PHYSICAL REVIEW A **86**, 033201 (2012)

Explosion, ion acceleration, and molecular fragmentation of methane clusters in the pulsed beam of a free-electron laser

B. Iwan,[1] J. Andreasson,[1] M. Bergh,[1,*] S. Schorb,[2] H. Thomas,[2] D. Rupp,[2] T. Gorkhover,[2] M. Adolph,[2] T. Möller,[2] C. Bostedt,[2]
J. Hajdu,[1] and N. Tîmneanu[1,†]
[1]*Laboratory of Molecular Biophysics, Institute of Cell and Molecular Biology Uppsala University,*
Husargatan 3, Box 596, S-75124 Uppsala, Sweden
[2]*Institut für Optik und Atomare Physik, Technische Universität Berlin, Eugene-Wigner-Bldg. EW 3-1,*
Hardenbergstrasse 36, D-10623 Berlin, Germany

(Received 19 April 2012; revised manuscript received 14 August 2012; published 4 September 2012)

X-ray lasers offer new possibilities for creating and probing extreme states of matter. We used intense and short x-ray pulses from the FLASH soft x-ray laser to trigger the explosions of CH_4 and CD_4 molecules and their clusters. The results show that the explosion dynamics depends on cluster size and indicate a transition from Coulomb explosion to hydrodynamic expansion in larger clusters. The explosion of CH_4 and CD_4 clusters shows a strong isotope effect: The heavier deuterons acquire higher kinetic energies than the lighter protons. This may be due to an extended inertial confinement of deuterons vs. protons near a rapidly charging cluster core during exposure.

DOI: 10.1103/PhysRevA.86.033201 PACS number(s): 36.40.Wa, 32.80.Fb, 52.50.Jm

Free-electron lasers (FEL's) can be used to trigger and monitor ultrafast transitions in targets, ranging from free atoms [1] to atomic clusters [2–4], biological objects [5,6], and solid samples [7–9]. In this paper we follow the x-ray–induced explosion of methane (CH_4) and heavy methane (CD_4) clusters and compare the results to the explosion of the individual molecules. Clusters are eminently suitable to study size-dependent phenomena in the explosion dynamics; we employed clusters containing 1000 to 250 000 molecules and corresponding to sizes of 4–32 nm diameter. Molecular clusters bridge the gap between isolated molecules and bulk condensed material. An understanding of ultrafast explosion dynamics in clusters of various dimensions has relevance to imaging by "diffraction before destruction" [10], plasma physics, and fusion research [11,12].

The target response to an intense x-ray pulse depends on the wavelength, the intensity of the field, and the size of the sample. Photoionization liberates electrons, which can escape from small samples, and these positively charged objects undergo a Coulomb explosion. The probability of electrons escaping from a cluster depends on its size [13–15]. In larger objects, photoelectrons elicit secondary electron cascades and these create additional ionizations. As the overall positive charge of the sample increases during the pulse, photoelectrons will not be able to escape the growing positive potential [13,16]. Trapped photoelectrons create more cascades, and the electrons move inward to neutralize the core of the cluster, leaving behind a positively charged outer layer which then peels off [17–21]. As a result, large samples burn from the outside inward. The core of such large objects expands hydrodynamically due to the growing electron pressure within [17,18]. Theoretical studies predict a transition from Coulomb explosion to hydrodynamic expansion with increasing sample size [13].

The study of Coulomb explosion of molecular clusters with intense infrared lasers has shown the advantage of using heteronuclear molecules, such as CH_4 or CD_4, to analyze the dynamics of the explosion [22,23]. In a heteronuclear cluster, the light ions can gain additional energy during the explosion by interacting with multiply charged heavy ions (C^{n+}). This kinematic effect would be indicative of a Coulomb process, while in a hydrodynamics expansion all the cluster constituents are expected to gain the same energy. We find that the explosion of CH_4 and CD_4 clusters shows an isotope effect detectable for the fastest ions: The heavier deuterons acquire significantly higher kinetic energies than the lighter protons. We surmise that this may be due to an extended inertial confinement of deuterons, as these stay near the highly charged cluster core longer as compared to the protons.

