S-matrix study on alignment dependence of single ionization of molecular ions with different active orbitals*

Li Yan(李 燕)[a], Jia Xin-Yan(贾欣燕)[b]†, Yang Shi-Ping(杨世平)[a]‡, Li Wei-Dong(李卫东)[c], and Chen Jing(陈 京)[b,d]

[a] *Department of Physics, Hebei Normal University, Shijiazhuang* 050016, *China*
[b] *Institute of Applied Physics and Computational Mathematics, P. O. Box* 8009, *Beijing* 100088, *China*
[c] *Institute of Theoretical Physics and Department of Physics, Shanxi University, Taiyuan* 030006, *China*
[d] *Center for Applied Physics and Technology, Peking University, Beijing* 100871, *China*

(Received 15 January 2010; revised manuscript received 23 February 2010)

The orientation-dependent single ionization rate of the diatomic molecular ion H_2^+ with different active orbitals in an intense field is studied by using S-matrix theory. Our results show that the orientation-dependent single ionization probability of H_2^+ is greatly dependent on the symmetry and the electron density distribution of its initial states, and it can be used to identify the excited state of the molecular ion in the dissociation process.

Keywords: alignment molecule, ionization probability, molecular orbits

PACC: 3380E, 3450H

1. Introduction

The interactions between atoms and molecules and high-intensity ultrashort laser pulses have been attracting much attention during recent years.[1−18] However, since a molecule has more degrees of freedom than an atom, it becomes more complicated to investigate both experimentally and theoretically. Molecular intrinsic characters are responsible for their interesting phenomena,[19−23] but they are far from being well understood in theory. It is well known that the ionization of the molecule is strongly dependent on the symmetry of the initial electronic state and the alignment of the molecule,[24−29] and the *ab initio* numerical treatment of molecular ionization is much more demanding than that of the atomic case. Therefore, the strong field approximation (SFA) theory or the tunnelling model is even more desirable in the molecular case.

Molecular H_2 (D_2^+), as the simplest diatomic representation of a molecule, is thought of as a key to understanding molecular dynamics and has been studied intensively in recent years.[30] Molecular H_2 can be ionized in a laser field to produce H_2^+. In the rescattering mechanism, the first photoelectron driven back by the field when its direction reverses excites the H_2^+ ion to an excited electronic state and then the ion can be dissociated or further ionized by the laser field.[31−34] The identification of the state, which determines the sequent ionization and dissociation process, plays a key role in understanding the problem. The theoretical simulation of the process is still a challenge so far.

In this paper, the S-matrix method[35] is used to investigate the single ionization process of the H_2^+ molecular ion with different active orbitals. Through studying the alignment-dependent single ionization rate of H_2^+, one can deduce which excited state the ion is in and achieve some insights into the effect of molecular active orbitals on the ionization process and/or the dissociation process. Our results show that the alignment-dependent single ionization probability of the molecular ion H_2^+ is sensitive to the electron density distribution of the active orbital, which may pro-

*Project supported by the National Natural Science Foundation of China (Grant No. 10674087), the National Basic Research Program of China (Grant No. 2006CB806000), the Hebei Provincial Natural Science Foundation (Grant No. A2008000136), the Project of National Center for Educational Techonology of the Ministry of Education of China (Grant NCET-08-0883), and the Program of TYAl of Shanxi Province and China Academy of Engineering Physics Foundation (Grant No. 2008B0102007).

†Corresponding author. E-mail: xyjia@live.cn
‡E-mail: yangshipingok@163.com

© 2010 Chinese Physical Society and IOP Publishing Ltd

vide a new way to detect the inner character of the molecular ion. With the alignment-dependence of the single ionization rate of H_2^+, one can deduce the electronic orbital distribution of the molecular ion in the dissociation process, which can provide important information about the molecular dynamics in an intense laser field.

