

Communication: Determining the structure of the N₂Ar van der Waals complex with laser-based channel-selected Coulomb explosion

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We experimentally reconstructed the structure of the N₂Ar van der Waals complex with the technique of laser-based channel-selected Coulomb explosion imaging. The internuclear distance between the N₂ center of mass and the Ar atom, i.e., the length of the van der Waals bond, was determined to be 3.88 Å from the two-body explosion channels. The angle between the van der Waals bond and the N₂ principal axis was determined to be 90° from the three-body explosion channels. The reconstructed structure was contrasted with our high level *ab initio* calculations. The agreement demonstrated the potential application of laser-based Coulomb explosion in imaging transient molecular structure, particularly for floppy van der Waals complexes, whose structures remain difficult to be determined by conventional spectroscopic methods. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4871205>]

One of the fundamental tasks of physicists, chemists, and biologists is to probe molecular structure and its time evolution.^{1–3} For some rigid molecules, the structural parameters can be determined by measuring the infrared and Raman spectra. However, it is still difficult for spectroscopic methods in analyzing structures of van der Waals complexes because of the limitation of experimental sensitivity and resolution.^{4,5} Especially for some floppy van der Waals complexes, their structures cannot be determined by spectroscopic analysis because of the large vibrational amplitudes of van der Waals bonds.⁶ In this context, Coulomb explosion offers possibly a novel approach for imaging molecular structure whether the target is a rigid molecule or a floppy van der Waals complex. This technique was pioneered by Vager and co-workers in accelerator-based experiments, where individual molecular targets were accelerated to a velocity of several percent of the speed of light and then passed through a thin solid film.⁷ As a result, multiple electrons are suddenly stripped off and multiply charged molecular ions are therefore produced. Due to the repulsion of Coulomb force, the multiply charged molecular ions are quickly fragmented, undergoing the process of so-called Coulomb explosion. The molecular structure can be then deduced from momentum vectors of correlated fragments produced in the explosion process.

Coulomb explosion has also been achieved for molecules by synchrotron light radiation,^{8,9} ion impact,^{10–12} and a short intense laser pulse.^{13–15} Among them, the laser-based Coulomb explosion has attracted much attention because it has the advantage of high temporal resolution. Now, laser-based Coulomb explosion has been demonstrated to be

a feasible approach to image the structure of short-lived intermediates,^{16,17} small van der Waals complexes,^{18,19} as well as chiral molecules.²⁰ However, two big challenges tend to hinder the application of laser-based Coulomb explosion imaging technique. The first challenge arises from the complicated laser-molecule interaction.²¹ The molecular structure might be modified during the multiple ionization process and thus the reconstructed structural parameters for ions cannot represent the structure of the molecules before the laser irradiation. Some experimental criteria are required to be established to ascertain whether the molecular structure is kept unchanged during the multiple ionization process. The second challenge of Coulomb explosion imaging is the lack of the accurate *ab initio* many-body dissociation potential surface for multiply charged molecular ions. Thus Coulomb potential approximation is normally applied in the reconstruction of molecular structure. However, there is a large discrepancy between the Coulomb potential and the *ab initio* potential, especially when the internuclear distance is small. Therefore, structural parameters reconstructed from Coulomb potential approximation cannot always describe the real structure of multiply charged molecular ions.

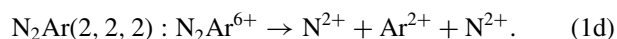
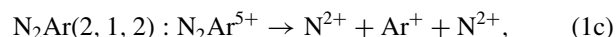
Multiple ionization followed by Coulomb explosion has been extensively studied for molecules under intense femtosecond laser fields with different pulse durations.^{22–28} The results have demonstrated that the nuclear motion can be frozen for molecules in the process of multiple ionization by using ultrashort laser pulses.^{14,25,28} Thus, the reconstructed structure of the molecular ion before explosion can represent the structure of the neutral precursor molecules when such ultrashort laser pulses are applied. In addition, we have carefully compared the Coulomb potential and the *ab initio* potential for describing the fragmentation dynamics of molecular

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ions. The results indicate that Coulomb potential approaches the *ab initio* potential closely when the internuclear distance is larger than 2.1 Å.^{15,28} van der Waals bonds usually have large equilibrium internuclear distances. Thus Coulomb potential is accurate enough to describe the explosion dynamics of van der Waals bond. Therefore, laser-based Coulomb explosion is suitable for imaging the molecular structure of small van der Waals complexes. As a prototypical van der Waals complex to study the interaction between a rare gas atom and a diatomic molecule, extensively theoretical calculations have been carried out for the N₂Ar van der Waals complex even though the experimentally measured spectral data are very scarce.²⁹⁻³¹ In this Communication, we experimentally reconstructed the structure of the N₂Ar van der Waals complex with laser-based channel-selected Coulomb explosion imaging technique. We found that the channel-independent reconstructed structures can be utilized as a criterion to judge whether the molecular structure is kept unchanged during the multiple ionization process. The reliability of the reconstructed molecular structure was verified by our high level *ab initio* calculations.

