Time-resolved photoelectron spectra of Br\textsubscript{2} molecule in intense laser field

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Received 15 November 2005; in final form 11 May 2007
Available online 24 May 2007

Abstract

The time-dependent-wave-packet method has been applied to calculate the photoelectron spectra of Br\textsubscript{2} molecule with zero time delay. Meanwhile, Br\textsuperscript{+} ion that mainly resulted from the dissociation of Br\textsubscript{2} (C\textsuperscript{1}P\textsubscript{u}) can be seen in the photoelectron spectra of Br\textsubscript{2} molecule. We presume that more Br atoms will be ionized later, as the dissociation is nearly complete. In addition, it is found that Br\textsuperscript{+} (X\textsuperscript{2}Σ\textsubscript{g}+) has the largest increasing rate as the increase of the laser intensities.

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1. Introduction

The study of molecules in intense laser fields has become a considerable activity area in recent years [1–7], and the multi-photon ionization spectra of different molecules have been studied extensively [8–15]. Nugent-Glandorf et al. have applied two-color photoionization dynamics to study the laser-excited Br\textsubscript{2} molecule [16]. They predict that UV-pump/soft X-ray probe photoelectron spectroscopy method is a powerful way to probe the dissociation dynamics of neutral molecules within ultra-fast time scale [17,18]. However, as a widely used theoretical model, time-dependent-wave-packet method can be used to simulate this novel pump-probe experiment. In addition, the transient state resulted from the ionization of the dissociative excited state wave packet can also be analyzed by the time-resolved photoelectron spectra. Here, we employ the time-dependent-wave-packet method to simulate the ionization process of Br\textsubscript{2} molecule.

\[ \text{Br}_2(X^1Σ_g^+) \xrightarrow{\text{pump}} \text{Br}_2^+(C^1Π_u) \rightarrow 2\text{Br} \rightarrow \text{Br}_2^+(X,A,B), \text{Br}^+, e^- \]

Firstly, the pump pulse induces a transition, and Br\textsubscript{2} molecule is ionized by the probe pulse shortly after it is prepared in a dissociating state C\textsuperscript{1}Π\textsubscript{u}, shown in Fig. 1. The five-state (ground, valence, three ionic states) model is employed to study this ionization and dissociation processes of Br\textsubscript{2} molecule.

2. Theoretical method

The Hamiltonian for the vibration motion of Br\textsubscript{2} molecule can be written as

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

where R is the inter-nuclear separation, and μ is the reduced mass of the molecule, thus the potential matrix \( V(R, t) \) can be written as

\[
\begin{pmatrix}
V_X & W_{XC} & 0 & \cdots & 0 \\
W_{CX} & V_C & 0 & \cdots & 0 \\
0 & 0 & V_1+E_{l,1} & 0 & \cdots & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots & \ddots \\
0 & 0 & \cdots & \cdots & 0 & \cdots \\
0 & 0 & \cdots & \cdots & \cdots & 0 \\
0 & 0 & \cdots & \cdots & \cdots & \cdots & 0 & V_1+E_{l,n}
\end{pmatrix}
\]

(2)
where $V_I$ refers to the potential energy of $X^2\Sigma^+_g$, $A^2\Pi_u$ or $B^2\Sigma^+_u$ state. The item $E_{I,n}$ ($n = 1, 2, \ldots, 90$) is the electron kinetic energies of the ionic state, and each of these continuous ionic states is detatched by 30 discrete states noted by $n$ going from 1 to 30, which leads to a total of 90 channels. The length of the radial grid about the nuclear motion is calculated by 30 a.u. with 0.01 a.u. spacing. So $V_I + E_{I,n}$ ($n = 1, 2, \ldots, 90$) denotes the potential energies of the discrete set of continuum states. Here X and C are used as the ground and valence state, respectively, and their interaction potential can be written as $W_{XC} = \mu_{XC} E(t)$, where $E(t) = E_0 \cos(\omega t) + E_0' \cos(\omega' t + \phi)$, $\phi$ denotes the phase, and the difference between $t$ and $t'$ is the delay-time. In the the item $E(t)$, $E_0 = 5.338 \times 10^{-9} \sqrt{I}$, $E_0' = 5.338 \times 10^{-9} \sqrt{I'} \exp(-(t'-t_0)^2/2\sigma^2)$, and $f(t) = \exp(-(t-t_0)^2/2\sigma^2)$ is the pulse envelope function, $I$ and $I'$ denote the laser intensities with the unit of W/cm², $t_0$ is the central value of the pulse, $\omega$ and $\omega'$ are the central frequencies, $\sigma$ and $\sigma'$ are relevant to the laser full width at half maximum. Because the interaction between the ionic and the excited states indirectly got by the method of the previous works [19-22] cannot affect our results we have neglected it in our theoretical model. The time-dependent Schrödinger equation is solved by ‘split-operator-Fourier’ method.

$$\psi(t + \delta t, R) = \exp\left(-\frac{iH_1}{2\hbar} \delta t\right) \psi(t, R) \times \exp\left(-\frac{iH_2}{\hbar} \delta t\right) + O(\delta t^2)$$

where

$$H_1 = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2}$$

$$H_2 = V(R, t)$$

The time-dependent wave function is advanced using the second-order split-operator scheme, and the time interval $\Delta t = 0.2$ fs is found to be suitable for the converged results in this five-state model. The exponentiation $\exp\left(-\frac{i\hbar}{2\mu} \delta t\right) \psi(t, R)$ is performed by the spectra method, which utilizes the fast Fourier transformation (FFT) [23–31].