2. Model

Using the S-matrix theory,[35,36] the single ionization rate of a molecule or a molecular ion in a linearly polarized laser field with vector potential $\boldsymbol{A}(t) = A_0\boldsymbol{\varepsilon}\cos\omega t$ is given by

$$W = 2\pi N_e \sum_{n=n_0}^{\infty} \int |T_{\boldsymbol{p}n}|^2 \delta(E_p + I_p - n\omega)\mathrm{d}\boldsymbol{p}_n, \quad (1)$$

where N_e is the number of equivalent electrons in the highest occupied molecular orbital (HOMO), and $T_{\boldsymbol{p}n}$ denotes the amplitude of the n-photon process

$$T_{\boldsymbol{p}n} = \frac{1}{T}\int_0^T \Psi_p^*(\boldsymbol{r},t)V_F(t)\,\Psi_0(\boldsymbol{r},\boldsymbol{R},t)\mathrm{d}\boldsymbol{r}\mathrm{d}t. \quad (2)$$

Here $\Psi_0(\boldsymbol{r},\boldsymbol{R},t) = \mathrm{e}^{\mathrm{i}\,I_p t}\Phi_0(\boldsymbol{r},\boldsymbol{R})$ is the wavefunction of the initial electron state, with $\Phi_0(\boldsymbol{r},\boldsymbol{R})$ being the wavefunction of the molecular valence orbital, and $I_p \equiv \kappa^2/2$ the ionization energy of the molecule; $V_F(t)$ is the interaction of the molecule with the laser field

$$V_F(t) = \boldsymbol{r}\cdot\boldsymbol{E}(t), \quad (3)$$

in the length gauge, $\boldsymbol{E}(t) = -\partial\boldsymbol{A}(t)/\partial t = E_0\boldsymbol{\varepsilon}\sin\omega t = A_0\omega\boldsymbol{\varepsilon}\sin\omega t$. The final state is given by the Volkov wavefunction

$$\Psi_p(\boldsymbol{r},t) = \exp\left[\mathrm{i}(\boldsymbol{p}+\boldsymbol{A}(t))\cdot\boldsymbol{r} - \frac{\mathrm{i}}{2}\int^t(\boldsymbol{p}+\boldsymbol{A}(t))^2\mathrm{d}t'\right] \quad (4)$$

with quasienergy $E_p = p_n^2/2 + U_p$, where $p_n^2/2 = n\omega - U_p - I_p$ represents the kinetic energy of the emitted electron on absorbing n photons. The minimum number of photons needed is $n_0 = [(U_p+I_p)/\omega]_\mathrm{int}+1$, where $[x]_\mathrm{int}$ denotes an integer part of variable x and $U_p = E_0^2/(4\omega^2)$ is the ponderomotive energy. The SFA is adopted, in which it is assumed that the initial bound state of the molecular or ion is unaffected by the laser field while the final state dose not feel the presence of the binding potential. Using Eqs. (3) and (4), amplitude (2) can be transformed into

$$T_{\boldsymbol{p}n} = \frac{1}{T}\int_0^T \mathrm{d}t\exp\left[\mathrm{i}\left(\frac{p^2}{2}+I_p+U_p\right)t\right]E_0\sin\omega t \times\exp\left[\mathrm{i}\left(\frac{E_0^2}{8\omega^3}\sin 2\omega t + \frac{E_0}{\omega^2}\boldsymbol{\varepsilon}\cdot\boldsymbol{p}\sin\omega t\right)\right] \times\widetilde{\Phi}_0(\boldsymbol{p}+\boldsymbol{A}(t)) \quad (5)$$

with

$$\widetilde{\Phi}_0(\boldsymbol{M}) = \int \exp[-\mathrm{i}\,\boldsymbol{M}\cdot\boldsymbol{r}](\boldsymbol{\varepsilon}\cdot\boldsymbol{r})\,\Phi_0(\boldsymbol{r},\boldsymbol{R})\mathrm{d}\boldsymbol{r}, \quad (6)$$

where $\boldsymbol{M} \equiv \boldsymbol{p} + \boldsymbol{A}(t)$.