Here, the structure of the N₂Ar van der Waals complex is described by using coordinates of R and θ . R is defined as the internuclear distance between the N₂ center of mass and the Ar atom, and θ is the angle between the van der Waals bond and the N₂ principal axis. The N≡N bond length is presumably the equilibrium distance R_e 1.0977 Å of the neutral nitrogen molecules because the weak van der Waals interaction slightly affects the N≡N bond length. The two N atoms are identical for the N₂Ar van der Waals complex. When θ is 90°, the van der Waals complex belongs to C_{2v} group and the two nitrogen atoms have the permutation symmetry. The symmetry can be preserved in the momentum configuration if the two nitrogen atomic ions carry the same charge in the three-body Coulomb explosion process.⁷ Therefore, we select some symmetric three-body fragmentation channels (1a)–(1d) to analyze. Such symmetric fragmentation channels produce one argon atomic ion and two nitrogen atomic ions with the same charge state,



The description of the experimental method and the two-dimensional momentum distributions can be found in the supplementary material for the correlated atomic ions generated in the three-body fragmentation of N₂Ar ions by 780 nm, 25 fs laser pulses at an intensity of 1.3×10^{15} W/cm².³² There are two kinds of chemical bonds for the N₂Ar van der Waals complex. One is the weak van der Waals bond between the N₂ center of mass and the Ar atom. The other is the strong covalent bond between the two identical N atoms. The three-body fragmentation can occur through Coulomb explosion or the sequential process. In the case of Coulomb explosion process,

the two chemical bonds break simultaneously and the three atomic ions are produced almost at the same time. The permutation symmetry can be preserved in the final momentum distributions for the two nitrogen atomic ions. In the case of sequential fragmentation process, the two bonds break one after the other with a time interval comparable to the molecular rotational period of the intermediate. Thus, the permutation symmetry will be destroyed because the fragmentation of the intermediate is always accompanied by its rotation.

To clarify the fragmentation mechanism, we display the experimental data for channels (1a)–(1d) in Newton diagrams in Figures 1(a)–1(d). The momentum vector of the argon atomic ion is represented by an arrow fixed at one arbitrary unit. The momentum vectors of the two nitrogen atomic ions are normalized to the length of the argon atomic ion momentum vector and mapped in the left of the plot. A circle structure will be exhibited in the Newton diagram if the sequential three-body fragmentation dominates.^{11,15} However, a pair of crescent-shaped structure was observed for all channels (1a)–(1d). The observation demonstrates that the van der Waals bond and the covalent bond break simultaneously or with an interval much smaller than the rotational period of the intermediate. In other words, the three-body fragmentation occurs through Coulomb explosion process. Thus, the permutation symmetry was preserved in the momentum distribution of the atomic ions from the three-body fragmentation. Figure 1(e) shows the normalized event counts as a function of the angle between P_{NN'} and P_{Ar}. The vector P_{NN'} is defined as the difference of the momentum vectors between the two identical nitrogen atomic ions and P_{Ar} as the momentum vector of the argon atomic ions. The distribution can be well simulated by a Gaussian function with a peak at 90°. This single-peak distribution further indicates that the three-body fragmentation occurs through Coulomb explosion process.¹⁰ These measurements demonstrate that the two nitrogen atomic ions have the permutation symmetry in the momentum configuration. Correspondingly, the two nitrogen atomic ions have the permutation symmetry in the space configuration and the van der Waals complex ions before explosion belong to C_{2v} group. Therefore, θ is determined to be 90° for N₂Arⁿ⁺ with $n = 3-6$.

