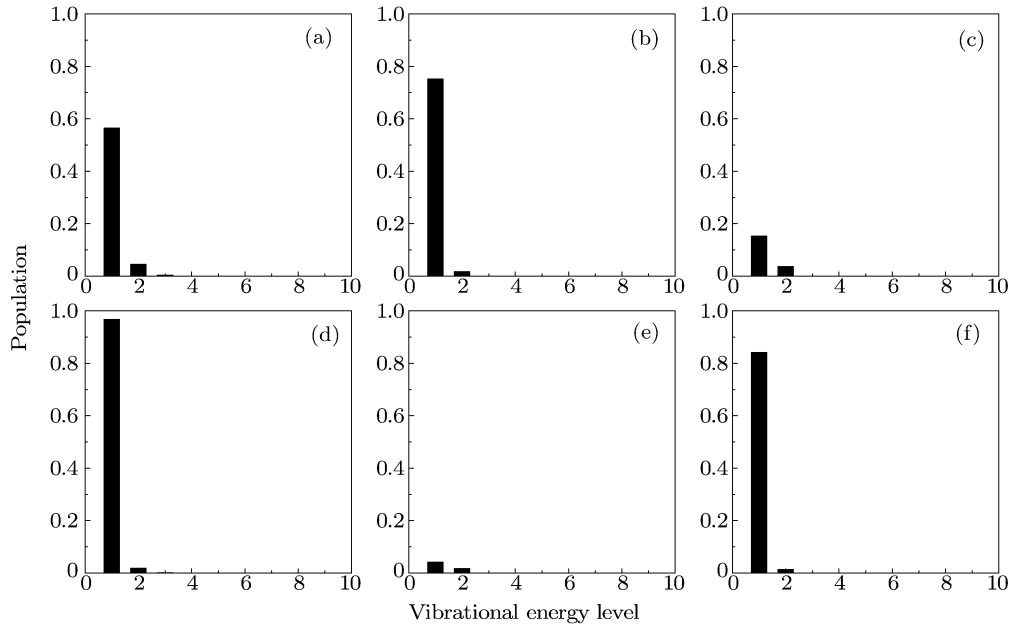


Fig. 4. Populations of each vibrational level in lower electronic state with the increase of the pulse width: (a) 35 fs, (b) 40 fs, (c) 45 fs, (d) 50 fs, (e) 55 fs, and (f) 60 fs.

Next, we calculate the influence of the laser wavelength which is varied from 350 nm to 430 nm with the pulse intensity fixed at 1.0×10^{15} W/cm^2, and pulse width at $\tau = 50$ fs. The simulation results are depicted in Fig. 6, which gives the variation tendency of vibrational distribution with the wavelength in the lower state. It is found that the vibrational population in the lower state changes also periodically with the increase of the laser wavelength, and more populations occupy the first vibrational energy level. What displayed in Fig. 7 is the vibrational distribution in the upper state. From it we can find an interesting phenomenon, i.e., the population in each vibrational energy level has some regular changes. With increasing laser wavelength, the vibrational state which has the most population will shift from the seventh one to the second one.