$$\exp\left(\frac{i\hbar}{4\mu} \frac{\partial^2}{\partial R^2}\right) \psi(t, R) = F^{-1} \exp\left(\frac{i\hbar}{4\mu} \frac{\partial^2}{\partial R^2}\right) F \psi(t, R)$$

where

$$F[f] = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \exp(ikR) f(R) dR$$

As is known, $H_1$ and $H_2$ can be diagonalized in momentum and coordinate space, respectively. The wave function is transformed into momentum or coordinate space during the process of our calculation. The parameters such as the laser intensities, the pulse duration, etc. used in our calculation are the same as those of the experiment [17,18].

As is known, the number and energies of photons absorbed can be easily got, and the intensity of the corresponding binding energy subtracted from the photoelectron kinetic energy is proportional to the total probability of the wave function. Thus, the photoelectron spectrum is calculated directly from the norm of the nuclear wave packets $\psi(t, R)$ ($t = t_1$).

$$P(\epsilon) = \int dR \psi^*(t_1, R) \psi(t_1, R)$$

where $\epsilon$ denotes the electron kinetic energies.

### 3. Results and discussion

Fig. 2 shows the photoelectron spectra of Br₂ molecule, in which the valence level can be seen clearly. Firstly, the Br₂ molecule is promoted to the excited state, and then ionized instantaneuosly with zero time delay, which results in the occurrence of three peaks marked by the resulting ionic states $X^2\Sigma^+_g$, $A^2\Pi_u$ and $B^2\Sigma^+_u$ with the binding energies...
higher than 10 eV. These peaks should be attributed to the removal of the \(3\sigma_u\), \(1\pi_u\) and \(2\sigma_u\) electrons, respectively, and the first peak with the position about 8.6 eV shows the photoelectron feature of the dissociated state \(C^1H_u\), which confirms the prediction of Nugent-Glandorf et al.’s experiment [17,18]. On the other hand, \(Br_2\) molecule is ionized from the flatter part of the dissociative curve, in the case at about 3 Å. Compared with the initial equilibrium bond distance about 2.2 Å, this elongated bond distance is included in the regime that atomic behavior is to be considered. In Fig. 3, it is shown that the calculated atomic-like peaks occur with the constant binding energy about 11.85 eV, which indicate that these peaks should arise from the dissociated state \(C^1H_u\) that also rises and decays on the nearly constant binding energy, and these decays that resulted from the ac Stark shift will lead to smearing out of valence-state resonances into the background no matter how complicated the behavior of the valence state has become. Meanwhile, it is seen that the signal counts of \(Br^+\) increase with the longer delay time, and the peaks become narrower at latter time delays than those of early ones. So we presume that the \(Br^+\) ion peaks should result from the third and fourth processes of the whole ionization processes [17,18], i.e., more \(Br\) atoms will be ionized later as the dissociation is nearly complete.

The signals of the transient state changing with the time delays from \(-33\) fs to \(+165\) fs in steps of 33 fs are shown in Fig. 4. We find that the transient signal is slightly delayed in time, which agrees with the experimental results [17,18]. As is known, \(Br_2\) molecule will be ionized sooner after it has moved out on the dissociative curve, which makes the energy deposited into the kinetic energy of the \(Br\) atoms. So, it can be predicted that the \(Br^+\) atom signals should occur within the short time scale (about 10–20 fs), which is in agreement with the presumption that some signals due to atoms should appear at very early time delays [17]. However, the atomic signals will keep almost unchanged until longer time delays when the dissociation is nearly complete, where more \(Br\) atom will be ionized.

During the simulation of the ground absorption process, we find that the populations of the ionic states are relevant to the laser intensities, shown in Fig. 5. It is identified that different ion states shows different populations of the total wave function for a given laser intensity, e.g., the population of the \(X^2\Sigma^+\) state is about five times that of \(B^2\Sigma^+\) state when \(5.0 \times 10^{14}\) W/cm\(^2\) laser intensity is used. Although all the populations of the three different states \(X^2\Sigma^+\), \(A^2\Pi_u\) and \(B^2\Sigma^+\) increase with the adding of the laser intensities from \(5.0 \times 10^{14}\) to \(9.0 \times 10^{14}\) W/cm\(^2\), \(Br^+_2 (X^2\Sigma^+)\) state has the largest increasing rate. So it can be concluded that
the photoelectron spectra of Br₂ molecule are dominated by Br₂⁺ (X2Σ⁺g) state with the increase of the laser intensities.

4. Conclusions

In summary, the photoelectron spectra of Br₂ molecule have been calculated with the time-dependent-wave-packet method. We find that the peak of the transient state is slightly delayed in time, which indicates that after the Br₂ wave packet has moved out of the dissociative curve, it will be ionized as soon as possible, but more Br atoms will be ionized at later time delays. In addition, the populations of the three different ionic states are shown to change with the laser intensities. So, the vibrational motion of the nuclei and the dissociation of the Br₂ molecule are shown definitely.

References