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Cluster-assisted generation of multi-charged ions in nanosecond laser ionization of pulsed hydrogen sulfide beam at 1064 and 532 nm*

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The multi-charged sulfur ions of S^{q+} ($q \leq 6$) have been generated when hydrogen sulfide cluster beams are irradiated by a nanosecond laser of 1064 and 532 nm with an intensity of $10^{10} \sim 10^{12}$W·cm^{-2}. S^{6+} is the dominant multi-charged species at 1064 nm, while S^{4+}, S^{3+} and S^{2+} ions are the main multi-charged species at 532 nm. A three-step model (i.e., multiphoton ionization triggering, inverse bremsstrahlung heating, electron collision ionizing) is proposed to explain the generation of these multi-charged ions at the laser intensity stated above. The high ionization level of the clusters and the increasing charge state of the ion products with increasing laser wavelength are supposed mainly due to the rate-limiting step, i.e., electron heating by absorption energy from the laser field via inverse bremsstrahlung, which is proportional to λ^2, λ being the laser wavelength.

Keywords: cluster, multi-charged ion, inverse bremsstrahlung absorption, electron impact ionization
PACC: 3280

1. Introduction

Coulomb explosion (CE) of molecule clusters, e.g. benzene, ammonia, methyl iodide, etc, induced by nanosecond laser field with intensity as low as 10^9–10^{12}W·cm^{-2} has been reported recently.[1−4] Multiply charged atomic ions of C^{q+} ($q \leq 4$), N^{q+} ($q \leq 5$) and H^+ with kinetic energy of several tens to over a thousand of eV released from the Coulomb potential of the multi-charged clusters have been detected. An interesting result is that these multi-charged ions show apparent dependence on the laser wavelength, i.e. the charge states and the ratio of the multiply charged ions to the total ion yields increase with increasing wavelength.[3,4] Conventionally, femto- and picosecond lasers with an intensity of 10^{13}–10^{18}W·cm^{-2} are used to induce CE processes and produce the highly charged atomic ions.[5−12] Some theoretical and computational models have been proposed to explain these laser–matter interaction processes.[12−17] Despite the differences among these models, the foundation is the field-ionization, as the electric field strength at an intensity of 10^{14}W·cm^{-2} is strong enough to strip off at least one of the valence electrons directly from the atoms or molecules. But all these models can hardly be used to explain the multi-charged atomic ions produced at a laser intensity of 10^9–10^{12}W·cm^{-2} used in our experiments. A preliminary interpretation has been made to account for the generation of these highly charged ions and their wavelength dependence. The multielectron ionization of the molecules is attributed to the electron impact ionization when the initial multiphoton ionized electrons are caged in the cluster and heated by the laser field through inverse bremsstrahlung (IB) to sufficiently high energies. More different cluster systems need to be studied to enhance our comprehension of the processes. Here we choose hydrogen sulfide to study the production of highly charged atomic ions from CE under the present laser intensity and its wavelength dependence.

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2. Experiment

The experimental setup has been presented previously.[1−4,18,19] Stated briefly, neat hydrogen sulfide gas at 0.1–0.4 MPa was introduced into the source chamber of a Wiley–McLaren type time-of-flight mass spectrometer (TOFMS) by a pulsed valve (General Valve Series 9, ϕ 0.5 mm), to the ionization chamber through a skimmer (ϕ3 mm). The pressure in the ionization chamber was varied from 2×10^{-4} Pa to 1×10^{-3} Pa depending on the valve opening duration and the pressure of the carrier gas. The fundamental 1064 nm and its harmonic 532 nm output from commercial Nd:YAG lasers (New Wave Tempest ∼100mJ@ 532 nm/5ns or Spectron SL800 ∼200 mJ @ 532 nm/25 ns) were focused by a quartz lens (f ∼ 75 mm) to provide an intensity of 10^{10}–10^{12}W/cm^2. The distance of valve to the focal point was 110mm. The ions produced were first accelerated by the extraction electric field, and then detected by a dual microchannel plates (MCP, ϕ 35 mm) after 500 mm field-free drift. The voltage on the extraction plate was 1850 V. The ion signals were recorded by a digital A/D card (2G, Gage82G) by averaging over 200 laser shots.