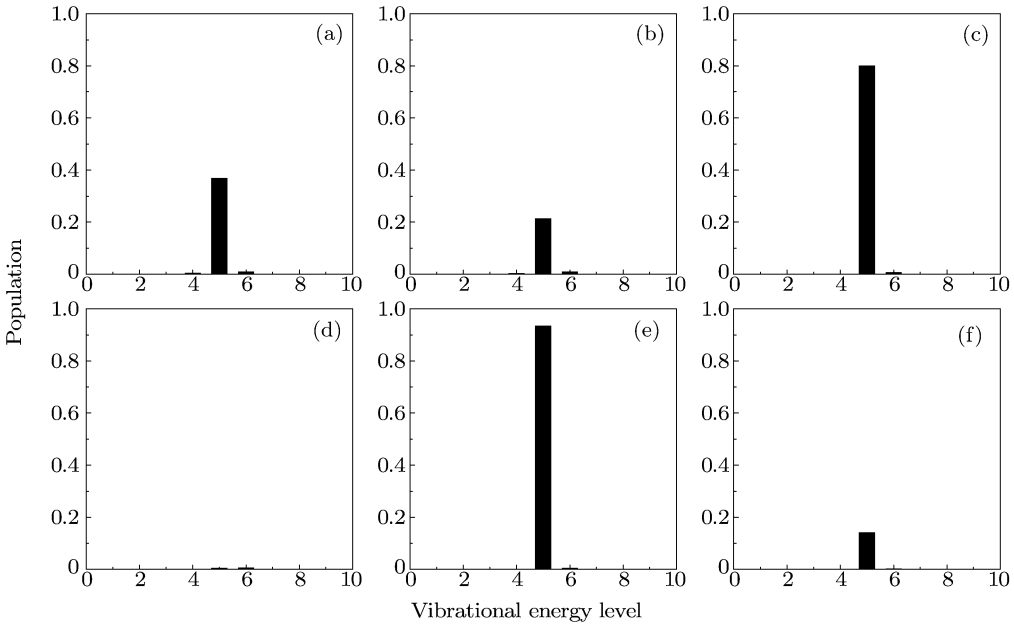


Fig. 5. Populations of each vibrational energy level in upper electronic state with the increase of the pulse width: (a) 35 fs, (b) 40 fs, (c) 45 fs, (d) 50 fs, (e) 55 fs, and (f) 60 fs.

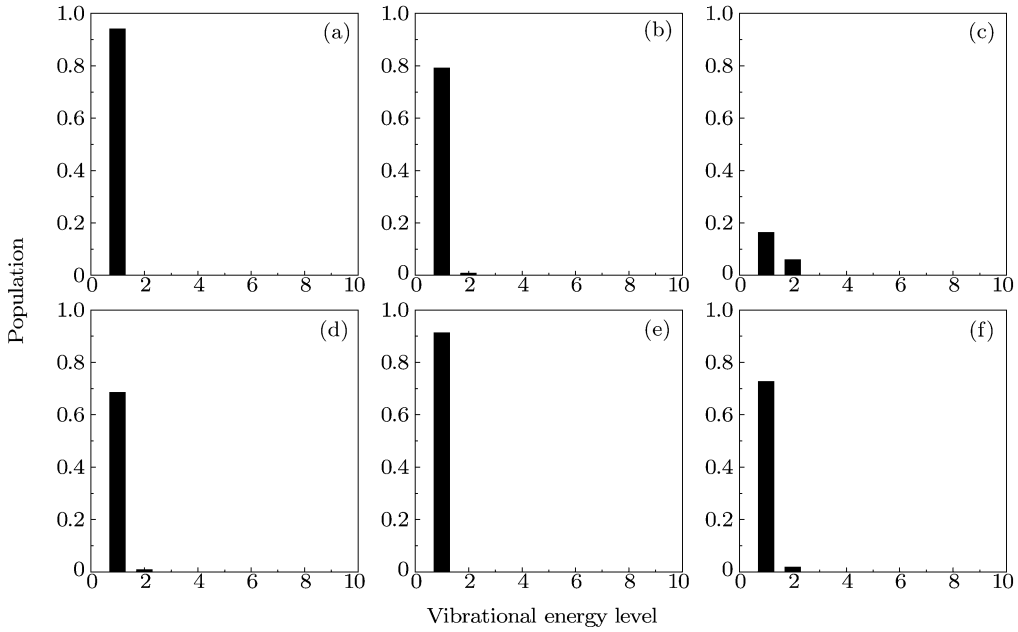


Fig. 6. Population of each vibrational energy level in lower state with the increase of the wavelength: (a) 350 nm, (b) 370 nm, (c) 385 nm, (d) 400 nm, (e) 420 nm, and (f) 430 nm.

To further illustrate the influence of the external field on population in each vibrational energy level, we perform a simulation with two separated pulses. In the calculation, the laser parameters for the pump laser are as follows: the pulse intensity 1.2×10^{13} W/cm^2, the centre wavelength $\lambda = 380$ nm, and the pulse width $\tau = 50$ fs; for the probe pulse, the intensity 1.5×10^{12} W/cm^2, the centre wavelength $\lambda = 390$ nm, and the pulse width $\tau = 40$ fs. The simulation results are depicted in Figs. 8 and 9 which give the variation tendency of vibrational distribution with the delay time in the lower and upper states, respectively. It is shown that, when only one laser pulse is used, the first vibrational state is the most probable state occupied.

