Study on wave packet dynamics of $E^1\Sigma_g^+$ state of Li_2 with femtosecond-resolved photoelectron spectra*

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Wave packet dynamics of the Li_2 molecule are investigated by using the time-dependent quantum wave packet method, and the time-resolved photoelectron spectra of the Li_2 molecule are calculated. The time-resolved wave packet theory is used to reasonably interpret the phenomena of the photoelectron spectra for different parameters. Our calculation shows that the loss of the wave packets in the shelf state area of $E^1\Sigma_g^+$ plays a prominent role in the process of photoionization with the increase of the delay time. Moreover, the oscillation of the wave packet on the $E^1\Sigma_g^+$ curve symbolizes a decreasing process of energy.

Keywords: time-dependent wave packet, photoelectron spectra, pump-probe
PACC: 3300, 3365, 3380E

1. Introduction

Alkali metals are interesting systems for various research areas, such as Bose–Einstein condensation, metal clusters or coherent control. In their own right, they are also regarded as simple model systems, suitable for theoretical studies. Correspondingly, femtochemistry has made remarkable progress during the last two decades, and more and more scientists have paid attention to the dynamical research on the femtosecond time scale.[1−5] Besides, an important effort has been devoted to the development of the ultrashort and intense laser pulse, thereby opening a new research domain in molecular dynamics and molecular spectroscopy.[6−9] The molecular motion has been studied since the introduction of femtosecond laser systems. One typical example is the study of molecule wave packets by using pump-probe techniques.

There have existed plenty of data for the Li_2 molecule, concerning both the bound states and the photoionisation continuum.[10,11] In some ultrafast pump-probe experiments on Li_2[12−14] there was employed an initial state selection, from which the wave packet was launched. This process greatly simplifies the preparation of the wave packet. Moreover, in several studies[15−21] the system of Li_2 in three-step photoionisation was investigated by using ultrafast pump-probe spectroscopy and Lorenzo *et al.*[20] presented a quantum dynamical simulation of the ultrafast photoionisation of Li_2. In Refs. [18], [20], [22], the pump-probe experimental setup was described in detail.

In the present paper, excited states $A^1\Sigma_u^+$ and $E^1\Sigma_g^+$ are both employed to calculate the photoelectron spectra (PES). The potential energy curves and pump-probe processing of the Li_2 molecule in the two-color laser field are depicted in Fig. 1.[21] Here, we present a theoretical investigation of Li_2, in which both the pump and probe pulses are considered by using the exact quantum mechanics, and the dynamics of all states is dealt with by the wavepacket dynamics method invoking the rotating wave approximation (RWA). By analysing intuitional images presented in this work, we can investigate the dynamical process of wave packet in $E^1\Sigma_g^+$ state. The time-resolved photoelectron spectra (TRPES) are calculated by considering three electronic states for the Li_2 molecule: the initial state $A^1\Sigma_u^+$, the intermediate state $E^1\Sigma_g^+$, and the electronic state $X^2\Sigma_g^+$ (or $X^2\Sigma_u^+$) of Li_2^+. The electronic degrees of freedom are limited to the three electronic surfaces, i.e. A, E, and I (for ionic), corresponding to the surfaces $A^1\Sigma_u^+$, $E^1\Sigma_g^+$ and the electronic state surface of Li_2^+, $X^2\Sigma_g^+$ (or $X^2\Sigma_u^+$), respectively. As shown in Ref. [18], a cw laser provides a launch state by exciting a transition from the ground state to the energy level of $A^1\Sigma_u^+$, and two femtosecond pulses, namely a pump pulse and a

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probe pulse, are employed. Here, we only pay attention to the pump-probe step. Initially, in the pump step, the wave packet that resides on the potential energy surface of the first excited state of the Li_2 molecule, (A), can be detached by the pump pulse, thereby forming a new wave packet on the potential energy surface of $E^1\Sigma_g^+$. During the delay time, the new wave packet transmits on the $E^1\Sigma_g^+$ state. After that, the new wave packet is excited into the potential energy surface of the electronic state ($X^2\Sigma_g^+$ or $X^2\Sigma_u^+$) for Li_2^+ ion by the probe pulse.