3. Results and analysis

3.1. Laser ionization of hydrogen sulfide at 1064 nm

The time of flight (TOF) mass spectra of hydrogen sulfide beam ionized by 1064 nm laser at an intensity of 3×10^{12}W·cm^{-2} at different laser shot delays to the pulse valve opening are shown in Fig.1. The duration of laser pulse is about 5 ns. The electric field strength in the extraction region is 185 V/cm (the space focus condition of the TOFMS). The delays are (a) 270, (b) 320, (c) 620, (d) 1220, and (e) 1520μs. The spectra of Figs.1(a) and 1(e) contain only those from mono-charged ions of H^+ and H_xS^+ (with some background ions of OH_x^+ and CH_x^+), which are typical multiphoton ionization (MPI) products. The peak profile of H_xS^+ is not of Gauss distribution, which is probably due to the overlap of S^+, HS^+, and H_2S^+ and the space charge effect caused by the Coulomb repelling among neighbouring ions in and/or between clusters. As the duration of delay are set at 320, 620, and 1220 μs, there appear some multi-charged ions of $S^{q+}(q = 2, 3, 6)$. The peaks of S^{6+} and H^+ ions split into two parts labelled as S_f^{6+}, S_b^{6+}, H_f^+, and H_b^+, representing the ions flying to and away from the detector. As is known, the densities of the clusters and molecules are different at the different parts of the pulsed beam. The middle part of the beam always contains high density of clusters and monomers and the cluster size is usually larger, while the head and tail parts display a much lower density and the cluster size is usually smaller. The appearance of multicharged ions of S^{q+} and the splitting peaks of H^+ in Figs.1(b), 1(c) and 1(d) are perhaps the results of laser interaction with hydrogen sulfide clusters of a larger size. The overall signal intensity increases from about 50 in Fig.1(a) to 1000 in Fig.1(c) and then decreases to about 40 in Fig.1(e), which runs parallel to the density distribution of the beam, and this is consistent with the previous studies in which we have proposed the cluster-assistant generation of the multiply ionized atomic ions.[1]

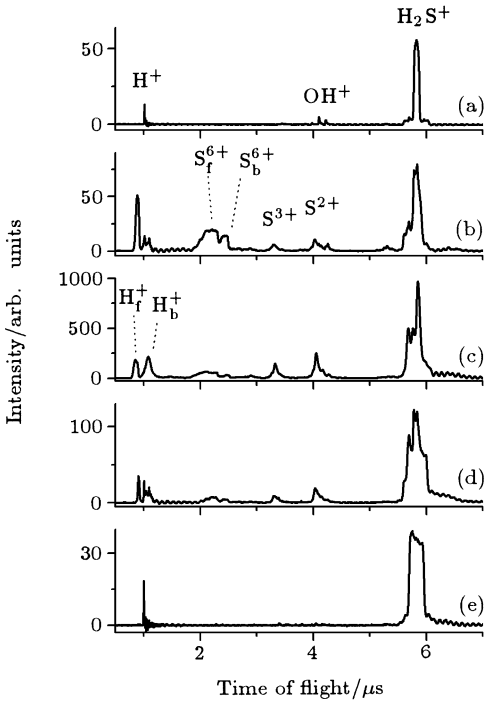


Fig.1. TOF mass spectra of hydrogen sulfide clusters irradiated by 1064 nm laser with an intensity of 3×10^{12}W·cm^{-2}. The delay times of the laser shot to the valve opening are (a) 270, (b) 320, (c) 620, (d) 1220, and (e) 1520μs.

