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Rovibrational Formation of Ultracold NaH Molecules Induced by an Ultrashort Laser Pulse *

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The formation of the NaH molecule from unaligned ultracold atoms via photoassociation (PA) is theoretically investigated by numerically solving the time-dependent Schrödinger equation including the vibrational and rotational degrees of freedom. The PA processes via one- and two-photon excitations are described. The calculated results show that the associated molecule can be prepared to a desired rovibrational state of the ground electronic state for NaH. Compared with the one-photon association probability, the two-photon association probability is obviously enhanced.

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With the rapid development of ultrashort laser pulse technology, the laser control of atomic and molecular dynamics is an interesting and active research subject.[1−6] As a reversed process of photodissociation, photoassociation (PA) is an effective way to form cold and ultracold molecules. In a PA process, the binding of colliding atoms can be facilitated by means of an external field, which induces a free-to-bound transition, forming a molecule in either its electronic excited state or the ground state. Many theoretical and experimental schemes for controlling the PA process have been proposed.[7−11] Kosloff *et al.*[12,13] presented an optimizing control scheme for PA dynamics. By using the magneto-optical trap (MOP) theory, a total conversion of colliding atom pairs to molecules is estimated to calculate the PA signal. Engel *et al.*[14] employed the local control theory to investigate the PA process driven by the shaped laser pulse. Koch *et al.*[15] focused their attention on the coherent control to improve the PA probability and produce ultracold molecules in the vibrational ground state. Korolkov *et al.*[16] studied the vibrationally state-selective PA process steered by the chirped laser pulse. de Lima *et al.*[17] employed a one-dimensional model to calculate the PA probability. Feng *et al.*[18,19] investigated the transfer efficiency from the atoms to molecules by using stimulated Raman adiabatic passage method and discussed the resonance condition for producing ultracold molecules.

In the present work, we study the PA dynamics of the ultracold colliding atoms Na and H driven by femtosecond laser pulses. The PA processes via one- and two-photon excitations are described.

In a femtosecond laser field, the colliding atoms Na and H combine to form a NaH molecule. The ground-state potential energy curve and the transition processes for NaH are depicted in Fig. 1. The potential energy curve and the permanent dipole moment of NaH are obtained from Refs. [20,21]. In the Born–Oppenheimer frame,[22] the wave function ψ is calculated by solving the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\psi(R,\theta,t)=\hat{H}\psi(R,\theta,t). \tag{1}$$

In this work, since the linearly polarized laser pulses are used, the molecular magnetic quantum number M is conserved. It is assumed that the initial magnetic quantum number $M=0$, which is equivalent to ignoring the $\partial\varphi$ term (φ azimuthal angle) in a full three-dimensional Hamiltonian.[23] The Hamiltonian with an azimuthal symmetry is given by

$$\begin{aligned}\hat{H}&=\hat{T}_k+\hat{T}_\theta+\hat{V}(R)+\hat{W}(R,\theta,t)\\&=\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial R^2}-\frac{\hbar^2}{2mR^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right]\\&\quad+\hat{V}(R)+\hat{W}(R,\theta,t),\end{aligned} \tag{2}$$

where $\hat{V}(R)$ denotes the field-free potential energy function of the ground state $X^1\Sigma^+$ for NaH. The laser-molecule interaction $\hat{W}(R,\theta,t)$ is expressed as

$$\hat{W}(R,\theta,t)=-\mu(R)\varepsilon(t)\cos\theta, \tag{3}$$

where μ is the permanent dipole moment, and θ the angle between laser electric field direction and the molecule axis. The electric field of laser pulse is given by

$$\varepsilon(t)=\varepsilon_0 f(t)\cos(\omega t), \tag{4}$$

where ε_0 and ω are the amplitude and frequency of laser pulse, respectively, and $f(t)$ denotes the Gaussian pulse envelope

$$f(t)=\exp\left[-4\ln 2\cdot\left(\frac{t}{\tau}\right)^2\right], \tag{5}$$

where τ is the full width at half maximum (FWHM) of laser pulse.