Coulomb potential approximation is always applied in the reconstruction of molecular structure, since it is very difficult to obtain the accurate *ab initio* potential energy surface for three-body fragmentation of multiply charged molecular ions. However, our previous studies indicated that Coulomb potential can be applied only when it approaches the *ab initio* potential at bond lengths larger than 2.1 Å.¹⁵ In the case of the N₂Ar van der Waals complex, the N≡N bond length is the equilibrium distance R_e 1.0977 Å of the neutral nitrogen molecules. Obviously, Coulomb potential is not suitable to describe the three-body fragmentation dynamics for the channels (1a)–(1d). Noticeably, the bond length is nearly 4 Å for the weak van der Waals bond between the argon atom and the nitrogen molecule. Then, the van der Waals bond fragmentation to produce nitrogen molecular ion and argon atomic ion, which is actually a manner of two-body explosion, can be described by Coulomb potential. So the bond length for the weak van der Waals bond can be determined by analyzing

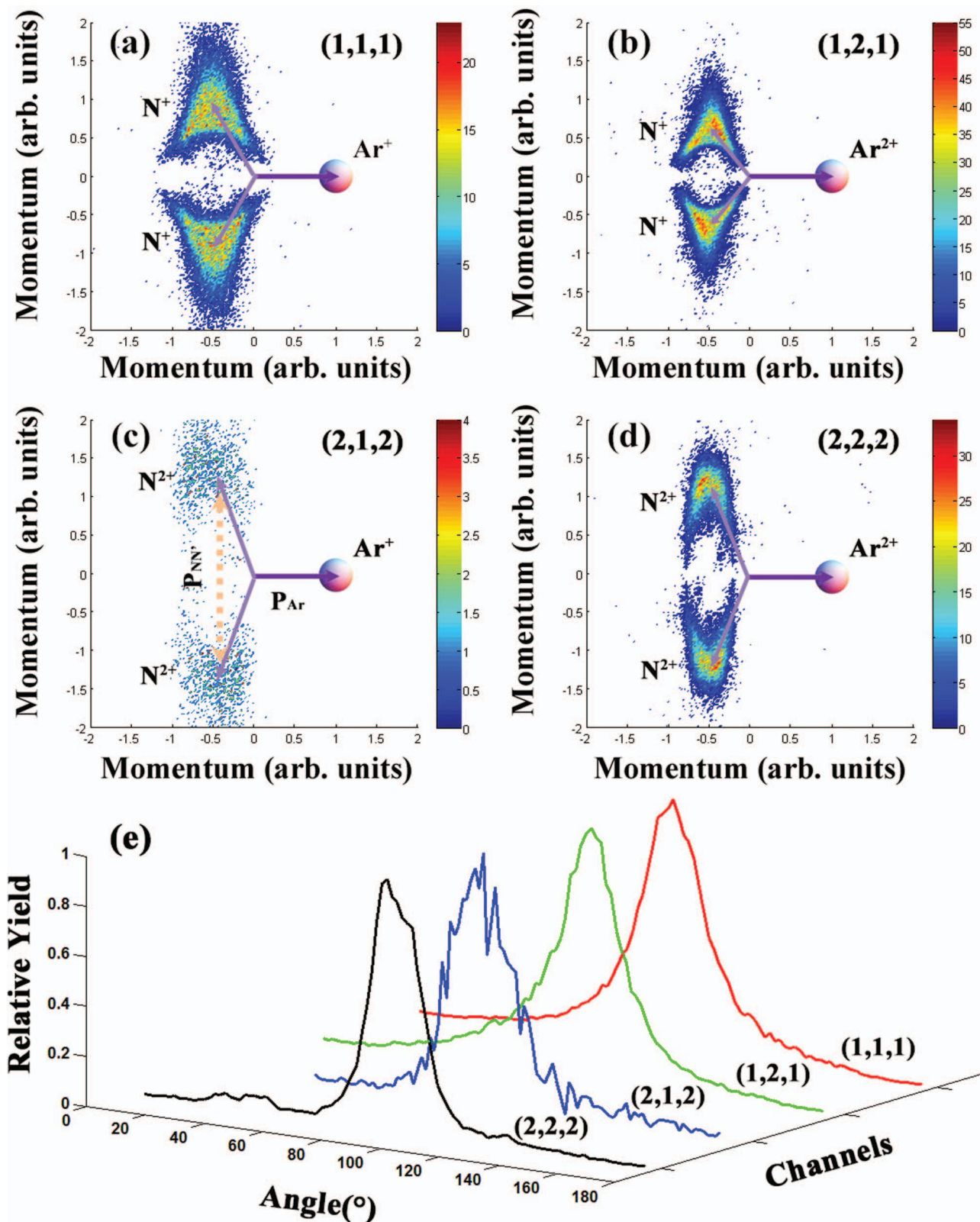
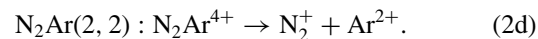
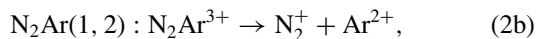
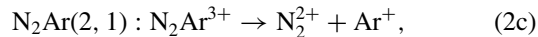
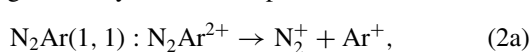