The peak shape of a specific ion often contains information of distribution of its initial position and velocity. By changing the ratio of the static electric field strengths in the extraction and acceleration regions, the decoupling of the position and ve-

locity information of the product ions may be realized. Mass spectra were taken by increasing the electric field from 185 V/cm in Fig.2(a) to 309 V/cm in Fig.2(b) and 463 V/cm in Fig.2(c) at laser intensity of 3×10^{12}W·cm^{-2}, while the voltage on the repeller was fixed at 1850V. As we can see, there are two types of multi-charged ions in the mass spectra. The first type of ions is S^{2+} and S^{3+}, whose peaks are integrated ones. These peaks are thin and sharp when the electric field is adjusted to the space focusing condition in Fig.2(a), and then become broader when the electric field is out of space-focusing in Fig.2(b) and Fig.2(c). Another type of ions is S^{6+} whose peak split into forward and backward parts that are broadly apart in Fig.2(a), and then get closer and closer when the extraction field increases from Fig.2(b) to Fig.2(c).

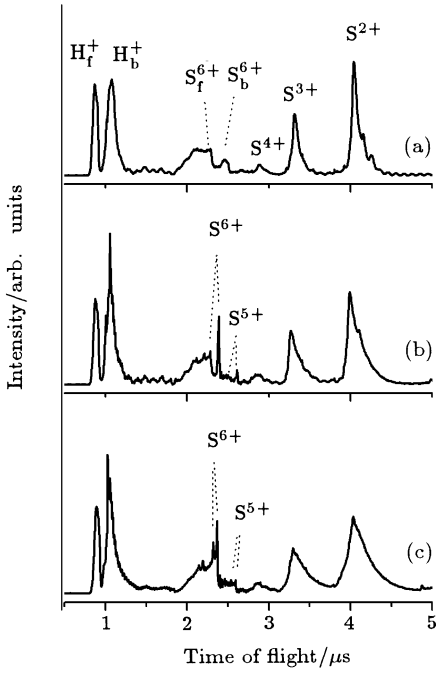


Fig.2. TOF mass spectra of hydrogen sulfide clusters irradiated by 1064nm laser ionization at the extraction electric fields of (a)185 , (b) 309 and (c) 463V/cm. The voltage on the repeller is fixed at 1850 V.

The kinetic energy (KE) of S^{6+} ions is larger than 200 eV, and the energy distribution is very broad. The KEs of S^{2+}, S^{3+} ions is only tens of eV, much smaller than S^{6+} ion, but S^{2+}, S^{3+} ions have a wide space distribution. We are led to the speculation that the two groups of ions, i.e. S^{q+} (q = 6, 7) and S^{q+} (q = 2, 3) may be produced in different ways. The S^{6+} ions with large KE may be the direct explosion particles from the highly ionized cluster; while S^{2+} and S^{3+} with large space distribution are probably produced in the following two ways: (1) the energetic electrons escaping from the clusters collision–ionize the surrounding molecules of H_2S to produce these ions, and (2) the exploding particles, i.e. S^{6+}, collision–ionize the H_2S to produce the ions. Both cases can result in the large space distribution.

To investigate the influence of the laser power on this interaction process, the laser intensity is decreased from 3×10^{12}, to 7×10^{11} or 2×10^{11}W·cm^{-2}, and the TOF mass spectra are shown in Figs.3(a)–3(c) respectively. As we can see, the sulfur ions of S^{6+}, S^{2+} and S^{3+} are the main multi-charged ion products at the three laser powers. The intensity of these multi-charged ions is about several tenths that of the H_xS^+ ions, and the corresponding parts of the mass spectra are enlarged 5 times for clarity in Figs.3(b) and 3(c). As the laser intensity decreases from Fig.3(a) to Fig.3(c) by more than one order, the ion species and their relative yields show no apparent changes except for the decreasing intensity of the overall ionic products. The peak splittings of S^{6+} and H^+ also decrease with the decrease of laser power from Fig.3(a) to Fig.3(c). The peaks of H_xS^+ ions (x=0, 1, 2) are clearly distinguishable in Fig.3(c), which can be ascribed to space charge effect and the change of kinetic energies of these ions.