The Fourier grid Hamiltonian (FGH) method[24] and Legendre polynomials are used to calculate the

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radial and angular parts of the rovibrational eigenfunction of the ground electronic state. In the representation of Legendre polynomials, the angular momentum operator is diagonal and expressed as

$$L^2 = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial}{\partial\theta}\Big) = -\frac{\partial}{\partial\xi}(1-\xi^2)\frac{\partial}{\partial\xi}, \quad (6)$$

where $\xi = \cos\theta$. When the Legendre polynomials $P_l(\cos\theta)$, $l = 0, 1, 2, \cdots, n_j$, are used as angular basis set, the Gaussian–Legendre quadrature points are used as grid points.

Before propagating the time-dependent wave packet, its initial form must be defined. In the present study, the initial wave function at $t = 0$ is described by the Gaussian wave packet[16,25]

$$\psi(R,\theta,t=0) = \Big(\frac{2}{\pi d_0^2}\Big)^{\frac{1}{4}} \exp\left[ik_0 R - \left(\frac{R-R_0}{d_0}\right)^2\right] \times P_l(\cos\theta), \quad (7)$$

where d_0 denotes the width of the initial wave packet, and R_0 is the initial distance between Na and H atoms. The collision energy is given by

$$E = \frac{\hbar^2}{2m}\Big(k_0^2 + \frac{1}{d_0^2}\Big), \quad (8)$$

where $\hbar k_0$ and m are the initial momentum and the reduced mass of NaH, respectively.

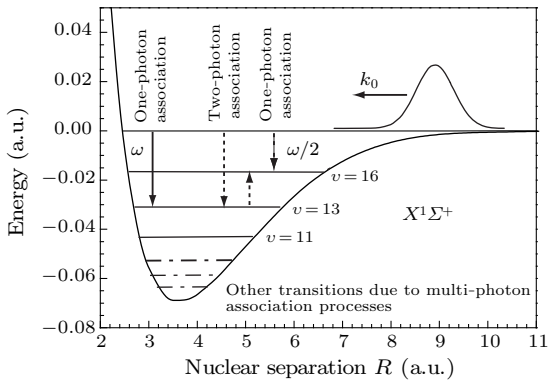


Fig. 1. The field-free potential energy curve of the ground state $X^1\Sigma^+$ and the transition processes for NaH.

The time-dependent Schrödinger equation is numerically solved by using the split operator method. The time-dependent rovibrational population on the rovibrational state $|v, j\rangle$ is calculated by

$$P_{v,j}(t) = |\langle v, j|\psi(R,\theta,t)\rangle|^2, \quad (9)$$

and the vibrational population on the $|v\rangle$ vibrational state is given by

$$P_v(t) = \sum_j P_{v,j}(t). \quad (10)$$

In the PA process, the colliding atoms Na and H move towards a small internuclear distance and form the NaH molecule in rovibrational state $|v, j\rangle$ by absorbing one or two photons, as shown in Fig. 1. In general, the PA probability depends on the properties of the initial wave packet.[26] In the present work, we take k_0 as $-2.0\hbar/a_0$, where a_0 is the Bohr radius. The width of the initial wave packet d_0 is chosen to be $10.6a_0$ in order to avoid large momentum uncertainty. The laser pulse frequency is determined by $\omega = (E_v - E_c)/\hbar$.