FIG. 1. Three-body fragmentation process of N₂Ar ions. (a)–(d) Newton diagram and (e) relative yield as a function of the angle between P_{NN'} and P_{Ar} (see text).

the following two-body Coulomb explosion channels,



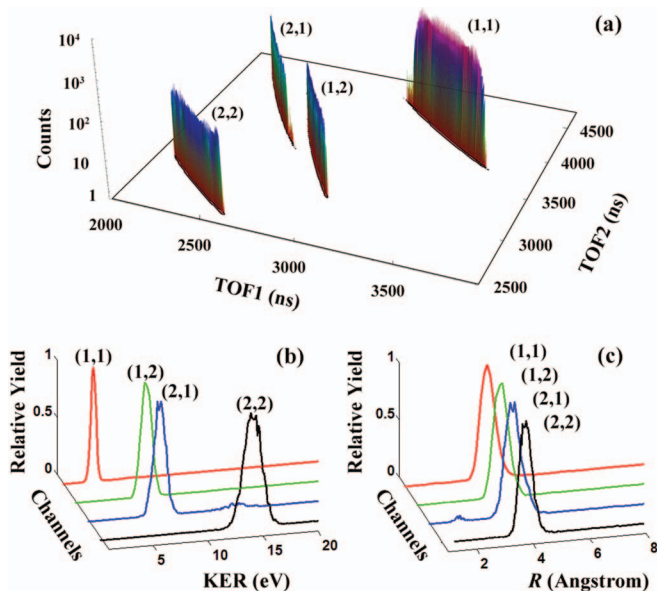


FIG. 2. Two-body fragmentation process of N_2Ar ions. (a) Coincidence time-of-flight map, (b) kinetic energy release distributions, and (c) the reconstructed internuclear distances between the N_2 center of mass and the Ar atom.

Figure 2(a) shows the coincidence time-of-flight map of ions produced in the two-body fragmentation of N_2Ar by 780 nm, 25 fs laser pulses at an intensity of 1.3×10^{15} W/cm². Each island (n,m) represents an explosion channel $N_2Ar^{(n+m)+} \rightarrow N_2^{n+} + Ar^{m+}$. Figure 2(b) shows the kinetic energy release (KER) distributions of the two-body fragmentation channels shown in (2a)–(2d). The KER exhibits almost similar shapes with the peak around 3.7 eV for the (1,1) channel, 7.4 eV for (1,2) and (2,1) channels, and 14.8 eV for (2,2) channel. Based on the KERs, the internuclear distance R before explosion can be derived under the Coulomb potential approximation, as shown in Figure 2(c). R represents the internuclear distance between the N_2 center of mass and the Ar atom, which is determined to be 3.88 Å for N_2Ar^{n+} with $n = 2-4$ and is shown to be channel-independent.

From the above analysis for the three-body and two-body Coulomb explosion channels, the structural parameters of θ and R are derived for the van der Waals complex after multiple ionization. Interestingly, θ and R are shown to be channel-independent, which are 90° and 3.88 Å, respectively. How are these structural parameters after multiple ionization related to the structure of the neutral van der Waals complex before the laser irradiation? One might think that the molecular structure is modified during the multiple ionization. The reconstructed structural parameters for ions cannot represent the structure of the van der Waals complex before the laser irradiation. Indeed, some experimental observations have shown that the internuclear distance could be stretched and the structure could be changed during the multiple ionization of molecules induced by intense laser fields.^{13,14,28} If the molecular structure is modified during the ionization process, the reconstructed structural parameters will be associated with specific channels and thus exhibit channel-dependence.^{13,14,28} However, our observation for the case of N_2Ar is that the reconstructed structural parameters do not depend on the channel from