The observations were made at the FLASH free-electron laser in Hamburg [24]. Molecular clusters of methane (CH_4) and fully deuterated methane (CD_4) were produced by adiabatically expanding methane gas through a conical nozzle [Fig. 1(a)] [14]. Different cluster sizes were obtained by varying the gas backing pressure (1.8 bar $< p <$ 18 bar) at a fixed temperature of the nozzle of 160 K. Using the empirical Hagena scaling law [25], the mean number $\langle N \rangle$ of molecules per cluster can be estimated in the range of 1×10^3 to 2.5×10^5. At fixed pressure and temperature, the size distribution can be described by a log-normal distribution [26]. Deviations from the empirical formula have been reported for CD_4 clusters produced at room temperature [26]. These suggest that the Hagena parameter, while it may overestimate the average cluster size, is useful as a scaling parameter for the cluster formation. Based on the Hagena scaling law, the average cluster sizes correspond to radii between 2.46 nm to 15.5 nm for spherical clusters at liquid methane density.

The clusters were delivered into a vacuum chamber and illuminated by 15-fs soft x-ray pulses at a wavelength of $\lambda = 13.5$ nm ($E_{ph} = 92$ eV). FLASH was operating at a 5-Hz repetition rate, and the pulse energy fluctuated between 20–53 μJ (mean = 43 μJ) as measured with a gas monitor detector

---

[*] Present address: Swedish Defense Research Agency, S-14725 Tumba, Sweden.

[†] nicusor@xray.bmc.uu.se

©2012 American Physical Society

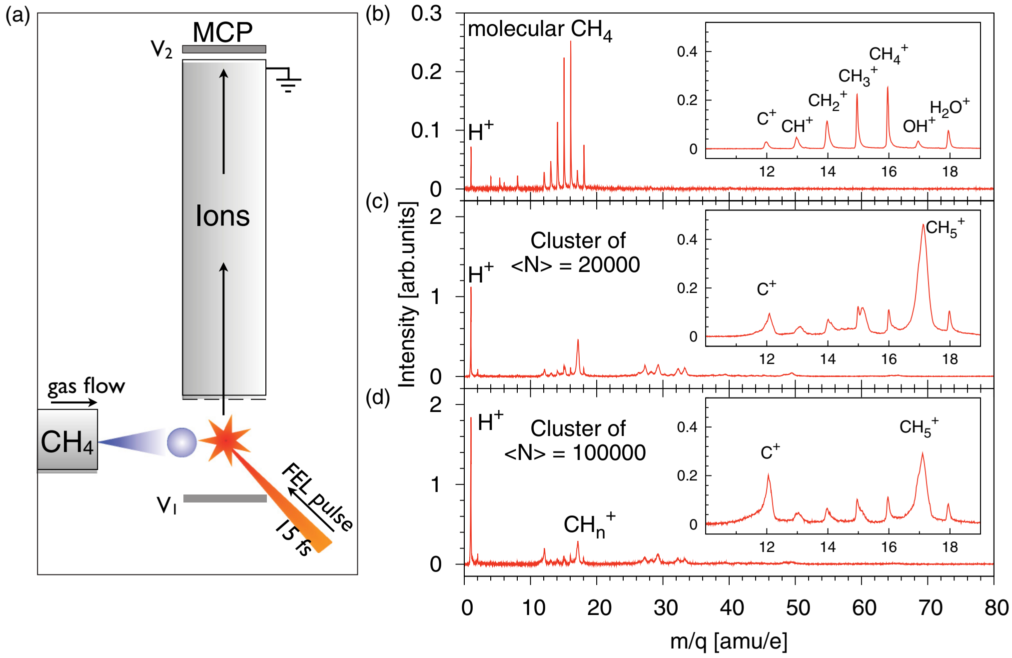

FIG. 1. (Color online) Experimental setup and mass over charge spectra for methane molecules and clusters irradiated by single laser pulses. (a) Clusters produced through supersonic expansion of gas are exposed to 15-fs-long soft x-ray pulses at $\lambda = 13.5$ nm, with an average intensity of 5×10^{14} W/cm^2. Positively charged ions from cluster fragmentation are accelerated by an electric field between a repeller plate $V_1 = 1000$ V and the grounded field-free drift tube, and are detected by a multichannel plate (MCP) detector $V_2 = -2600$ V. (b) The spectrum for CH_4 molecules shows a weak H^+ signal, signature peaks for typical fragments $CH_n{}^+$, and the water background. The insert shows a zoom into the region from $m/q = 12$ to 18. (c) and (d) Spectra of methane clusters show a significant increase in the H^+ and C^+ peaks. The signal of $CH_5{}^+$, a sign of molecular recombination, reaches a maximum for $\langle N \rangle = 20\,000$ molecules. Note the different scales on the vertical axes.