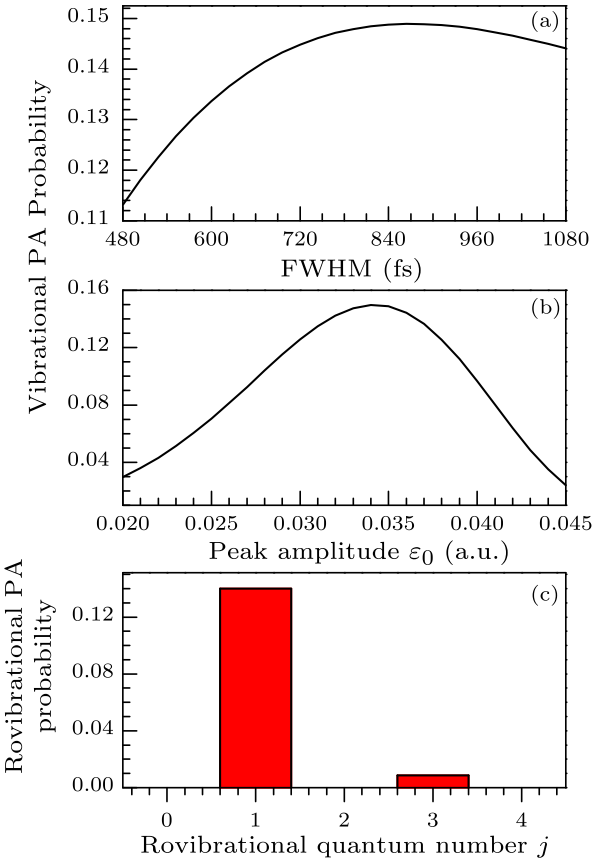


Fig. 2. (a) P_{13} versus FWHM at $\varepsilon_0 = 4.3\times10^{13}\,\mathrm{W/cm^2}$, (b) P_{13} versus laser intensity at $\tau = 840\,\mathrm{fs}$, and (c) the rovibrational association probability $P_{13,j}$ versus rotational quantum number j at $\varepsilon_0 = 4.3\times10^{13}\,\mathrm{W/cm^2}$ and $\tau = 840\,\mathrm{fs}$.

First, we consider the PA process induced by one-photon excitation. The central wavelength of laser pulse is chosen to be $\lambda = 3210\,\mathrm{nm}$, which satisfies the resonance condition $\hbar\omega = E_{13} - E_c$. The change of the vibrational population P_{13} with the FWHM τ of laser pulse is shown in Fig. 2(a), where the peak intensity of laser pulse is fixed at $4.3\times10^{13}\,\mathrm{W/cm^2}$. We can find that the PA probability increases as τ changes from 480 to 840 fs. At about $\tau = 840\,\mathrm{fs}$, the PA probability reaches its maximum. When $\tau > 840\,\mathrm{fs}$, the PA probability decreases with the increase of τ. The shorter laser pulse in the time domain, the broader its frequency bandwidth in the frequency (or energy) domain. Thus, it is difficult to control the associated molecule to a desired quantum state by utilizing ultrashort laser pulse. From Fig. 2(a), we can find that the

population can not be transferred completely to the desired quantum state and the maximal vibrational population $P_{13} = 0.148$.

Figure 2(b) illustrates P_{13} as a function of laser intensity at a fixed $\tau = 840\,\text{fs}$ at which the PA probability takes its maximal value, as shown in Fig. 2(a). We can see that the PA probability is very sensitive to the peak intensity of laser pulse. The maximal value $P_{13} = 0.148$ at the peak intensity $\varepsilon_0 = 4.3 \times 10^{13}\,\text{W/cm}^2$. It is noteworthy that photodissociation (PD) may take place simultaneously with the PA process.[4] With a weaker laser pulse, for example, $\varepsilon_0 < 4.3 \times 10^{13}\,\text{W/cm}^2$, the PD process has a small effect on the PA reaction and P_{13} increases with ε_0. When $\varepsilon_0 > 4.3 \times 10^{13}\,\text{W/cm}^2$, however the PD probability increases and the PA probability decreases with the increase of laser intensity, as shown in Fig. 2(b). Figure 2(c) shows the final rovibrational population on the $\upsilon = 13$ vibrational state after the laser pulse is over. The associated NaH molecule is mainly prepared on the $|\upsilon = 13, j = 1\rangle$ state via $\Delta j = 1$ transition.