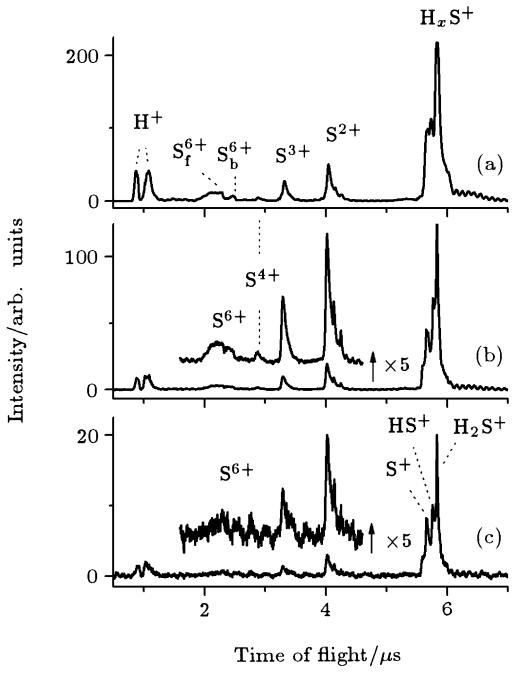


Fig.3. TOF mass spectra of hydrogen sulfide clusters irradiated by 1064 nm laser at intensities of (a) 3×10^{12}, (b) 7×10^{11} and (c) 2×10^{11}W·cm^{-2}.

3.2. Laser ionization of hydrogen sulfide at 532 nm

In order to investigate the influence of laser wavelength on the production of multi-charged ions, the experimental procedure of laser ionization of hydrogen sulfide was repeated at 532 nm. Similar to the results at 1064 nm, the multi-charged ions of S^{q+} could be detected only when the laser shoots at the dense middle part of the pulsed molecular beam, while if the laser shoots at the head and tail parts of the beam, the product ions consist solely of mono-charged ion species which are typical MPI products (the mass spectra are not given here). Figure 4 shows some typical mass spectra obtained at different laser intensities of (a) 1×10^{12}, (b) 5×10^{11}, (c) 1×10^{11} and (d) 3×10^{10}W·cm^{-2}, when the extraction electric field is set at 185 V/cm. In fact, the overlaps of the backward and forward peaks of S^{q+} make it difficult to properly assign the peaks. So we increase the extraction field from 185, 231, 463, 617 to 925 V/cm, and obtain the five mass spectra, as shown in Fig.5 from curve *e* at the bottom to curve *a*. The splitting backward and forward parts of the multi-charged ion peaks get closer and closer from curve *e* to curve *a*, and finally form integrated peaks which can be easily assigned to S^{2+}, $S^{3+}$and S^{4+} ions, as shown in curve *a*.

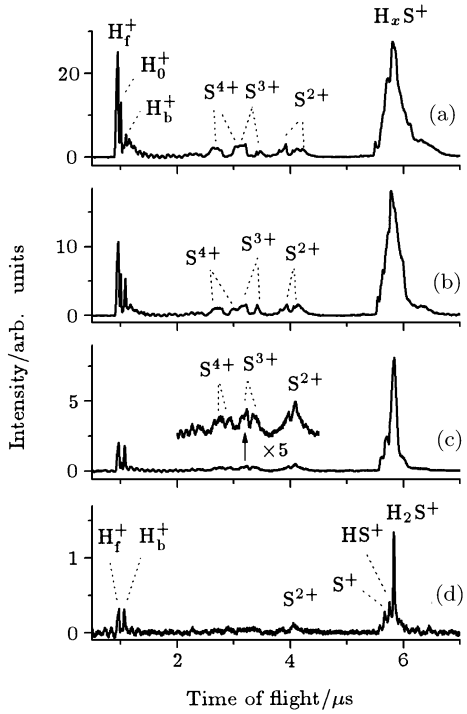


Fig.4. TOF mass spectra of hydrogen sulfide clusters ionized by 532 nm laser at laser intensities of (a)1×10^{12}, (b)5×10^{11}, (c)1×10^{11} and (d)3×10^{10}W·cm^{-2}.