(GMD) [27]. The beam line transmission was 64%, and the transmitted beam was focused to a spot size of 20 μm at the interaction point [24,27]. The intensity of the focused beam on the sample was between $10^{13} - 10^{15}$ W/cm^2, with the mean value at 5×10^{14} W/cm^2. This corresponds to a transmitted intensity of a pulse with a 43-μJ reading on the GMD.

The positively charged ions were detected by ion time-of-flight (TOF) spectrometry (Fig. 1). The spectra were calibrated by simulating ion trajectories through the TOF, using SIMION [28]. The calibration enabled the conversion of flight times to mass-over-charge (m/q) distributions and identification of specific peaks. The ion kinetic energies were determined after background subtraction. Simulations indicate that the effect of the extracting electric field (0.08 V/μm) on the cluster explosion was negligible. The maximum detected kinetic energy for H^+ and D^+ ions was obtained from the leading edge of the ion peak with a 95% confidence level in the signal-to-noise ratio (SNR). Subsequent analyses of ion yields and energy distributions were performed for all individual experiments with fixed average cluster sizes, and for all energies of the incident FEL pulse averaged in bins of ± 1 μJ around the mean (data from GMD).

A qualitative inspection of the mass spectra in Fig. 1(b)–1(d) reveals a size dependency in the fragmentation of methane clusters. These measurements used pulses with 5×10^{14} W/cm^2 intensity. The spectrum for molecular methane [Fig. 1(b)] had a weak proton signal at $m/q = 1$ and showed peaks of methane fragments (CH_n^+, $1 \leqslant n \leqslant 4$). There were no higher molecular adducts. Figures 1(c) and 1(d) show spectra from methane clusters of $\langle N \rangle = 20\,000$ (6.7-nm radius) and $\langle N \rangle = 100\,000$ molecules (11.5-nm radius), respectively. These spectra exhibit additional higher charged adducts and an increased overall ion yield. The proton peaks were significantly higher in the two cluster spectra than in the spectrum of molecular methane.

The formation of protonated methane $CH_5{}^+$ [29] was a dominant feature in the spectra of methane clusters [Figs. 1(c) and 1(d)]. The $CH_5{}^+$ ion was only observed in the fragmentation patterns of clusters, and its presence is indicative of molecular recombination due to reactions between ions and molecules. The cluster spectra also showed signals for higher adducts ($C_nH_m{}^+$, $n \geqslant 2$).

The results for these two different cluster sizes show that molecular recombination is influenced by the cluster size. With increasing cluster size, a change in the proportion of the adduct ions took place, together with a strong increase in the H^+ and C^+ peaks in the larger of the two clusters. These data provide signs that molecular recombination depends on the explosion time of the clusters.

A quantitative analysis of the ion yield in the TOF spectra is shown in Fig. 2. Figure 2(a) shows H^+ yields from methane clusters and D^+ yields from heavy methane clusters as a function of the gas jet backing pressure at 5×10^{14} W/cm^2 pulse intensity. The yields of H^+ and D^+ ions grew linearly with increasing pressure, and the same behavior was observed for C^+ ions in both sets of sample. This behavior is to be expected, as the total number of methane molecules in the interaction volume increases linearly with the backing pressure