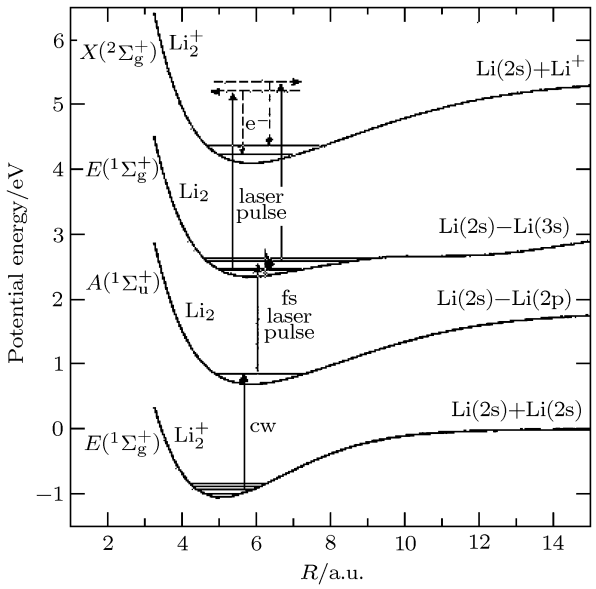


Fig. 1. Three-step 'preparation-pump-probe' scheme of Li_2 molecule. The potential energy curves of the X, A and E electronic states of Li_2 molecule each are shown as a function of inter-nuclear distance R. The potential curve associated with the ground electronic state of Li_2^+ is also shown here.

2. Theoretical treatment

To calculate the TRPES of the Li_2 molecule, we perform the three-state (the A state, the E state, and the ionic state of Li_2 molecule) quantum mechanical calculations, and chose wave packet in the vibrational ground state of $A^1\Sigma_u^+$ as the initial wave packet. The rotational degree of freedom in our treatment is frozen because of the ultrashort interaction time between Li_2 molecule and the femtosecond laser pulses. Invoking the Born–Oppenheimer approximation and neglecting the coupling between the core and photoelectron, we write the Hamiltonian for the vibration motion of the molecule as

$$H = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2}\boldsymbol{I} + \boldsymbol{V}(R,t), \tag{1}$$

where $\boldsymbol{I}$ is the identity matrix, R is the inter-nuclear separation, and μ is the reduced mass of the molecule, while the potential matrix $\boldsymbol{V}(R,t)$ can be explicitly written as[23−31]

$$\boldsymbol{V}(R,t) = \begin{pmatrix} V_{\rm AA} & W_{\rm AE} & 0 & 0 & \cdots & 0 \\ W_{EA} & V_{\rm EE} & W_{\rm EI} & \cdots & \cdots & W_{\rm EI} \\ 0 & W_{\rm IE} & V_{\rm II}+E_{\rm I,1} & 0 & \cdots & 0 \\ \vdots & \vdots & 0 & \ddots & \cdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & W_{\rm IE} & 0 & 0 & \cdots & V_{\rm II}+E_{\rm I,n} \end{pmatrix}. \tag{2}$$

Here, A, E and I represent the $A^1\Sigma_u^+$ state of Li_2 molecule, the $E^1\Sigma_g^+$ state of Li_2 molecule and the electronic state of Li_2^+ ion, respectively, and for the continuum state of the Li_2^+ ion, the free electron–ion pair states are detached by 40 discrete states. V_{ii} (i= A, E, I) refer to the potential matrix elements of the molecule in the absence of any laser field. $V_{\rm II}+E_{{\rm I},n}$ $(n=1,2,\ldots,40)$ denote the total energies of the discrete set of continuum states in the part of the free electron–molecule pair states. $E_{{\rm I},n}$ are the electron kinetic energies related to the discretized set of free electron-ion pair states. Other nonzero off-diagonal matrix elements are given by

$$W_{ij} = W_{ji} = \mu_{ij}\cdot E(t), \tag{3}$$

where μ_{ij} (i= A, E, I) and $E(t)$ are the dipole matrix elements and the external field, respectively. The dipole matrix elements μ_{ij} are the same as those in Ref. [10]. The shape of the laser pulse is chosen to be

$$E(t) = \sqrt{8\pi I/c}f(t)(\cos\omega t), \tag{4}$$

where $f(t) = \exp\left(-(t-t_0)^2/2\sigma^2\right)$ is the pulse envelope function, I is the laser intensity, c is the velocity of light in vacuum, t_0 is the central value of the pulse, ω is the central frequency, and σ is relevant to the laser full width at half maximum (FWHM).

