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Theoretical study of femtosecond photoionization for the Na_2 molecule

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Abstract. Multiphoton ionization of the Na_2 molecule by a single phase shaped femtosecond laser pulse has been theoretically studied using time-dependent quantum wave packet method including the effect of molecular rotation. We analyze the temporal development of the population and further discuss the molecular motion by mapping the rovibrational wave packet propagation in the excited state. The calculated results show a strong dependence of the kinetic energy-resolved photoelectron spectra on the laser chirp directions and the pulse duration.

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Key words: multiphoton ionization, photoelectron spectra, time-dependent wave packet, effect of rotation

1 Introduction

With the rapid development of laser technology, femtosecond laser pulses have opened the possibility to observe or to control the real-time molecular dynamics [1,2]. Compared to atoms, molecules exhibit complex behavior due to their multi-center nature, which introduces additional vibrational and rotational degrees of freedom. Many interesting phenomena, such as bond softening and hardening [3,4], above-threshold ionization (ATI) and dissociation (ATD) [5,6], adiabatic passage of light-induced potentials (APLIP) [7], and more, have been explored. To illustrate the matter-field interaction process, femtosecond pump-prob photoelectron spectroscopy has become a useful tool in ultrafast molecule science [8,9]. As a prototype, a large number of experimental and theoretical

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studies using the pump-prob technology have been made on dynamics of the sodium dimer in laser fields [10–13].

In Ref. [14], the authors reported the observation of the coherent control of the Na_2 molecular multi-photon ionization process in a single phase shaped pulse experiment, where the carrier frequency ω_0 is 618 nm. In the experiment, starting from a Fourier-transform limited 40 fs pulse, either an up-chirp (+3500 fs^2) or a down-chirp (-3500 fs^2) is introduced. The measured kinetic energy photoelectron spectra showed a strongly chirp- and pulse-duration-dependent behavior and revealed that for down-chirp the population in neutral state may be higher, but the up-chirp led to a higher ionization yield.

In present work, we theoretically stimulate the Na_2 molecular multi-photon ionization process in Ref. [14] including the effect of rotation using time-dependent quantum wave packet method. As the torque exerted by laser fields on molecules can lead to molecular alignment, the effect of rotation should be taken into account to obtain quantitative agreement with experiment. In Ref.[14], the photoelectron spectra had been calculated using time-dependent perturbation theory [13,15]. Compared with their work, the dynamics of the Na_2 molecule is dealt with accurate non-perturbation quantum mechanics method in this letter. The paper is organized as follows: in Section 2, the theoretical method is summarized. The numerical results and their discussions are presented in Section 3, and Section 4 contains the conclusion.

2 Theoretical method

In accordance with the experimental conditions the calculations are performed include four electronic states, the ground state X $^1\Sigma_g^+$, A $^1\Sigma_u^+$, 2 $^1\Pi_g$, and the ionic ground state Na_2^+ $^2\Sigma_g^+$, as shown in Fig. 1. For convenience we refer to the four electronic states as $|X\rangle$, $|A\rangle$, $|2\rangle$, and $|I\rangle$ states, respectively. The nuclear wave functions Ψ are obtained by solving the time-dependent Schrödinger equation

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

with

$$\Psi=\begin{pmatrix}\Psi_X\\ \Psi_A\\ \Psi_2\\ \Psi_I\end{pmatrix}. \tag{2}$$

In this work we consider the initial magnetic quantum number M of the Na_2 molecule to be zero. In the linearly polarized laser field, M is conserved, which is equivalent to ignoring the ∂_ϕ term (ϕ azimuthal angle) in a full three-dimension Hamiltonian. Then the kinetic energy operator $\hat{T}(R,\theta)$ can be expressed as [16,17]

$$\hat{T}(R,\theta)=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial R^2}-\frac{\hbar^2}{2mR^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}), \tag{3}$$