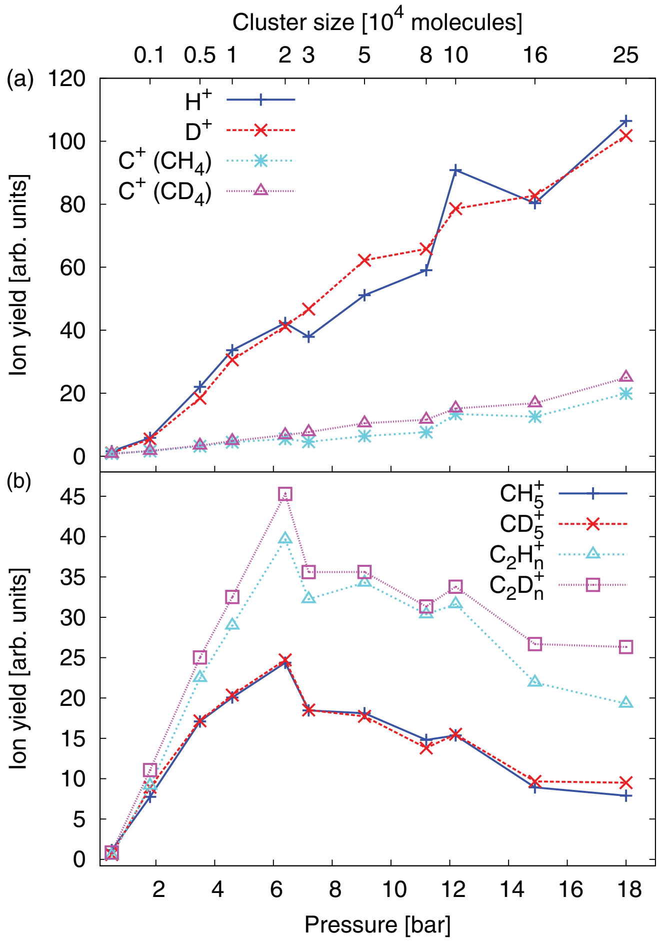

FIG. 2. (Color online) Ion yields from fragmented methane clusters as a function of backing pressure and cluster size. (a) Ion yields for H^+ and D^+ from pure and deuterated methane are increasing as a function of gas jet pressure and number of molecules in the cluster. The FEL intensity is 5×10^{14} W/cm^2. (b) Under the same conditions, ion yields for the molecular fragments $CH_5{}^+$ and $CD_5{}^+$ reach a maximum at the cluster size of $\langle N \rangle = 20\,000$ molecules (radius of 6.7 nm).

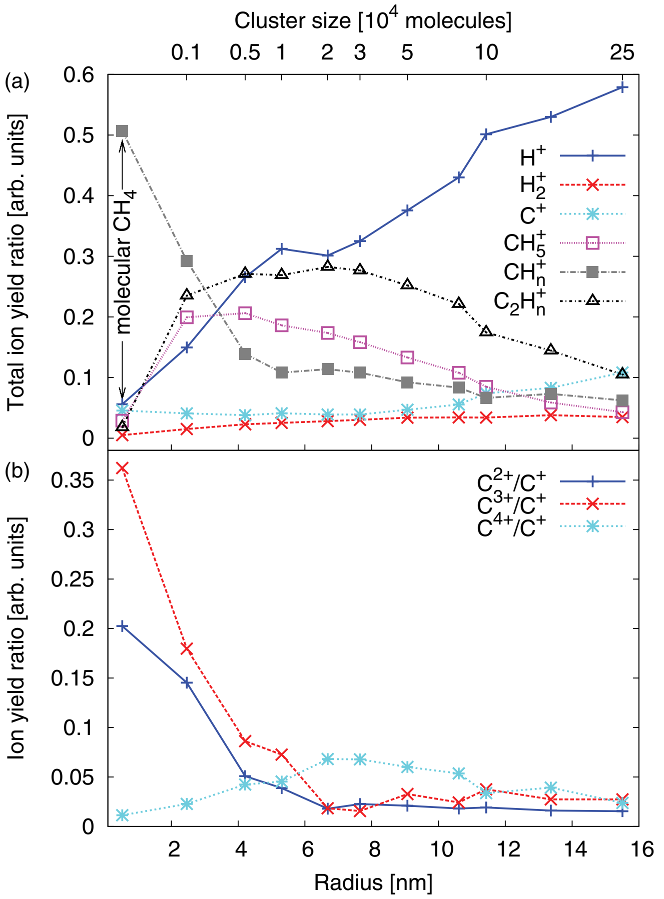

FIG. 3. (Color online) Normalized ion signals as a function of cluster size. (a) Contribution of different ion yields, normalized to the total ion yield is shown for the CH_4 experiment. The $CH_n{}^+$ and $C_2H_n{}^+$ data contain all adducts with one or two carbon atoms (except for $CH_5{}^+$ shown separately). The data points at close to zero size correspond to the single-molecule (no clustering) experiment. Higher charge states of carbon have a contribution below 20% of the single ionized carbon. (b) Ion yield ratio for higher charge states of carbon from pure methane clusters (C^{2+}, C^{3+}, C^{4+}) to the singly charged carbon ion (C^+). The carbon yields from CD_4 clusters show similar behavior.