For homonuclear diatomic molecules H_2, we assume that the internuclear axis is along the z axis, and the linear polarization laser field is in the y–z plane. According to the linear combination of atomic orbitals and molecular orbitals (LCAO-MO) approximation,[37−40] the two-centred single-electron molecular wavefunction of $1s\sigma_g$, $1s\sigma_u$, $2p\pi_u$ and $2p\pi_g$ can be combined as an appropriate superposition of scaled hydrogen $1s$ and $2p$ atomic orbitals as follows:

$$\Phi_{1s}^{\sigma_g}(\boldsymbol{r},\boldsymbol{R}) = \frac{[\phi_{1s}^{\sigma_g}(\boldsymbol{r}-\boldsymbol{R}/2)+\phi_{1s}^{\sigma_g}(\boldsymbol{r}+\boldsymbol{R}/2)]}{\sqrt{2[1+S_{1s}^{\sigma_g}(R)]}}, \quad (7)$$

$$\Phi_{1s}^{\sigma_u}(\boldsymbol{r},\boldsymbol{R}) = \frac{[\phi_{1s}^{\sigma_u}(\boldsymbol{r}-\boldsymbol{R}/2)-\phi_{1s}^{\sigma_u}(\boldsymbol{r}+\boldsymbol{R}/2)]}{\sqrt{2[1-S_{1s}^{\sigma_u}(R)]}}, \quad (8)$$

$$\Phi_{2p}^{\pi_u}(\boldsymbol{r},\boldsymbol{R}) = \frac{[\phi_{2p}^{\pi_u}(\boldsymbol{r}-\boldsymbol{R}/2)+\phi_{2p}^{\pi_u}(\boldsymbol{r}+\boldsymbol{R}/2)]}{\sqrt{2[1+S_{2p}^{\pi_u}(R)]}}, \quad (9)$$

$$\Phi_{2p}^{\pi_g}(\boldsymbol{r},\boldsymbol{R}) = \frac{[\phi_{2p}^{\pi_g}(\boldsymbol{r}-\boldsymbol{R}/2)-\phi_{2p}^{\pi_g}(\boldsymbol{r}+\boldsymbol{R}/2)]}{\sqrt{2[1-S_{2p}^{\pi_g}(R)]}}, \quad (10)$$

whereas

$$S_j^{(n)}(R) = \int \mathrm{d}\boldsymbol{r}\phi_j^{(n)}(\boldsymbol{r}+\boldsymbol{R}/2)\phi_j^{(n)}(\boldsymbol{r}-\boldsymbol{R}/2) \quad (11)$$

denotes the atomic orbital overlap integral. The wavefunctions of the atomic orbitals are given as:

$$\phi_{1s}(\boldsymbol{r}) = \frac{1}{\sqrt{\pi}}\kappa^{3/2}\exp(-\kappa\boldsymbol{r}), \quad (12)$$

$$\phi_{2px}(\boldsymbol{r}) = \kappa^{5/2}\frac{\boldsymbol{r}}{\sqrt{\pi}}\exp(-\kappa\boldsymbol{r})\sin\theta\cos\varphi, \quad (13)$$

where θ and φ are the polar angle and the azimuthal angle with respect to the molecular axis. Taking the molecular wavefunction of $1s\sigma_g$ Eq. (7) for example, we have

$$\widetilde{\Phi}_0(\boldsymbol{M}) = \frac{2\cos(\boldsymbol{M}\cdot\boldsymbol{R}/2)\int \exp(-\mathrm{i}\,\boldsymbol{M}\cdot\boldsymbol{r})(\boldsymbol{\varepsilon}\cdot\boldsymbol{r})\Phi_{1s}(\boldsymbol{r})\mathrm{d}\boldsymbol{r} - 2\,\mathrm{i}\sin(\boldsymbol{M}\cdot\boldsymbol{R}/2)(\boldsymbol{\varepsilon}\cdot\boldsymbol{R}/2)\int \exp(-\mathrm{i}\,\boldsymbol{M}\cdot\boldsymbol{r})\Phi_{1s}(\boldsymbol{r})\mathrm{d}\boldsymbol{r}}{\sqrt{2[1+S_{1s}^{\sigma_g}(R)]}}. \quad (14)$$

Similarly, the single ionization rate for the homonuclear diatomic molecular ion H_2^+ in an intense field can also be correctly calculated by Eq. (1) with corresponding parameters.