The time-dependent Schrödinger matrix equation can be written as

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\begin{pmatrix}\psi_{\mathrm{A}}\\ \psi_{\mathrm{E}}\\ \psi_{\mathrm{I}}\\ \vdots\\ \vdots\\ \psi_{\mathrm{I}n}\end{pmatrix} = \begin{pmatrix} H_{\mathrm{AA}} & H_{\mathrm{AE}} & 0 & 0 & \cdots & 0\\ H_{EA} & H_{\mathrm{EE}} & H_{\mathrm{EI}} & \cdots & \cdots & H_{\mathrm{EI}}\\ 0 & H_{\mathrm{IE}} & H_{\mathrm{II}}+E_{\mathrm{I},1} & 0 & \cdots & 0\\ \vdots & \vdots & 0 & \ddots & \cdots & \vdots\\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots\\ 0 & H_{\mathrm{IE}} & 0 & 0 & \cdots & H_{\mathrm{II}}+E_{\mathrm{I},n}\end{pmatrix}\begin{pmatrix}\psi_{\mathrm{A}}\\ \psi_{\mathrm{E}}\\ \psi_{\mathrm{I}}\\ \vdots\\ \vdots\\ \psi_{\mathrm{I}n}\end{pmatrix}, \tag{5}$$

where ψ_i (i=A, E) and $\psi_{\mathrm{I}n}$ ($n = 0, 1, \ldots, 40$) denote the wave functions of the bound states and the quasi-continuum states (discrete states) respectively; the diagonal elements can be expressed as

$$H_{ii} = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2}I_{ii} + V_{ii}(R,t); \tag{6}$$

the off-diagonal elements can be expressed as

$$H_{ij} = H_{ji} = W_{ij} = \mu_{ij}\cdot E(t). \tag{7}$$

The above matrix equation can be solved by using the 'split-operator Fourier' method.[24−30] The evolution of the wave packets with time can be expressed as

$$\Psi(R, t+\delta t) \approx U_{\mathrm{T}}^{1/2}(R,t)U_{\boldsymbol{V}}U_{\mathrm{T}}^{1/2}(R,t)\Psi(R,t), \tag{8}$$

where U_{T} and U_{V} denote the kinetic and potential energy evolution operators, respectively. The kinetic energy evolution operator is given by

$$U_{\mathrm{T}} = \exp\left[-\frac{\mathrm{i}\,\delta t}{\hbar}T_{\mathrm{R}}\right] = F^{-1}\exp\left[-\frac{\mathrm{i}\,\hbar k^2\delta t}{2\mu}\right]F, \tag{9}$$

where F denotes the Fourier transform

$$F[f] = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\mathrm{d}R'\mathrm{e}^{\mathrm{i}\,kR'}f(R'). \tag{10}$$

The potential energy evolution operator is calculated by [23,24]

$$\begin{aligned} U_{\mathrm{V}} &= \exp\left[-\frac{\mathrm{i}}{\hbar}\boldsymbol{V}\delta t\right] = \boldsymbol{M}\exp\left[-\frac{\mathrm{i}}{\hbar}\boldsymbol{M}^{\mathrm{T}}\boldsymbol{V}\boldsymbol{M}\delta t\right]\boldsymbol{M}^{\mathrm{T}}\\ &= \boldsymbol{M}\begin{pmatrix}\exp(-\mathrm{i}\,\lambda_1\delta t/\hbar) & 0 & \cdots & 0\\ 0 & \exp(-\mathrm{i}\,\lambda_2\delta t/\hbar) & \cdots & 0\\ \vdots & \vdots & \ddots & \vdots\\ 0 & 0 & \cdots & \exp(-\mathrm{i}\,\lambda_n\delta t/\hbar)\end{pmatrix}\boldsymbol{M}^{\mathrm{T}}, \end{aligned} \tag{11}$$

where $\boldsymbol{M}$ denotes the unitary matrix, the superscript T represents the transpose of the matrix, and λ_1, $\lambda_2, \ldots, \lambda_n$ are the eigenvalues of the matrix $\boldsymbol{V}$.