[25]. Further analysis of the total H^+ and D^+ signal showed that about 75% of the contribution came from ions produced from clusters, and the rest were low energetic ions coming from the ionization of free molecules. The high energetic ions originate from the clusters and their yield showed a similar linear rise with backing pressure.

Figure 2(b) shows a significant maximum in the yield of $CH_5{}^+$ ($CD_5{}^+$) and $C_2H_n{}^+$ ($C_2D_n{}^+$) ions as a function of cluster size. The peak is located at a cluster size of 20 000 molecules (6.7-nm cluster radius). The yield of these ions decreased in clusters that contained more than 20 000 molecules. This behavior contrasts sharply with the linear increase in the yield of H^+, D^+, and C^+ ions [Fig. 2(a)] as a function of cluster size, and hints to the existence of a decay channel for these adducts in larger clusters. The decrease in the yield of these ions in larger clusters is probably connected to the longer lifetime of big cluster, following illumination (see below). It is conceivable that $CH_5{}^+$ and $C_2H_n{}^+$ adducts lose protons through collisions, and there are more collisions during expansion of large clusters than of small clusters, which disintegrate faster. In contrast, the proton and deuteron yields show a steady growth [Fig. 2(a)], which is in agreement with this proposition.

Figure 3 indicates that electron-ion recombination processes are also influenced by sample size. The measured ionization states of carbon depend on cluster size [Fig. 3(b)]. Carbon ions with higher charge states (C^{4+}) reach a maximum abundance relative to singly charged C^+ ions for a cluster of $\langle N \rangle = 20\,000$ molecules. The normalized abundance of the different ionic species is shown in Fig. 3(a). In the case of single molecules, the ionization mainly broke bonds in the CH_4 molecule, and the total yield was dominated by ions containing a single carbon atom ($CH_n{}^+$). With increasing cluster size, adducts with higher masses were formed through molecular recombination. A key parameter in the fragmentation of molecular clusters with femtosecond soft x-ray pulses is the lifetime of the charged cluster. This scales with cluster