3. Results and discussion

Figure 1 shows the plots for the tunnelling ionization rate of parallel-aligned H_2 molecules, calculated by the S-matrix theory, as a function of electric field strength at a wavelength of 800 nm, internuclear separation $R = 2.0$ a.u. (atomic units) and ionization potential $I_p = 0.5684$ a.u. This indicates that our results are in good agreement with the numerical result presented by Saenz in Ref. [41]. The deviations possibly come from the simplified LCAO-MO approximation and the SFA[42] adopted in our S-matrix theory, which neglects the atomic binding potential in the propagation of the electron in the continuum and the laser field when the electron is in the bound state.

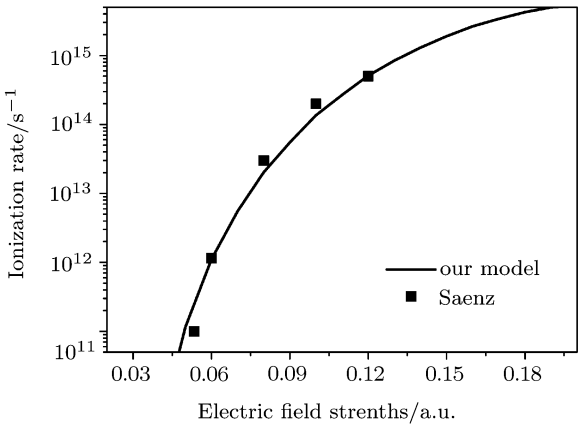


Fig. 1. Comparison of the single ionization rate of H_2 given by IMST and the result of Sanenz.

Applying Eq. (1) to molecular ion H_2^+, the alignment dependences of single ionization probabilities of H_2^+ from initial states $1s\sigma_g$, $1s\sigma_u$, $2p\pi_u$ and $2p\pi_g$ with different symmetries are investigated. Figure 2 shows the plots for the polar coordinate representation of single ionization rates of molecular ion H_2^+ with different active valence orbitals versus the molecular alignment angle θ with respect to the laser field polarization direction. Figures 2(a) and 2(b) show the plots for the ionization probabilities of H_2^+ for bonding $1s\sigma_g$ and anti-bonding $1s\sigma_u$ orbits, respectively while figures 2(c) and 2(d) show those for bonding $2p\pi_u$ and anti-bonding $2p\pi_g$ orbits, respectively. The internuclear separation is $R = 2$ a.u., and the corresponding electronic binding energies of these states are $E_{1s\sigma_g} = -1.1026$ a.u., $E_{1s\sigma_u} = -0.6675$ a.u., $E_{2p\pi_u} = -0.4288$ a.u., and $E_{2p\pi_g} = -0.2267$ a.u. In order to make a convenient comparison, we have normalizated the maximum ionization probability to one. Figure 2(a) shows that the ionization probability has a maximum for the parallel alignment and a minimum for the perpendicular one with the $1s\sigma_g$ orbital. It decreases monotonically with the increase of alignment angle θ due to the fact that the electron tunnelling between potential wells is maximum for the parallel alignment. Figure 2(b) shows that the single ionization rate of H_2^+ with initial state $1s\sigma_u$ at $I = 1\times10^{14}$ W/cm^2 has a maximum probability for the parallel alignment and a minimum for the perpendicular alignment, i.e., the tunnelling is significantly suppressed for perpendicular alignment molecules with $1s\sigma_u$ orbital. Figure 2(c) shows a sharp minimum for the parallel alignment H_2^+ at $I = 1\times10^{13}$ W/cm^2 and it is shown in Fig.2(d) that the ionization probability of H_2^+ at $I = 1\times10^{12}$ W/cm^2 reaches its maximum at about 45°.