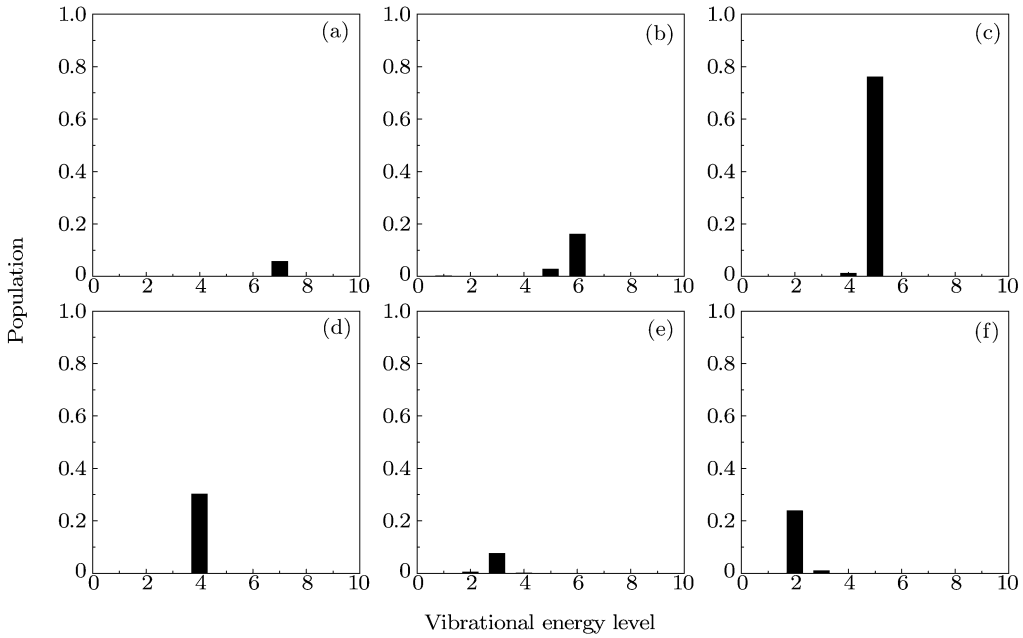


Fig. 7. Population of each vibrational energy level in upper state with the increase of the wavelength: (a) 350 nm, (b) 370 nm, (c) 385 nm, (d) 400 nm, (e) 420 nm, and (f) 430 nm.

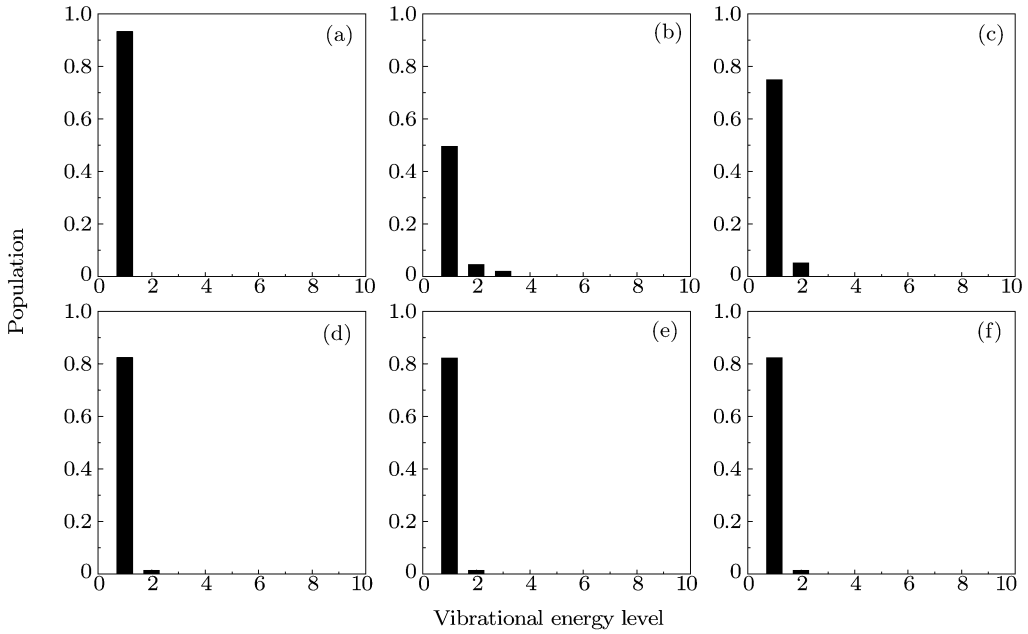


Fig. 8. The variation of population of each vibrational energy level in the lower state with the delay time of the two laser pulses: (a) first laser only, (b) 0 fs, (c) 50 fs, (d) 100 fs, (e) 150 fs, and (f) 200 fs.