Therefore, expression (8) can be rewritten as

$$\Psi(R, t+n\delta t) \approx \left[\prod_{k=0}^{n-1}U_{\mathrm{T}}^{1/2}(R, t+k\delta t)U_{\boldsymbol{V}}U_{\mathrm{T}}^{1/2}(R, t+k\delta t)\right]\Psi(R,t). \tag{12}$$

In this paper, the time internal $\delta t = 0.2$ fs is found to be suitable for the converged result.

Once the wave function $\Psi(R,t)$ is determined, the population in each electronic state can be written as

$$P_i(t) = \int \mathrm{d}R|\Psi_i(R,t)|^2 \quad i = \mathrm{A},\ \mathrm{E},\ \mathrm{I}{+}1,\ldots,\ \mathrm{I}+n. \tag{13}$$

And the photoelectron spectrum can be expressed as follows:

$$P(E) = \lim_{t\to\infty}\int \mathrm{d}R\sum_i |\Psi_{\mathrm{I}i,E}(R,t)|^2 \quad i = 1, 2, \ldots, n. \tag{14}$$

3. Results and discussion

In the present calculations, the wave packet in the vibrational ground state of $A^1\Sigma_u^+$, which is the metastable state of Li_2, is selected as an initial wave packet. And the values of parameters, i.e. intensity and FWHM of pump (806 nm) and the probe (806 nm) pulses are the same as those in the experiment of Lorenzo *et al.*[20] In Figs. 2 and 3, the simulated time-resolved photoelectron spectra are shown.

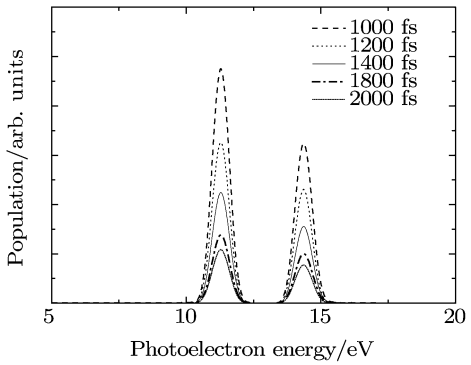


Fig. 2. Photoelectron spectra of Li_2 molecule obtained by theoretical calculation. The different values of delay time Δt, i.e. Δt = 1000, 1200, 1400, 1800, and 2000 fs are corresponding to different lines, separately. The pump (806 nm) and the probe (806 nm) pulses have Gaussian profiles of duration (FWHM) $\tau_1 = \tau_2 = 260$ fs.

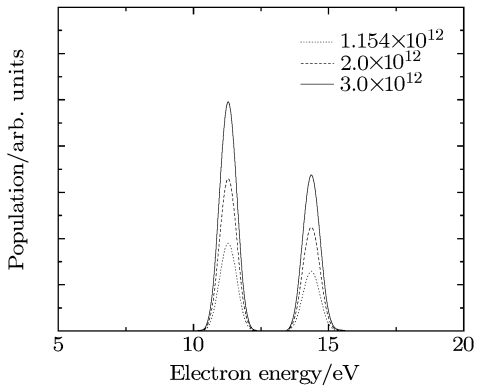


Fig. 3. Comparison of photoelectron spectrum of Li_2 molecule among different intensities of probe pulse.