To further describe the PA process, in Fig. 3, we plot the time-dependent image of wave packet $|\psi(R,t)|^2$ in the coordinate space. At $t = 200\,\text{fs}$, the initial wave packet moves into potential well ($R < 10\,\text{a.u.}$), and H associates with Na. The association process lasts until $t \approx 700\,\text{fs}$. When the PA process ends, a part of $|\psi(R,t)|^2$ is located in the region of $R < 8\,\text{a.u.}$. From Fig. 3 we can observe an obvious interference picture of wave packet in the PA process. In our treatment, the width of the initial wave packet is larger than that of the potential well. In the association process, different parts of the wave packet correspond to different directions of momenta. A part of wave packet returns at the inner turning point ($R \approx 2.5\,\text{a.u.}$) and meets with other part that still movies to the left, and thus leads to the interference picture of wave packet.[27]

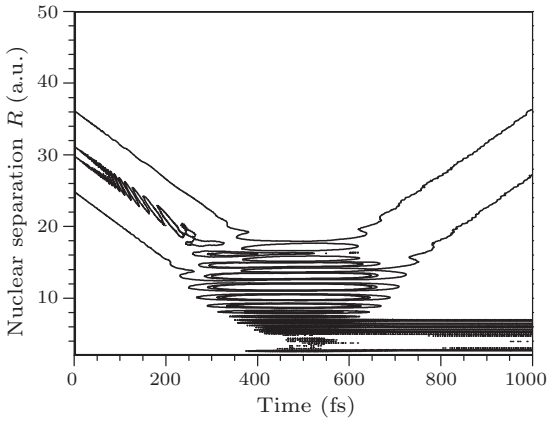


Fig. 3. The evolution of wave packet $|\psi(R,t)|^2$ with time in coordinate space at $\varepsilon_0 = 4.3 \times 10^{13}\,\text{W/cm}^2$ and $\tau = 840\,\text{fs}$.