When the pump and probe pulses are employed and the delay time is 0 fs, more vibrational states will be occupied by particles although the total population in the lower state decreases, while in the upper state, more population will occupy the fifth vibrational energy level. When the delay time is 50 fs, the population in the lower state increases and the population in the upper state decreases. In this case, the fourth vibrational energy level in the upper state has more population. When the delay time is 100 fs, the phenomena above are more obvious. However the cases for much larger delay time than 100 fs are peculiar, i.e., the population in each vibrational energy level is almost unchanged.

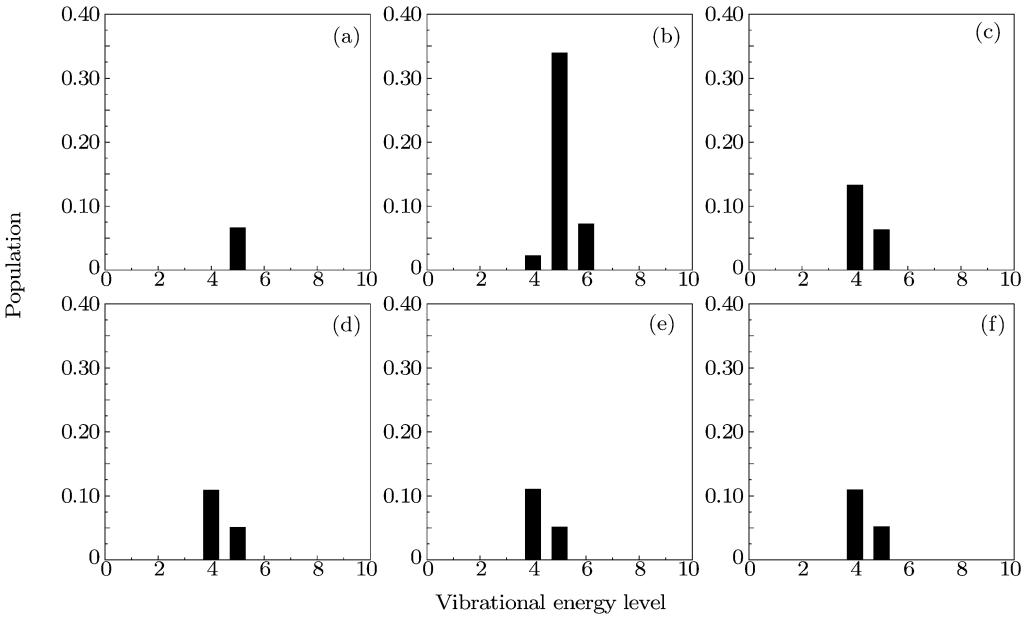


Fig. 9. The variation of population of each vibrational energy level in the upper state with the delay time of the two laser pulses: (a) first laser only, (b) 0 fs, (c) 50 fs, (d) 100 fs, (e) 150 fs, and (f) 200 fs.

3.2. Discussion

The phenomena given above are the consequences of LMI. When a two-level system is subjected to laser fields, the populations on both the lower and upper states will change periodically with time.[39] This changing tendency can be interpreted by Rabi oscillation (Fig. 10), an effect which has been well established and understood in atomic and molecular systems.[40−42] After the laser pulse moved away, the population left in each state will keep the same as the one in the right wing of the pulse is. However, for different laser wavelengths and intensities, the frequencies of Rabi oscillation are different, which leads to the different population left in each electronic state.

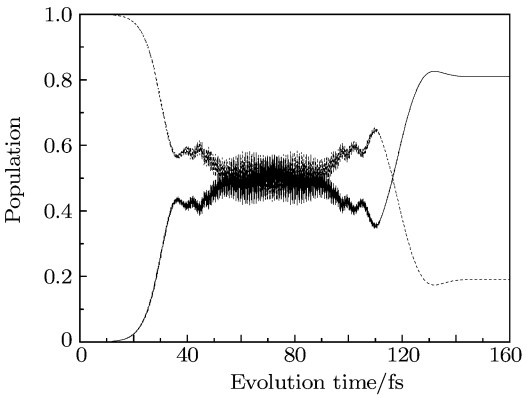


Fig. 10. Rabi oscillation occurring in the ground state (dashed line) and the excited state (solid line) for a two-level system subjected to a laser pulse.