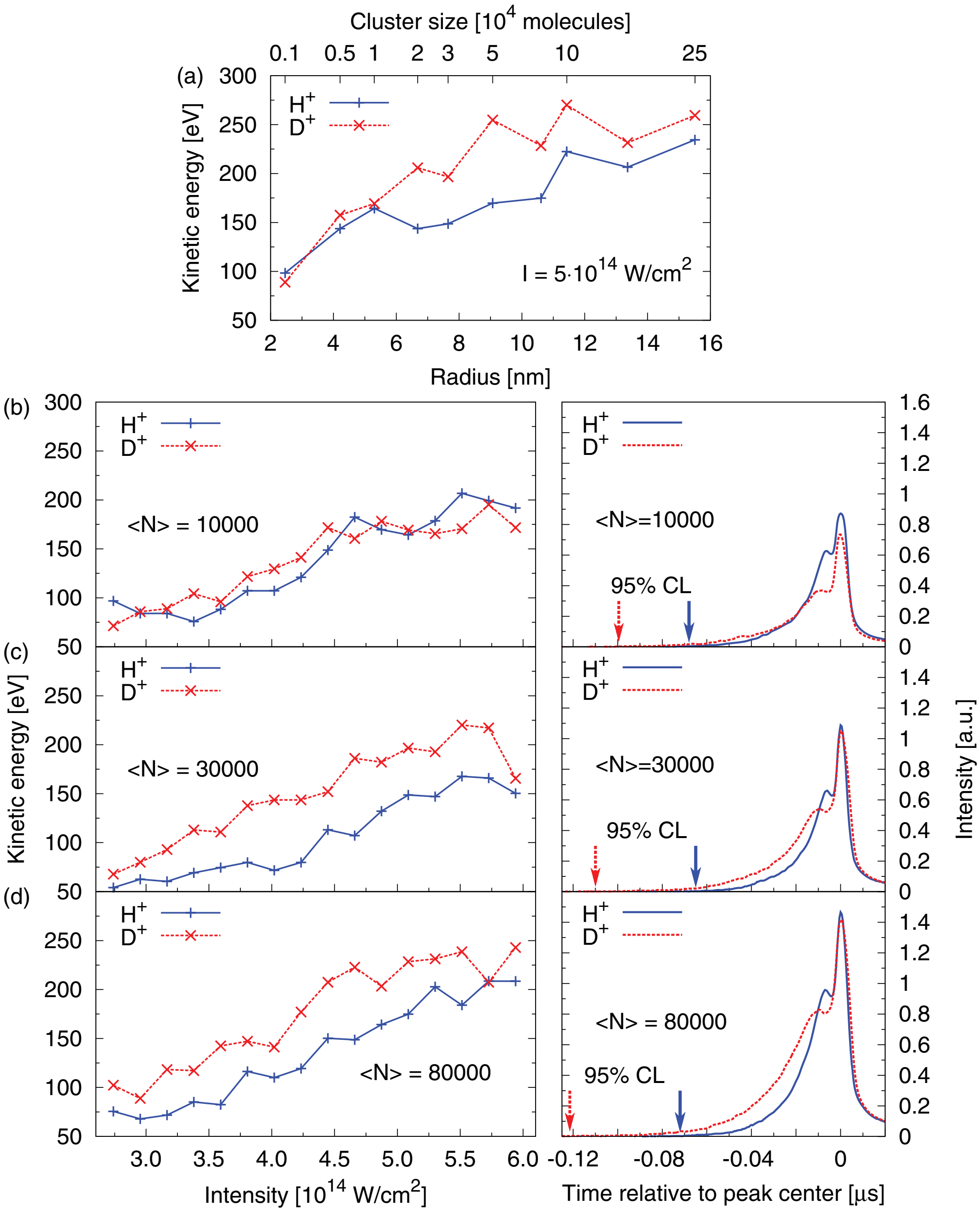

FIG. 4. (Color online) Highest detected kinetic energy of hydrogen and deuterium ions from molecular clusters. (a) The maximum detected kinetic energy, with a confidence level (CL) of 95%, for light ions (H^+ and D^+) from CH_4 and CD_4 clusters, is shown as a function of cluster size. The average pulse energy is 43 μJ (intensity 5×10^{14} W/cm^2). (b), (c), and (d) Kinetic energy of H^+ and D^+ ions from pure and deuterated methane as a function of pulse energy for fixed cluster sizes of (b) 10 000 molecules, (c) 30 000 molecules, and (d) 80 000 molecules. Deuterium ions from larger clusters (6.7-nm radius and higher) tend to be more energetic than hydrogen ions. The panel on the right shows the shape of the H^+ and D^+ peaks in the TOF data. The highest signal values of the two peaks were aligned by moving them to a reference time $t = 0$. Pulse intensity is 5×10^{14} W/cm^2, and the arrows show the time where signal is detected above background at 95% confidence level. The kinetic energy of the particles scales with $(\Delta t)^2$/mass.

size and influences the production of intermediate adducts, notably protonated methane $CH_5{}^+$. Such adducts have been observed in other type of experiments probing the ion-molecule chemistry, for example, electron impact ionization on methane clusters [30] and helium droplets doped with methane clusters [31]. These experiments used electrons of 20–70 eV to fragment the clusters and have observed a series of protonated and unprotonated cluster ions. These experiments happen on a longer time scale, in contrast to our experiment, which is almost instantaneous. In our case, the recombination happened after the ionizing femtosecond laser pulse had left the cluster, during the time the sample transited from liquid density to rarefaction.

Deuterons had systematically higher kinetic energies than protons in all experiments on clusters. The difference was size-dependent (Fig. 4). Cluster size, the total charge build-up, and Coulomb repulsion are determining factors in the explosions, and influence ion acceleration. Figure 4(a) shows the maximum measured kinetic energies for H^+ and D^+ ions as a function of cluster size at a pulse intensity of 5×10^{14} W/cm^2. Measured kinetic energies were between 50 and 300 eV, depending on the cluster size. The largest difference between the kinetic energies of protons and deuterons was 150 eV in clusters of 50 000 molecules [Fig. 4(a)].