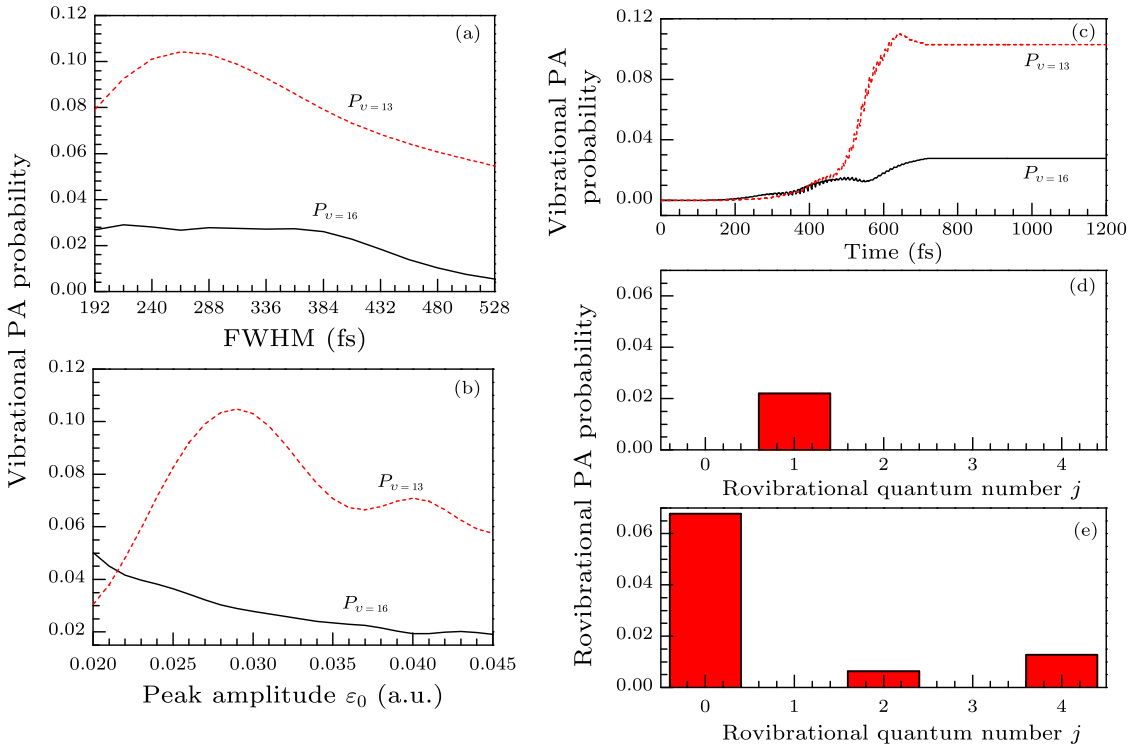


Fig. 4. (a) P_{16} and P_{13} versus FWHM at $\varepsilon_0 = 3.6 \times 10^{13}\,\text{W/cm}^2$, (b) P_{16} and P_{13} versus laser intensity at $\tau = 288\,\text{fs}$, (c) P_{16} and P_{13} versus time, (d) $P_{16,j}$ versus rotational quantum number j, and (e) $P_{13,j}$ versus j. In panels (c)–(e), $\varepsilon_0 = 3.6 \times 10^{13}\,\text{W/cm}^2$ and $\tau = 288\,\text{fs}$.

We then discuss the PA process via the two-photon excitation. Figure 4(a) shows the vibrational populations P_{13} and P_{16} versus the FWHM τ, where $\varepsilon_0 = 3.16 \times 10^{13}\,\mathrm{W/cm^2}$ and $\lambda = 6240\,\mathrm{nm}$. The vibrational population depends on the duration of the laser pulse, and the peak values of P_{13} and P_{16} appear at around $\tau = 288\,\mathrm{fs}$. Figure 4(b) illustrates the dependency of P_{13} and P_{16} on the peak intensity of laser pulse, where τ is fixed at 288 fs. The vibrational population is sensitive to the intensity of laser pulse, and the maximum of $P_{13} = 0.103$ is obtained. Compared with Figs. 2(a) and 2(b), with shorter and weaker laser pulse, we can obtain a larger PA probability with a maximal value $P_{\mathrm{tot}} = 0.206$ in the two-photon excitation, as shown in Figs. 4(a) and 4(b).

Figure 4(c) displays the time-dependent vibrational populations P_{13} and P_{16} at $\varepsilon_0 = 3.16 \times 10^{13}\,\mathrm{W/cm^2}$ and $\tau = 288\,\mathrm{fs}$. There are two channels through which the initial population is transferred from the continuum state to the $\upsilon = 13$ vibrational state. In the first channel, the population can be transferred through the intermediate states and the population transfer process is ruled by $\Delta j = \pm 1$ transitions. In the second channel, the two-photon transition path which is ruled by $\Delta j = \pm 2$ transitions is opened according to the parity selection rule for a polar molecule.[2,3] Figures 4(d) and 4(e) show the rotational populations on the different vibrational states. The PA process is steered by the rotational and vibrational excitations, and the associated molecule can be prepared to the desired rovibrational state, suggesting that the rotational degree of freedom should be considered in the PA process driven by strong ultrashort laser pulse.

In conclusion, we have theoretically studied the formation of the NaH molecule by means of the one- and two-photon photoassociation processes. The rotational degree of freedom of the molecule is taken into account in the calculation. By using an optimized laser pulse, a rovibrationally selective state $|\upsilon = 13, j = 1\rangle$ for the associated NaH molecule can be efficiently prepared via the one-photon association process. Two-photon association process can open more association channels in which odd- and even-order rotational transitions take place. Moreover, the evolution pictures of the rovibrational wave packet are plotted in the coordinate space, and the interference pattern of the wave packet is observed in the photoassociation process.

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