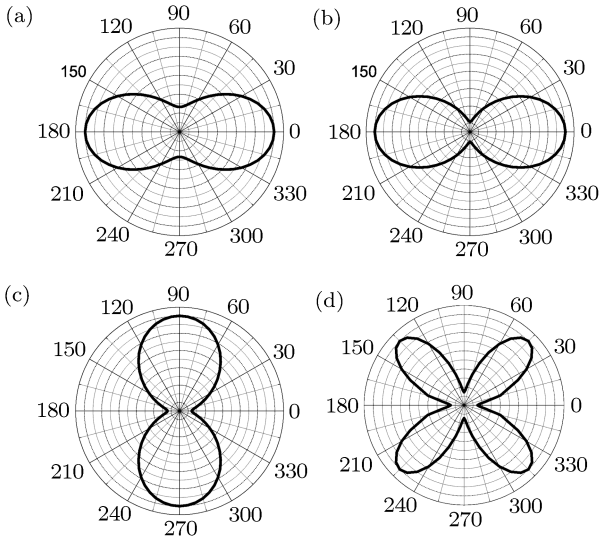


Fig. 2. Single ionization probabilities of H_2^+ with different active orbitals vesus the alignment angle θ. For (a) $1s\sigma_g$ orbital, $I = 5\times10^{14}$ W/cm^2 and $\omega = 0.057$ a.u.; for (b) $1s\sigma_u$ orbital, $I = 1\times10^{14}$ W/cm^2 and $\omega = 0.057$ a.u.; for (c) $2p\pi_u$ orbital, $I = 1\times10^{13}$ W/cm^2 and $\omega = 0.043$ a.u.; for (d) $2p\pi_g$ orbital, $I = 1\times10^{12}$ W/cm^2 and $\omega = 0.012$ a.u.

The wavefunctions of different initial states of the molecular ion H_2^+ corresponding to Figs. 2(a)–2(d) are plotted in Fig. 3, in which the nuclei of H_2^+ are located along the z axis at $z = \pm 1$. Further analysis of Fig. 2 indicates that the ionization probability may be assumed to be a function of the image of the contour of the electron distribution of the active molecular orbital. The $1s\sigma_g$ and the $1s\sigma_u$ electronic orbitals are quite similar in a sense that the electron clouds concentrate along the internuclear axis. Also, the $1s\sigma_u$ state shows a more strongly suppressed ionization probability than the $1s\sigma_g$ state for the perpendicular alignment, because there exists a nodal plane perpendicular to the molecular axis. It corresponds to a minimum of the electron cloud density along the laser field for the perpendicular alignment H_2^+ as shown in Fig. 3(b). Moreover, for anti-bonding of the $2p\pi_u$ orbital, the ionization probability tends to maximize when the laser polarization is perpendicular to the molecule's axis, consistent with its maximal electron cloud location (Fig. 3(c)). The ionization rate of the molecular ion in the $2p\pi_g$ orbital in Fig. 2(d) indicates that the alignment-dependent single ionization probability of H_2^+ is greatly dependent on the electron density distribution of the active molecular orbital (Fig. 3(d)). In general, the stronger the electron cloud distribution along the field polarization direction is, the larger the ionization rate will be. Comparing the alignment-dependent single ionization rates of H_2^+ with the structure of the molecular orbitals, we can deduce that the distribution of the active orbital of the molecular ion is closely related to the ionization rate.

