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Field dependence of state populations in pump-probe pulses

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ABSTRACT

The effects of pulse width, laser wavelength and laser intensity on the state populations of NaI molecule driven by a pump-probe pulse were studied via employing the time-dependent wave packet approach. Wave packet moves periodically with roundtrip time 1000 fs. That the wave packet bifurcates in the crossing region affects state populations. The excitation probability increases and dissociation probability decreases with increasing pulse width. The excitation probability approaches the maximum at the resonance pump wavelength 318 nm, and the dissociation probability decreases with increasing pump wavelength. The excitation probability increases with increasing pump intensity while the dissociation probability does not vary. The probe wavelength and probe intensity have no effect on state populations. The wave packet motion and selective distribution of state populations, excitation and dissociation of molecule can be achieved by adjusting laser parameters. The results can provide some important basis for realizing quantum manipulation of molecules experimentally.

1. Introduction

With the development of ultrashort and ultrastrong laser pulse technology, more and more researches have focused on the control of molecular dynamics in real time. Controlling the evolution of wave packet will be a benefit for light manipulation of molecular processes experimentally. State populations map the wave packet dynamic information of the electronic state, are found to be sensitive to the parameters of the laser fields, and have been studied in multi-level molecular systems [1–14].

NaI molecule is a typical molecule with an avoided crossing between two nonadiabatically coupled electronic states at internuclear distance 7 Å, and has been studied experimentally and theoretically. Braun et al. [1] and Charron and Suzor-Weiner [2] presented that the wave packet moves periodically on the electronic state potentials of NaI molecule, which induces the periodical variation of photoelectron spectra. Yao et al. [3,4] suggested that the first dissociation probability decreases with increasing pump wavelength. The photoelectron spectra are dependent on the delay time. Arasaki et al. [5,6] and Takatuka et al. [7] indicated that the total ion signal oscillates periodically with increasing delay time. Miao et al. [8,9] and Liu et al. [10] suggested that the delay time affects state populations and photoelectron spectra. Ma et al. [11] presented that the pump wavelength affects state populations. Zhao et al. [12] studied the influence of field-free orientation on the predissociation dynamics of the NaI molecule. Xiong et al. [13] presented that the wavelength affects state populations of CsI molecule, the populations of excited state approaches the maximum with the resonance excitation wavelength. Zhu et al. [14] suggested the delay time affects state populations of CsI molecule.

The studies on the nonadiabatic effects on state populations of NaI molecule above mostly focused on the influence of pump-probe delay time. The effects of the pulse width and laser intensity on state populations of NaI molecule have not been reported. This paper presents new data on the influence of pulse width, laser wavelength and intensity on state populations of NaI molecule driven by pump-probe pulses via time-dependence quantum wave packet method.

2. Computation details

Three states (the ground state X, the excited state A and the ion ground state I) are involved in the multiphoton ionization of NaI molecule [1–3], as shown in Fig. 1. The transition from X to A is induced by resonant one-photon absorption, then the excited molecule is ionized through single-photon absorption after the delay time, and the emitted photoelectron is detected from I.

The wave function for the three-state model can be written as

$$\boldsymbol{\Psi} = (\Psi_X, \Psi_A, \Psi_I)^T, \quad (1)$$

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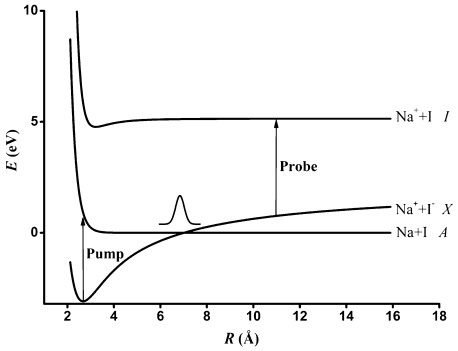

Fig. 1. Potential energy curves of NaI molecule.

where Ψ_X, Ψ_A and $\boldsymbol{\Psi}_I$ are the wave functions for the states X, A, and I, respectively. The ion ground state is a continuum state and can be discretized into a band of quasicontinuum states. The $\boldsymbol{\Psi}_I$ can be further expressed as

$$\boldsymbol{\Psi}_I = (\psi_1, \psi_2, \ldots, \psi_N)^T, \tag{2}$$

where N represents the number of discrete states of NaI ion. The wavefunctions $\boldsymbol{\Psi}_I$, within the Born-Oppenheimer approximation can be obtained by solving the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix}\Psi_X\\ \Psi_A\\ \psi_1\\ \psi_2\\ \vdots\\ \psi_N\end{pmatrix} = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2}\begin{pmatrix}\Psi_X\\ \Psi_A\\ \psi_1\\ \psi_2\\ \vdots\\ \psi_N\end{pmatrix} + \boldsymbol{V}(R,t)\begin{pmatrix}\Psi_X\\ \Psi_A\\ \psi_1\\ \psi_2\\ \vdots\\ \psi_N\end{pmatrix}, \tag{3}$$