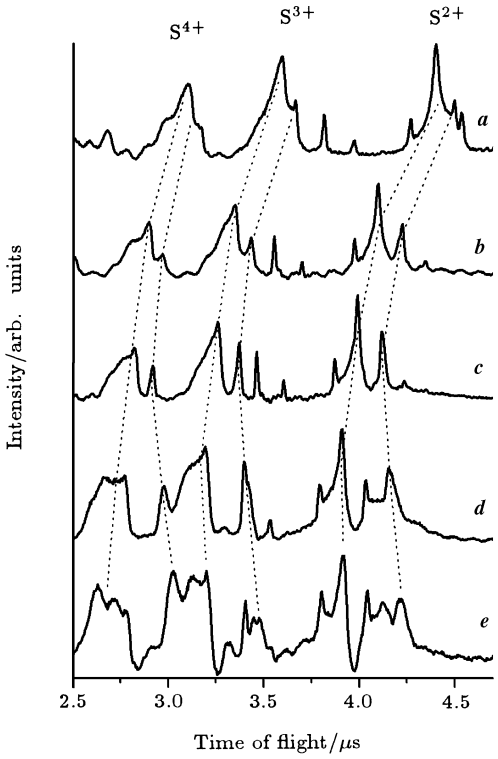


Fig.5. TOF mass spectra of hydrogen sulfide clusters under the extraction electric fields of curves *a* 185, *b* 231, *c* 463, *d* 617, and *e* 925 V/cm. The voltage on the repeller is fixed at 1850 V.

The kinetic energies of S^{4+}, S^{3+}, S^{2+} and H^+ in Fig.4(a) are 260, 110, 40 and 90 eV respectively according to the peak splitting. The large values of the KEs of these ions at 1064 and 532 nm indicate that these ions experience the Coulomb explosion of $(H_2S)_n^{q+}$ instead of the monomer $(H_2S)^{q+}$, because the Coulomb potential of $(H_2S)^{6+}$ monomer at its equilibrium structure can release at most $\sim$ 90 eV. And this is one of the reasons that we are confident of the participation of clusters even when we have not detected the cluster ions.

4. Discussion

As stated above, the main multi-charged ion products are S^{2+}, S^{3+} and S^{4+} at 532 nm, while S^{6+} is one of the main multi-charged ions at 1064 nm, even if the laser intensity of 532 nm in Fig.4(a) is higher than that of 1064 nm in Figs.3(b) and 3(c). The decreasing charge state of the atomic ions with laser wavelength is similar to our previous experiments of benzene and ammonia,[3,4] where C^{4+} and N^{5+} are the main products at 1064 nm; while C^{2+}, C^{3+}, N^{2+}, and N^{3+} are the main products at 532 nm. The peak splitting of these ions decreases with the decrease of the laser intensity, e.g. the S_b^{4+} and S_f^{3+} overlap in

Fig.4(a) to form one peak but become clearly split in 4(c). The overall ion yields decrease apparently with the decrease of the laser intensity, but the ratio of the multi-charged S^{q+} ions over the overall outputs does not drop apparently, as indicated in Figs.3 and 4. This insensitivity of the relative yield of the S^{q+} ions to the laser intensity is similar to our previous experimental results of benzene and ammonia,[3,4] in which the relative yields of C^{q+} and N^{q+} keep almost unchanged even when the laser intensity decreases by one order or more in magnitude.