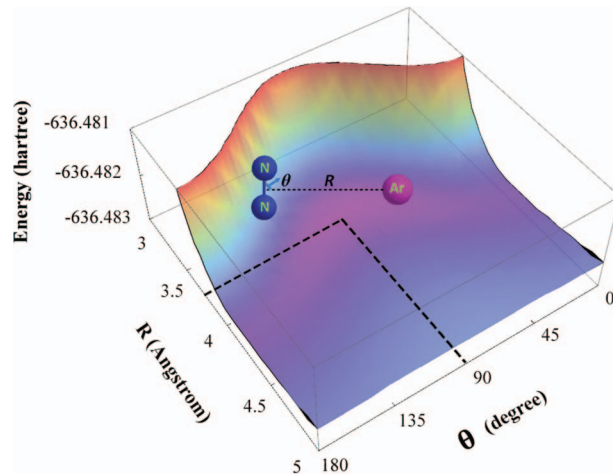


FIG. 3. Calculated PES of N_2Ar for the van der Waals bond dissociation varied with the coordinates of R and θ . The covalent $N \equiv N$ bond length is unchanged and fixed at 1.0977 Å.

which the molecular structure is reconstructed. The channel-independence indicates that the nuclear motion is frozen during the interaction between the van der Waals complex and the ultrashort 25 fs laser pulse. Thus, the determined configuration for the multiply charged ions can represent the configuration of the neutral N_2Ar before the laser irradiation, with θ being 90° and R being 3.88 Å.

In order to test the reliability of our reconstructed molecular structure, we calculate the potential energy surface (PES) of N_2Ar using the coupled cluster singles and doubles model including connected triples corrections (CCSD(T)) with aug-cc-pVQZ basis set.³³ For such van der Waals complexes, CCSD(T) has been proved to be a powerful method to obtain accurate potentials.³⁰ As shown in Figure 3, the located energy minimum corresponds to $\theta = 90^\circ$ and $R = 3.71$ Å. These parameters agree well with our experimentally reconstructed values, demonstrating that the structural reconstruction can be achieved for small van der Waals complexes by using the method of laser-based Coulomb explosion imaging.

In summary, we have experimentally studied three-body and two-body Coulomb explosion dynamics of N_2Ar driven by intense laser pulses. The structure of the N_2Ar molecular ion was reconstructed with the laser-based channel-selected Coulomb explosion imaging. The reconstructed structures are shown to be channel-independent, indicating that the nuclear motion is frozen during the interaction between the N_2Ar van der Waals complex and the ultrashort laser pulse. Therefore, the reconstructed structure of the multiply charged molecular ions can represent the structure of the N_2Ar van der Waals complex before the laser irradiation. This conclusion was supported further by our high level *ab initio* calculation. Altogether, the results show the great promise of laser-based Coulomb explosion in imaging transient molecular structures, particularly for floppy van der Waals complexes whose structures remain difficult to be determined by conventional spectroscopic methods.