Figures 4(b), 4(c), and 4(d) show the maximum detected kinetic energy of H^+ and D^+ ions as a function of pulse intensity for three fixed cluster sizes (10 000, 30 000, and 80 000 molecules). We exploited the stochastic fluctuations of the FEL to cover a larger range of pulse energies (20–53 μJ). The results show higher ion energies with increasing pulse intensity. The energy of D^+ ions was systematically higher in all measurements than the energy of protons. Classical molecular dynamics simulations [17] show that a mass difference would influence the energy distribution of accelerated ions during the pulse. H^+ ions would have a tendency to escape faster (and earlier) from a cluster, while D^+ ions would stay closer to the charged core as the core rapidly accumulates more charges. With pulses of Gaussian profiles, the rate of charge buildup starts slow and then increases steeply. As a result, D^+ ions would have an energy distribution that reaches higher energies than the energy distribution of protons, leading to a difference in the maximum detected energies. The energy distribution for C^+ ions is similar for carbon ions originating from clusters of CH_4 and CD_4. Fast-moving H^+ and D^+ ions remove positive charges from the cluster and also cool the system. As a result, carbon does not accelerate as much as these lighter ions.

Carbon has a relatively low photoionization cross section (0.65 Mb) at 92-eV incident photon energy. The size range of the clusters investigated here was much smaller than the attenuation length (1 μm) of 92-eV photons in liquid methane. This ensured a uniform ionization of the clusters during the pulse. We simulated the interaction of methane clusters with a FEL pulse using CRETIN [32], a non–local thermodynamic equilibrium plasma (non-LTE) code with radiation transfer and electron thermal conduction. The results gave an electron temperature of 4 eV after thermalization for all cluster sizes, and an average ionization of 0.5 per carbon atom at the end of the pulse (intensity: 5×10^{14} W/cm^2). Similar electron temperatures were observed in experiments with infrared lasers [12]. Our simulations account for electron impact ionization, which contributes significantly to the overall ionization of the clusters. It also treats electron-ion recombination (which happens within 10 fs) and electron-ion thermalization (which happens within about 100 fs). The simulations showed no significant differences in these processes as a function of sample size at these short time scales. Hydrodynamic expansion is a significantly slower process.

In a hydrodynamic expansion, larger samples are kept together for longer times as the sample burns from the outer layers toward its center at a steady rate. This rate is 0.01 nm/fs for methane clusters as calculated with CRETIN. Thus, the largest methane clusters used here are expected to explode in picoseconds, and this is consistent with the earlier observations on the explosion rates on nanosized polystyrene spheres [19]. As the cluster size increases, fragment composition would evolve from a state dominated by H^+ and C^+ toward a state where intermediate adducts and recombinant products can be observed. Bond formation requires extended interaction times, and this is only possible in larger clusters.

In conclusion, we performed experimental studies on the explosion dynamics of molecular CH_4 and CD_4 clusters in intense soft x-ray fields. We discovered a strong isotope effect in methane clusters exposed to intense X-ray pulses that, to our knowledge, was not observed in earlier infrared studies [22,23]. The deuterons spend a longer time than protons closer to the charged core and thus can reach higher kinetic energies. This isotope effect may be exploited at higher intensities and lower wavelengths to accelerate light ions to higher energies.

We thank Rolf Treusch, Matthias Duske, and the staff at FLASH for their help with the experiment, and Abraham Szoke and Mark Harris for useful comments on the manuscript. This work was supported by the following agencies: The Swedish Research Council, the Virtual Institute Program of the Helmholtz Association (VH-VI-302), the DFG Cluster of Excellence at the Munich Centre for Advanced Photonics, the DFG through Grant No. BO 3/69/2-2 to T. M., the European Research Council, and the Knut and Alice Wallenberg Foundation. Access to FLASH was supported by the European Union under Contract No. RII3-CT-2004-506008 (IA-SFS). The simulations were performed on resources provided by the Swedish National Infrastructure for Computing at UPPMAX, Projects No. s00111-71 and No. s00112-67.