The periodically changing tendency of the vibrational population with the laser intensity on both g and e states shown in Figs. 2 and 3 can be interpreted by Rabi oscillation. The laser intensity influences not only the Rabi oscillation frequency, but also the oscillation amplitude, which leads to the different population left in each electronic state. Since, for convenience to investigate the influence of laser pulses on the vibrational distribution, the population in each electronic state is projected to different vibrational states, it is natural that the vibrational population on each electronic state changes periodically with laser intensities. The phenomena shown in Figs. 4–7 can also be interpreted in the same way. Because of the Rabi oscillation and the influence of wavelength on its frequency,[42] with different pulse width and different wavelength, there will be also the different population left in each state after the laser pulse is moved away.

Generally, we often choose the ground vibrational state as the initial wave packet. Obviously when the laser field is absent, the particles are concentrated almost entirely on the ground vibrational state. After the pump pulse is over, because some particles have been excited to the upper state, the magnitude of the total population in the lower state is less than that before the pump pulse is applied. Since the ground vibrational state is the initial state with high stability, it is easy to understand that most of the population will remain in this state after the pulse is over. The

related phenomena are depicted in Figs. 2, 4 and 6.

In Figs. 3 and 5, the vibrational population in the upper electronic state has a common feature, i.e., the fifth vibrational state is the most probable one to be occupied. Considering that except the fifth vibrational state, other states are far from the resonance region, we can easily understand this so-called resonant phenomenon. In Fig. 7, we can find that with the increase of the laser wavelength, the resonance region shifts gradually from the seventh vibrational energy level to the second one. It is natural that the states closest to the resonance region will obtain most population.

In Figs. 8 and 9, it is found that when only one pulse is used, the fifth vibrational energy level closest to the resonance region is mostly occupied. When two pulses of the delay time 0 fs are used, for the first pulse the fifth vibrational energy level in upper electronic state is closest to the resonance region, while for the second pulse the fourth vibrational energy level in upper electronic state is closest to the resonance region. Because of the coupling between the two laser pulses, the population of the fifth vibrational energy level in the upper electronic state is dropped down to the second vibrational energy level in lower electronic state by the second laser. At the same time, the particles of the second vibrational energy level in the lower electronic state are excited to the sixth vibrational energy level in the upper electronic state by the first laser. Similarly the third vibrational energy level in the lower electronic state can also be populated by the second pulse. When the delay time is 50 fs, the coupling between two pulses is relatively small, besides the first vibrational state in the lower state and the fourth and fifth vibrational states in the upper state being populated, other most occupied state is the second one in the lower state. More population in the fourth vibrational level of the upper state is due to the influence of Rabi oscillation which makes more particles occupy the first vibrational level in the lower state and then be excited to the fourth vibrational level in the upper state when subjected to the second laser pulse. However, when the delay time is equal to or larger than 100 fs, since the coupling of them is very small, the populations in the fourth and fifth vibrational energy levels in upper electronic state and the first energy level in lower electronic state no longer change with the delay time. A small number of particles in the second vibrational energy level of the lower electronic state are from the population in the fifth vibrational level of the upper electronic state induced by the second laser.

4. Conclusions

In this paper, using the time-dependent wave packet method and taking the two-state system as an example, the variation tendency of vibrational distribution with laser parameters is investigated. It is found that the periodically changing tendency of the vibrational population with the laser parameters such as intensity, pulse width and wavelength is due to the Rabi oscillation. The key to the interpretion of the phenomena is the populations left in the upper and lower states, which can be projected to the related vibrational states after the pulses move away. The vibrational states closest to the resonance region can acquire the most probable distribution. As for the influence of the pulse delay time, it can be ascribed to the effect of the coupling between the two pulses. With the increase of the delay time, the coupling becomes weaker and its influence on the vibrational distribution in each electronic state becomes smaller gradually. The calculated results indicate that by changing the laser parameters we can control the evolution of a wave packet, and as a result, the population in each vibrational state can also be controlled. The above arguments will benefit the light manipulation of atomic and molecular processes.

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