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- ¹A. H. Zewail, *J. Phys. Chem. A* **104**, 5660 (2000); *Science* **328**, 187 (2010).
- ²K. J. Gaffney and H. N. Chapman, *Science* **316**, 1444 (2007).
- ³C. I. Blaga, J. Xu, A. D. Dichiaro, E. Sistrunk, K. Zhang, P. Agostini, T. A. Miller, L. F. DiMauro, and C. D. Lin, *Nature (London)* **483**, 194 (2012); M. Y. Ivanov, *ibid.* **483**, 161 (2012).
- ⁴X. B. Wang, H. K. Woo, and L. S. Wang, *J. Chem. Phys.* **123**, 051106 (2005).
- ⁵N. Moazzen-Ahmadi and A. R. W. McKellar, *Int. Rev. Phys. Chem.* **32**, 611 (2013).
- ⁶D. Bressanini and G. Morosi, *J. Phys. Chem. A* **115**, 10880 (2011).
- ⁷I. Plessner, Z. Vager, and R. Naaman, *Phys. Rev. Lett.* **56**, 1559 (1986); Z. Vager, R. Naaman, and E. P. Kanter, *Science* **244**, 426 (1989).
- ⁸R. K. Singh, G. S. Lodha, V. Sharma, I. A. Prajapati, K. P. Subramanian, and B. Bapat, *Phys. Rev. A* **74**, 022708 (2006).
- ⁹Z. D. Pesic, D. Rolles, R. C. Bilodeau, I. Dimitriu, and N. Berrah, *Phys. Rev. A* **78**, 051401(R) (2008).
- ¹⁰J. H. Sanderson, T. Nishide, H. Shiromaru, Y. Achiba, and N. Kobayashi, *Phys. Rev. A* **59**, 4817 (1999).
- ¹¹N. Neumann, D. Hant, L. P. H. Schmidt, J. Titze, T. Jahnke, A. Czasch, M. S. Schöffler, K. Kreidi, O. Jagutzki, H. Schmidt, and R. Dorner, *Phys. Rev. Lett.* **104**, 103201 (2010).
- ¹²M. R. Jana, P. N. Ghosh, B. Bapat, R. K. Kushawaha, K. Saha, I. A. Prajapati, and C. P. Safvan, *Phys. Rev. A* **84**, 062715 (2011).
- ¹³A. Hishikawa, A. Iwamae, and K. Yamanouchi, *Phys. Rev. Lett.* **83**, 1127 (1999).
- ¹⁴I. Bocharova, R. Karimi *et al.*, *Phys. Rev. Lett.* **107**, 063201 (2011).
- ¹⁵C. Wu, C. Wu, D. Song, H. Su, Y. Yang, Z. Wu, X. Liu, H. Liu, M. Li, Y. Deng, Y. Liu, L.-Y. Peng, H. Jiang, and Q. Gong, *Phys. Rev. Lett.* **110**, 103601 (2013).
- ¹⁶F. Legare, K. F. Lee, I. V. Litvinyuk, P. W. Dooley, A. D. Bandrauk, D. M. Villeneuve, and P. B. Corkum, *Phys. Rev. A* **72**, 052717 (2005).
- ¹⁷E. Gagnon, P. Ranitovic, X. M. Tong, C. L. Cocke, M. M. Murnane, H. C. Kapteyn, and A. S. Sandhu, *Science* **317**, 1374 (2007).
- ¹⁸B. Ulrich, A. Vredenborg, A. Malakzadeh, L. Ph. H. Schmidt, T. Havermeier, M. Meckel, K. Cole, M. Smolarski, Z. Chang, T. Jahnke, and R. Dorner, *J. Phys. Chem. A* **115**, 6936 (2011).
- ¹⁹J. Wu, M. Kuniski, L. Ph. H. Schmidt, T. Jahnke, and R. Dorner, *J. Chem. Phys.* **137**, 104308 (2012).
- ²⁰M. Pitzer *et al.*, *Science* **341**, 1096 (2013).
- ²¹K. Yamanouchi, *Science* **295**, 1659 (2002).
- ²²J. Purnell, E. M. Snyder, S. Wei, and A. W. Castleman, *Chem. Phys. Lett.* **229**, 333 (1994).
- ²³C. Cornaggia, *Phys. Rev. A* **54**, R2555 (1996).
- ²⁴K. W. D. Ledingham, D. J. Smith, R. P. Singhal, T. McCanny, P. Graham, H. S. Kilic, W. X. Peng, A. J. Langley, P. F. Taday, and C. Kosmidis, *J. Phys. Chem. A* **103**, 2952 (1999).
- ²⁵E. Baldit, S. Saugout, and C. Cornaggia, *Phys. Rev. A* **71**, 021403 (2005).
- ²⁶J. P. Brichta, S. J. Walker, R. Helsten, and J. H. Sanderson, *J. Phys. B* **40**, 117 (2007).
- ²⁷H. L. Xu, C. Marceau, K. Nakai, T. Okino, S. L. Chin, and K. Yamanouchi, *J. Chem. Phys.* **133**, 071103 (2010).
- ²⁸C. Wu, Y. Yang, Z. Wu, B. Chen, H. Dong, X. Liu, Y. Deng, H. Liu, Y. Liu, and Q. Gong, *Phys. Chem. Chem. Phys.* **13**, 18398 (2011).
- ²⁹K. Patel, P. R. Butler, A. M. Ellis, and M. D. Wheeler, *J. Chem. Phys.* **119**, 909 (2003).
- ³⁰C. R. Munteanu, J. L. Cacheiro, and B. Fernández, *J. Chem. Phys.* **121**, 10419 (2004).
- ³¹A. K. Dham, W. J. Meath, J. W. Jechow, and F. R. McCourt, *J. Chem. Phys.* **124**, 034308 (2006).
- ³²See supplementary material at <http://dx.doi.org/10.1063/1.4871205> for the description of the experimental method and the experimental data for plotting Fig. 1.
- ³³M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford, CT, 2009.