To reveal the mechanism underlying, we have to consider the laser–cluster interactions in three steps: the initial ionization events, the laser heating and ionizing process, and the exploding process. The multiphoton ionization is considered to be responsible for the generation of the initial electrons as the Keldysh adiabaticity parameter $\gamma >> 1$, even at the fundamental 1064 nm of maximum intensity of $3\times10^{12}\,\mathrm{W\cdot cm^{-2}}$.[20] The MPI generated electrons can leave from the cluster and go to infinity, which is identical to the MPI of molecules. These courses can produce the positively charged clusters and could be defined as 'outer ionization'. However, some of the electrons can also be caged in the cluster due to the rebound from collision with neighbouring particles and the trapping by the positively charged ion cores in the cluster, this could be defined as 'inner ionization'. We have made *ab initio* calculation of some possible structures of $(H_2S)_n$ $(n = 2-8)$ at the MP2 level. From the distance of about 4.3 Å between the two neighbouring sulfur atoms in the weakly bonded cluster, the density of the cluster is estimated to be about $\sim 10^{22}\,\mathrm{cm^{-3}}$, and this is nearly the solid density of the hydrogen sulfide. So it is reasonable to assume a high collision frequency of electrons with the neutrals and ions. This high collision frequency results in the key heating process of inverse bremsstrahlung, in which the electron heating rate can be expressed as:[21]

$$\begin{aligned}\frac{\mathrm{d}\varepsilon}{\mathrm{d}t} &\approx 2U_\mathrm{p}\times\nu = \frac{e^2 I\lambda^2}{4\pi^2\varepsilon_0 m_\mathrm{e}c^3}\times\nu \\ &= 1.86\times10^{-13} I\lambda^2\times\nu, \end{aligned} \quad (1)$$

where U_p is the ponderomotive potential of the laser field, I is the laser intensity in $\mathrm{W\cdot cm^{-2}}$, λ is the laser wavelength in μm, ν is the frequency of electron-neutral and/or electron–ion collision of an order up to $\sim10^{14}$. The time to heat the electrons to 100 eV by 1064 nm laser of intensity $\sim 10^{12}\,\mathrm{W\cdot cm^{-2}}$ is estimated to be $\sim 10^2$ ps.

The IPs of S^{q+} (q=1–8) are 10.36, 23.33, 34.83, 47.3, 72.68, 88.05, 230.93 and 328.22 eV respectively. When the electrons are heated to an energy higher than the corresponding IPs of the ions, the electron may collision–ionize the particles step by step to higher and higher charge states till there is a barrier to further ionization, i.e. the 8th IP. Since the electrons can be heated efficiently during the laser pulse in 5 ns, the electron collision ionization is deduced to be the main contribution to the multielectron ionization of the molecules in the cluster. As more electrons with enough energy escape from the multi- charged clusters, the positive cluster will explode and produce the observed multi-charged atomic ions with large kinetic energies. Some of the escaping electrons can also collision–ionize the surrounding gases to generate some single- or multi-charged ion species with very broad space distribution. Since the electron heating rate scales with λ^2, longer wavelength benefits the energy gaining of the electrons, the collision ionization and hence the final ionization level of the cluster.

In summary, the following processes can account for the production of different ion species:

$$(H_2S)_n \xrightarrow{\mathrm{MPI}} (H_2S)_n^+ + \mathrm{e}, \quad (2)$$

$$(H_2S)_n^+ \xrightarrow{\mathrm{MPID}} H_xS^+ + H_0^+, \quad (x = 0-2), \quad (3)$$

$$(H_2S)_n^+ + \mathrm{e} \xrightarrow{\mathrm{IBS-EI}} H_\mathrm{f}^+ + H_\mathrm{b}^+ + S_\mathrm{f}^{q+} + S_\mathrm{b}^{q+} + H_xS^+, \quad (4)$$

$$H_2S + \mathrm{e(escaping\ from\ clusters)} \xrightarrow{\mathrm{EI}} H_xS^+ + S^{q+}, \quad \mathrm{(Low\ KE)}, \quad (5)$$

$$H_2S + S^{q+}\mathrm{(exploding\ from\ clusters)} \xrightarrow{\mathrm{impact}} H_xS^+ + S^{m+}(m<q), \quad \mathrm{(Low\ KE)}. \quad (6)$$