Two characters of the spectra can be seen clearly in our result. First, from Fig. 2 we can find distinctly that each spectrum has two peaks. And the detailed explanation for the first character is presented in the following. As shown in Fig. 1, the probe pulse has sufficient energy to detach the $E^1\Sigma_g^+$ state of Li_2 molecule, and then forms the continuum state of Li_2^+ ion. The $X^2\Sigma_u^+$ is the fist excited state of Li_2^+ ion whose ground state is $X^2\Sigma_g^+$. And the two states correspond to the same asymptotic 2s limit just as show in Fig. 4 according to the data in Ref. [10]. Therefore, besides $X^2\Sigma_g^+$ state, the $X^2\Sigma_u^+$ state can also be permitted to transit from the $E^1\Sigma_g^+$ state by photodetachment. We also notice that compared with the potential energy curve of $X^2\Sigma_u^+$ state of Li_2^+ ion, the potential energy curve of $X^2\Sigma_g^+$ state is close to that of the $E^1\Sigma_g^+$ state of Li_2 molecule, i.e. the transition from the $E^1\Sigma_g^+$ state to the $X^2\Sigma_u^+$ state needs more energy than to the $X^2\Sigma_g^+$ state. Hence, we can draw the conclusion that the lower peaks corresponding to the higher electron kinetic energies in Figs. 2 and 3 are induced by the transition to the $X^2\Sigma_g^+$ state, while the higher peaks corresponding to the lower electron kinetic energies are induced by the transition to the $X^2\Sigma_u^+$ state.

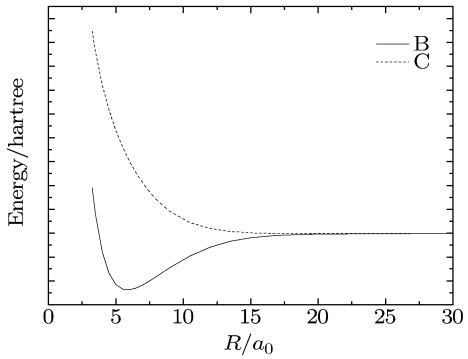


Fig. 4. Potential energy curves of $X^2\Sigma_g^+$ (solid line) and $X^2\Sigma_u^+$ (dash line) states of Li_2^+ ion according to the data in Ref. [10], which correspond to the same asymptotic 2s limit.

Secondly, it is seen obviously in Fig. 2 that the maximum of each peak decreases monotonically as pump-probe delay increases. With regard to the second character, time-resolved wave packet theory can be used to interpret the variety of spectra. At short delay time, the wave packet in the $E^1\Sigma_g^+$ state is mostly situated in short internuclear area. As delay time increases, the wave packet moves into the shelf state area of $E^1\Sigma_g^+$, where 'reflectron' and 'molecular cannon'[32] cases take place. The 'reflectron' is defined as the fact that wave packet reflects to bound region of potential energy surface, and 'molecular cannon' means that wave packet dissociates from weaker binding area.[33] As the movement of 'molecular cannon', part of the wave packet becomes a lost one. As a result, the rest part which still in the potential well will is weakened gradually with the increasing of delay time. In other words, the oscillating of the wave packet on the $E^1\Sigma_g^+$ curve is a decreasing process.

A comparison of TRPES of Li_2 molecule among different intensities of probe pulse is shown in Fig. 3. Different values of probe pulse intensity I, i.e. $I = 3.0 \times 10^{12}$, 2.0×10^{12} and 1.154×10^{12} W/cm^2 are corresponding to solid line, dash line and short dash line, respectively. In our calculation, the pump (806 nm) and probe (806 nm) pulses each have a Gaussian profile of duration $\tau_1 = \tau_2 = 260$ fs, and an intensity of pump pulse of 1.154×10^{12} W/cm^2 when delay time Δt is assumed to be 1000 fs, i.e. $\Delta t = 1000$ fs. From Fig. 3, We can see intuitionally that the variation of probe pulse intensity influences the amplitude of photoelectron's signal merely.

4. Conclusion

In this paper, the quantum mechanics method is employed to calculate the TRPES of the Li_2 molecule. We investigate the wave packet dynamical process of the $E^1\Sigma_g^+$ state by analysing intuitional images of the TRPES. The characters of PES with different parameters are explicated by using wave packet theory. According to our theoretical result, the losing of the wave packet in the shelf state area of $E^1\Sigma_g^+$ plays a prominent role in the process of photoionisation with the increase of delay time. The oscillation of wave packet on the $E^1\sum_g^+$ curve is found to be a decreasing process of energy. The results presented here are expected to provide a good testing ground for future theoretical investigations on the photoionisation spectra of alkali dimer.

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