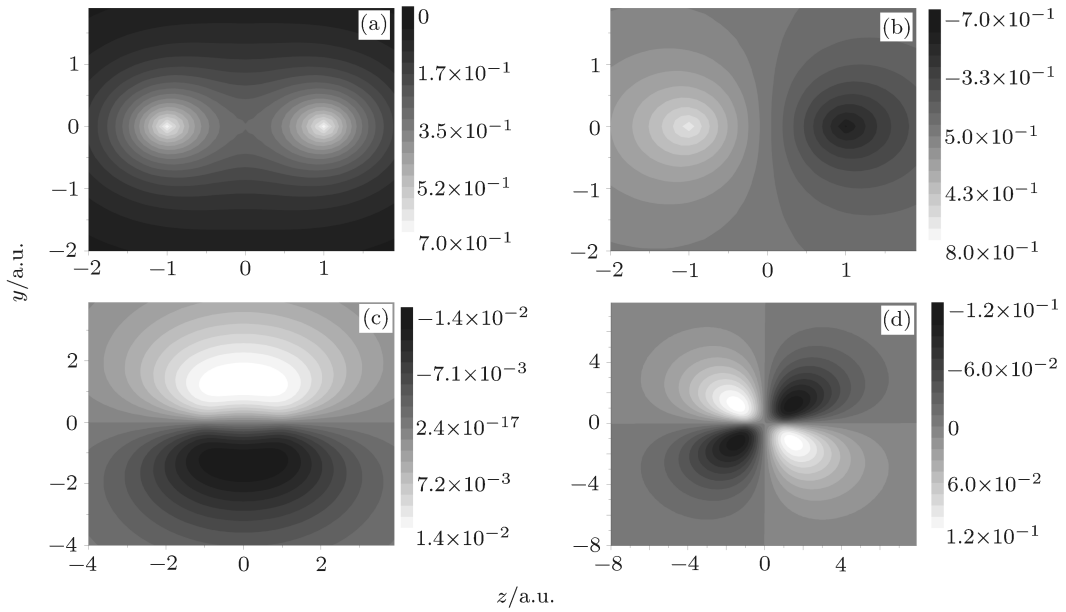


Fig. 3. Contour plot, in the (y, z)-plane, of the electronic wavefunction $\Psi(y, z)$ of H_2^+, with parameters being the same as those in Fig. 2.

Recently, experimental probes of molecular dynamics have entered the attosecond time scale. In the so-called "molecular clock" experiments, the nuclear dynamics of H_2^+ (D_2^+) after the first electron has been ionized away by the external field is studied because of the fast speed of its nuclear vibrational wave packet, and all excited states of H_2^+ (D_2^+) will be directly dissociated.[31−34] To identify the channel of interest, one must recognize which dissociation channel the protons come from. According to our calculation, measuring the orientation-dependent single ionization probability of the molecular ion can provide important information about identifying which excited state the ion stays in after the excitation. Moreover, it is noteworthy that the current calculation can also be extended to the cases of more complicated molecules like N_2, O_2 and even polyatomic molecules provided that the wavefunctions of their electronic states are given.

4. Conclusion

The alignment-dependent single ionization probabilities of diatomic molecular ions H_2^+ from different initial states $1s\sigma_g, 1s\sigma_u$, $2p\pi_u$ and $2p\pi_g$ in a linearly polarized laser field are investigated by S-matrix theory. Our results show that the alignment-dependent single ionization rates for different active orbitals are different, and they are greatly dependent on the symmetry and the electron density distribution of the active molecular orbital. Therefore, one can deduce the distribution of electron cloud density of the initial state of molecular ions, namely the excited state while the ion is dissociated, from the alignment-dependent single ionization probability, which can provide important information about the molecular dynamics in an intense laser field.