---

[1] L. Young *et al.*, Nature (London) **466**, 56 (2010).
[2] H. Wabnitz *et al.*, Nature (London) **420**, 482 (2002).
[3] C. Bostedt, M. Adolph, E. Eremina, M. Hoener, D. Rupp, S. Schorb, H. Thomas, A. R. B. de Castro, and T. Möller, J. Phys. B **43**, 194011 (2010).
[4] C. Bostedt *et al.*, Phys. Rev. Lett. **108**, 093401 (2012).
[5] H. N. Chapman *et al.*, Nature (London) **470**, 73 (2011).
[6] M. M. Seibert *et al.*, Nature (London) **470**, 78 (2011).
[7] H. N. Chapman *et al.*, Nature (London) **448**, 676 (2007).
[8] B. Nagler *et al.*, Nat. Phys. **5**, 693 (2009).
[9] J. Andreasson *et al.*, Phys. Rev. E **83**, 016403 (2011).
[10] R. Neutze, R. Wouts, D. van der Spoel, E. Weckert, and J. Hajdu, Nature (London) **406**, 752 (2000).
[11] I. Last, I. Schek, and J. Jortner, J. Chem. Phys. **107**, 6685 (1997).
[12] T. Ditmire, J. Zweiback, V. O. Yanovsky, T. E. C. G. Hays, and K. B. Wharton, Nature (London) **398**, 489 (1999).
[13] B. Ziaja, H. Wabnitz, F. Wang, E. Weckert, and T. Möller, Phys. Rev. Lett. **102**, 205002 (2009).
[14] C. Bostedt, H. Thomas, M. Hoener, T. Möller, U. Saalmann, I. Georgescu, C. Gnodtke, and J.-M. Rost, New J. Phys. **12**, 083004 (2010).
[15] T. Fennel, K.-H. Meiwes-Broer, J. Tiggesbäumker, P.-G. Reinhard, P. M. Dinh, and E. Suraud, Rev. Mod. Phys. **82**, 1793 (2010).
[16] C. Bostedt *et al.*, Phys. Rev. Lett. **100**, 133401 (2008).

[17] M. Bergh, N. Tîmneanu, and D. van der Spoel, Phys. Rev. E **70**, 051904 (2004).

[18] S. P. Hau-Riege, R. A. London, and A. Szöke, Phys. Rev. E **69**, 051906 (2004).

[19] S. P. Hau-Riege *et al.*, Phys. Rev. Lett. **104**, 064801 (2010).

[20] H. Thomas *et al.*, J. Phys. B **42**, 134018 (2009).

[21] U. Saalmann, J. Phys. B. **43**, 194012 (2010).

[22] I. Last and J. Jortner, Phys. Rev. Lett. **87**, 033401 (2001).

[23] M. Hohenberger, D. R. Symes, K. W. Madison, A. Sumeruk, G. Dyer, A. Edens, W. Grigsby, G. Hays, M. Teichmann, and T. Ditmire, Phys. Rev. Lett. **95**, 195003 (2005).

[24] W. Ackermann *et al.*, Nat. Photonics **1**, 336 (2007).

[25] O. Hagena and W. Obert, J. Chem. Phys. **56**, 1793 (1972).

[26] K. W. Madison, P. K. Patel, D. Price, A. Edens, M. Allen, T. E. Cowan, J. Zweiback, and T. Ditmire, Phys. Plas. **11**, 270 (2004).

[27] K. Tiedtke *et al.*, New J. Phys. **11**, 023029 (2009).

[28] D. A. Dahl, Int. J. Mass Spectrom. **200**, 3 (2000).

[29] G. Scuseria, Nature (London) **366**, 512 (1993).

[30] H. J. Yi, Y. S. Kim, C. J. Choi, and K.-H. Jung, J. Mass Spectrom. **33**, 599 (1998).

[31] C. Leidlmair, P. Bartl, H. Schäbel, S. Denifl, S. Yang, A. M. Ellis, and P. Scheier, Chem. Phys. Chem. **13**, 469 (2012).

[32] H. A. Scott, J. Quant. Spectrosc. Radiat. Transf. **71**, 689 (2001).