where μ is the reduced mass and R is the internuclear distance, while the potential matrix $\boldsymbol{V}(R,t)$ can be explicitly written as

$$\boldsymbol{V}(R,t) = \begin{pmatrix} V_{XX} & W_{XA} & 0 & 0 & \cdots & 0\\ W_{AX} & V_{AA} & W_{AI} & \cdots & \cdots & W_{AI}\\ 0 & W_{IA} & V_{II}+E_{I,1} & 0 & \cdots & 0\\ \vdots & \vdots & 0 & \ddots & \cdots & \vdots\\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots\\ 0 & W_{IA} & 0 & 0 & \cdots & V_{II}+E_{I,N}\end{pmatrix}, \tag{4}$$

where V_{XX}, V_{AA}, and V_{II} refer to the potential matrix elements of states X, A, and I in the absence of laser fields. $E_{I,k} = (k-1)\Delta E_I (k = 1, 2, \ldots, N)$ is the emitted photoelectron energy. Other nonzero off-diagonal matrix elements are given by

$$W_{XA} = W_{AX} = \mu_{XA}\{\varepsilon_1 f_1(t)\cos\omega_1 t + \varepsilon_2 f_2(t)\cos\omega_2(t-\Delta t)\}, \tag{5}$$

$$W_{AI} = W_{IA} = \mu_{AI}\{\varepsilon_1 f_1(t)\cos\omega_1 t + \varepsilon_2 f_2(t)\cos\omega_2(t-\Delta t)\}, \tag{6}$$

where μ_{XA} and μ_{AI} are the transition dipole matrix elements, ε_1 and ε_2 are the amplitudes of the pump and probe pulses, ω_1 and ω_2 are the angular frequencies. The envelopes of the pulses $f_1(t)$ and $f_2(t)$ take Gaussian form

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

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

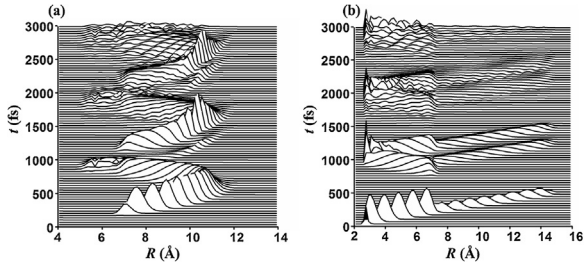

Fig. 2. The evolution of wave packet on (a) ground state X and (b) excited state A.

τ is the full width at half maximum (FWHM) of pulse and Δt is the delay time between the pump and probe pulses.

The time-dependent Schrödinger equation is solved by split-operator Fourier methods rigorously [15,16], once the wave function $\boldsymbol{\Psi}_i(R,t)$ is determined, the population on each electronic state can be written as [2,3,5,8–10,12,13]

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

The photoelectron spectrum can be obtained via [1,2,4–6,10]

$$P(E_{I,k}) = \lim_{t\to\infty}\int dR\left|\psi_k(R,t,E_{I,k})\right|^2, \quad (k = 1, 2, \ldots, N), \tag{10}$$

In the calculation, $E_{I,k}$ span over 0–1.2 eV and N equals 120.

3. Results and discussion

The effect of the delay time on the wave packet motion is considered. Fig. 2 shows the evolution of wave packet on the ground state and the excited state. The wave packet moves periodically with oscillation period 1000 fs. The wave packet moves on the excited state potential within 0–200 fs, reaches the crossing point (R = 7 Å) for the first time at 200 fs and bifurcates: most of the wave packet transfers to the ground state [Fig. 2(a)], only a small part still moves toward large internuclear distance on the excited state [Fig. 2(b)], which eventually dissociates into Na and I atoms. The wave packet on the ground state is reflected at the outer turning point (R = 11 Å) at 500 fs, returns to the crossing point at 800 fs and splits again, where most of the wave packet transfers to the excited state and a small component remains on the ground state. The similar periodical motion and bifurcation of wave packet have been referred to [1–8,10–12]. The wave packet propagates at different velocity on the ground state and on excited state after the second bifurcation, and returns to the crossing point at 1100 fs and 1200 fs, respectively, which results that the wave packet is composed of two envelopes, and is no longer a good-localization envelope, i.e. the nonadiabatic effect of NaI molecule becomes more and more obvious with increasing delay time. The wave packet on the ground state returns to the crossing point earlier than that on the excited state is referred to in Refs. [3,4,6].

The effect of the pulse width on state populations is considered. Fig. 3 demonstrates the evolution of state populations at different pulse width. All molecules are on the ground state initially until the pump laser excites them to the excited state, which makes the population of ground state declines [Fig. 3(a)], the population of excited state increases [Fig. 3(b)], and the sum population of three states is 1.0 [Fig. 3(c)]. The increase of the population on excited state increases (i.e. the excitation probability increases) with increasing pulse width. At 200 fs the wave packet of excited state reaches the crossing point (R = 7 Å) firstly and bifurcates: most of the wave packet transfers to the ground state with transfer probability P_X, while a small part remains on the excited state with transfer probability P_A, therefore the population of the ground state