5. Conclusion

The formation of multi-charged sulfur ions from hydrogen sulfide clusters irradiated by a nanosecond laser field has been studied in detail by TOF mass spectrometry. The charge state distribution of the multi-charged ion sulfur is strongly dependent on the laser wavelength. An extreme high ionization level has been observed, e.g. the outer-shell valence electrons in the clusters can be stripped off when hydrogen sulfide clusters are irradiated by a nanosecond laser at 1064 nm with laser intensity of only $10^{11}-10^{12}\,\mathrm{W\cdot cm^{-2}}$. The process of MPI triggering-inverse bremsstrahlung heating-electron collision–ionization has been proposed to explain the generation of these multi-charged ions at the above laser intensity. The increasing charge states of the ion products with increasing laser wavelength are ascribed to the possible rate-limiting step, i.e., electron heating by absorbing energy from the laser field via IB, which is proportional to λ^2.

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References

[1] Kong X L, Luo X L, Niu D M and Li H Y 2004 *Chem. Phys. Lett.* **388** 139
[2] Luo X L, Niu D M, Kong X L and Li H Y 2005 *Chem. Phys.* **310** 17
[3] Niu D M, Li H Y, Liang F, Wen L H, Luo X L, Wang B, Hou K Y and Zhang X X 2005 *Chem. Phys. Lett.* **403** 218
[4] Niu D M, Li H Y, Liang F, Wen L H, Luo X L, Wang B and Qu H B 2005 *J. Chem. Phys.* **122** 151103
[5] Frasinski L J, Codling K, Hatherly P, Barr J, Ross I N and Toner W T 1987 *Phys. Rev. Lett.* **58** 2424
[6] Snyder E M, Buzza S A and Castleman A W Jr. 1996 *Phys. Rev. Lett.* **77** 3347
[7] Junkel-Vives G C, Abdallah J, Jr., Blasco F, Stenz C, Salin F, Faenov A Ya, Magunov A I, Pikuz T A and Skobelev I Yu 2001 *Phys. Rev.* A **64** 021201
[8] Cornagia C, Lavancier J, Normand D, Morellec J and Liu H X 1990 *Phys. Rev.* A **42** 5464
[9] Shimizu S, Kou J, Kawato S, Shimizu K, Sakabe S and Nakashima N 2000 *Chem. Phys. Lett.* **317** 609
[10] Tzallas P, Kosmidis C, Graham P, Ledingham K W D, McCanny T, Hankin S M, Singhal R P, Taday P F and Langley A J 2000 *Chem. Phys. Lett.* **332** 236
[11] Wu C Y and Gong Q H 2001 *Chin. Phys.* **10** 36
[12] Li X, Ren H Z, Ma R, Chen J X, Yang H and Gong Q H 2004 *Chin. Phys.* **13** 1564
[13] Rose-Petruck C, Schafer K J, Wilson K R and Barty C P J 1997 *Phys. Rev.* A **55** 1182
[14] Boyer K, Thompson B D, McPherson A and Rhodes C K 1994 *J. Phys.* B **27** 4373
[15] Zuo T and Bandrauk A D 1995 *Phys. Rev.* A **52** 2511
[16] Ditmire T, Donnelly T, Rubenchik A M, Falcone R W and Perry M D *Phys. Rev.* A **53** 3379
[17] Last I and Jortner J 2004 *J. Chem. Phys.* **120** 1336
[18] Xiao X, Li H Y, Luo X L, Niu D M, Wen L H, Wang B, Liang F, Hou K Y and Zhang N Z 2005 *Acta Phys. Sin.* **54** 5098
[19] Xiao X, Li H Y, Luo X L, Niu D M, Wen L H, Wang B, Liang F, Hou K Y, Dong C and Shao S Y 2006 *Acta Phys. Sin.* **55** 661
[20] Keldysh L V 1965 *Sov. Phys. JETP* **20** 1307
[21] Krainov V P and Smirnov M B 2002 *Phys. Rep.* **370** 237