References

[1] Fittinghoff D N, Bolton P R, Chang B and Kulander K C 1992 *Phys. Rev. Lett.* **69** 2642
[2] Corkum P B 1993 *Phys. Rev. Lett.* **71** 1994
[3] Walker B, Sheehy B, DiMauro L F, Agostini P, Schafer K J and Kulander K C 1994 *Phys. Rev. Lett.* **73** 1227
[4] Becker A and Faisal F H M 1996 *J. Phys.* B **29** L197
[5] Hu B, Liu J and Chen S G 1997 *Phys. Lett.* A **236** 533
[6] Becker A and Faisal F H M 1999 *J. Phys.* B **32** L335
[7] Chen J, Liu J, Fu L B and Zheng W M 2000 *Phys. Rev.* A **63** 011404(R)
[8] Fu L B, Liu J, Chen J and Chen S G 2001 *Phys. Rev.* A **63** 043416
[9] Fu L B, Liu J and Chen S G 2002 *Phys. Rev.* A **65** 021406
[10] Chen J and Nam C H 2002 *Phys. Rev.* A **66** 053415
[11] Zhang S M 2004 *Chin. Phys.* **13** 481
[12] Gong Y B, Ma X G, Wang M S and Yang C L 2009 *Chin. Phys.* B **18** 5296
[13] Ma X G, Gong Y B and Qu Z J 2009 *Chin. Phys.* B **18** 1451
[14] Ma X G and Sun W G 2005 *Chin. Phys.* **14** 1792
[15] Jia X F, Li X W, Miao X Y, Shi W Q, Sun S Y, Xie Y and Zhang J F 2009 *Chin. Phys.* B **18** 2744
[16] Yang H, Gao K, Wu X J and Zhang S M 2008 *Acta Phys. Sin.* **57** 1640 (in Chinese)
[17] Gao K, Sun R, Wu X J, Yang H, Zhang S M and Zhou J 2007 *Acta Phys. Sin.* **56** 6378 (in Chinese)
[18] Gao K, Yang H and Zhang S M 2007 *Acta Phys. Sin.* **56** 5202 (in Chinese)
[19] Liu J, Ye D F, Chen J and Liu X 2007 *Phys. Rev. Lett.* **99** 013003
[20] Ye D F, Chen J and Liu J 2008 *Phys. Rev.* A **77** 013403
[21] Jia X Y, Li W D, Fan J, Liu J and Chen J 2008 *Phys. Rev.* A **77** 063407
[22] Li Y, Chen J, Yang S P and Liu J 2007 *Chin. Phys. Lett.* **24** 5
[23] Yang S P, Li Y, Jia X Y and Chen J 2010 *Chin. Phys.* B **19** 043303
[24] Litvinyuk I V, Lee K F, Dooley P W, Rayner D M, Villeneuve D M and Corkum P B 2003 *Phys. Rev. Lett.* **90** 233003
[25] Zeidler D, Staudte A, Bardon A B, Villeneuve D M, Dorner R and Corkum P B 2005 *Phys. Rev. Lett.* **95** 203003
[26] Li Y, Chen J, Yang S P and Liu J 2007 *Phys. Rev.* A **76** 023401
[27] Talebpour A, Larochelle S and Chin S L 1998 *J. Phys.* B **31** L49
[28] DeWitt M J, Prall B S and Levis R J 2000 *J. Chem. Phys.* **113** 1553
[29] Tong X M, Zhao Z X and Lin C D 2002 *Phys. Rev.* A **66** 033402
[30] Wang P Q, Sayler A M, Carnes K D, Xia J F, Smith M A, Esry B D and Ben-Itzhak I 2006 *Phys. Rev.* A **74** 043411
[31] Niikura H, Légaré F, Hasbani R, Bandrauk A D, Ivanov M Y, Villeneuve D and Corkum P B 2002 *Nature* **417** 917
[32] Niikura H, Légaré F, Hasbani R, Bandrauk A D, Ivanov M Y, Villeneuve D and Corkum P B 2003 *Nature* **421** 826
[33] Tong X M, Zhao Z X and Lin C D 2003 *Phys. Rev.* A **68** 043412
[34] Chen J, Fan J, Li Y and Yang S P 2007 *Phys. Rev.* A **76** 013418
[35] Muth-Böhm J, Becker A and Faisal F H M 2000 *Phys. Rev. Lett.* **85** 2280
[36] Gribakin G F and Kuchiev M Y 1997 *Phys. Rev.* A **55** 3760
[37] Usachenko V I and Chu S I 2005 *Phys. Rev.* A **71** 063410
[38] Kjeldsen T M and Madsen L B 2006 *Phys. Rev.* A **73** 047401
[39] Usachenko V I 2006 *Phys. Rev.* A **73** 047402
[40] Kamta G L and Bandrauk A D 2006 *Phys. Rev.* A **74** 033415
[41] Saenz A 2000 *Phys. Rev.* A **61** 051402R
[42] Faria C Figueira de Morisson and Lewenstein M 2005 *J. Phys.* B **38** 3251