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Highly charged carbon ions formed by femtosecond laser excitation of \( \text{C}_{60} \):
A step towards an x-ray laser

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We study the interaction of \( \text{C}_{60} \) molecules with intense (10–1000 TW/cm\(^2\)) femtosecond pulses of 790-nm wavelength. High charge states of carbon up to \( \text{C}^{8+} \) are produced in this intensity range, as determined by time-of-flight spectroscopy. These high charge states of carbon are produced at intensities more than an order of magnitude lower than would be required based on optical field ionization of isolated carbon atoms. From a line-shape analysis of the time-of-flight data, we derive the kinetic-energy distribution of the \( \text{C}^{\text{m+}} \) ions. We find average energies of up to a few hundred eV, indicating that these ions are released through Coulomb explosion of the \( \text{C}_{60} \) molecules once the charge buildup due to ionization becomes sufficiently high. I onic potentials of up to 200 V are derived from the kinetic-energy distributions. The ionic potential needed to retain electrons energetic enough to cause K-shell impact ionization is 392 V. This potential is not reached in case of ionization of \( \text{C}_{60} \) with 790-nm, 45-fs pulses since the disintegration of the cluster occurs on a time scale of a few femtoseconds, much shorter than the optical pulse. In this short time span, the heating of the cluster is not sufficient enough for higher charge states to be ionized. [S1050-2947(98)07812-3]

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I. INTRODUCTION

The interaction of ultrashort high-intensity laser pulses with matter has been the subject of intense theoretical and experimental research over many years. Besides the interest in developing a fundamental understanding of light-matter interaction under extreme high-intensity conditions, a major goal of many studies is the production of short-wavelength radiation and, more specifically, the realization of optically pumped x-ray lasers as a source of coherent, short-pulsed high-power x rays. The basic requirements for the realization of a recombination-pumped x-ray laser scheme are the production of highly charged ions to enable radiative inner-shell transitions, and the presence of a dense, cold-electron distribution to obtain an efficient pumping of these transitions through three-body recombination and collisional relaxation [1].

Most of the target materials previously investigated for laser-induced x-ray generation were either gases or solids, which were found to possess general characteristic advantages and disadvantages for potential x-ray laser applications. Optical field ionization (OFI) in the gas phase, which in the case of highly charged ions proceeds through tunneling, has been considered as a mechanism for production of cold electrons that could drive a recombination-pumped x-ray laser [2]. Experimental studies performed on plasmas formed from optical ionization of He, Ar, or Kr at relatively low densities (about 10\(^{10}\)cm\(^{-3}\)) and at laser intensities up to 100 PW/cm\(^2\) have shown that relatively low electron temperatures, in the range 10–50 eV [3], are obtained under these conditions. For the densities and at the intensities mentioned above, the dominant mechanism for plasma production is direct ionization of the atoms by the laser field. The ionization is primarily through tunneling of the electrons directly out of the atomic ground state [4]. The mechanism accounting for the temperature of the plasma is above-threshold ionization (ATI) [2], resulting from the excess energy the electron acquires in the laser field during ionization.

Another mechanism that could potentially lead to additional electron plasma heating is inverse bremsstrahlung. However, this mechanism only becomes important for plasma densities above 10\(^{20}\)cm\(^{-3}\). Thus, the electron temperature and density start rising considerably due to collisional heating and collisional ionization, respectively. As shown by Ditmire et al. [5], a helium plasma at the density of 10\(^{20}\)/cm\(^3\), excited by a 100 fs pulse with an intensity of 10 PW/cm\(^2\) will be heated to a temperature of about 100 eV.

Since OFI is the dominant mechanism for plasma production in low-density gases, strong optical fields and therefore extremely high intensities are required to reach a high degree of ionization. For example, from the barrier suppression model (BSM) [6,7], the threshold intensity for tunnel ionizing argon to a charge state of Ar\(^{9+}\) can be estimated to be 2000 PW/cm\(^2\). Obviously, this high intensity requirement of tunnel ionization forms a major drawback for a potential x-ray laser scheme based on gases, since a large number of ions and a large ionization volume will be required to produce sufficiently high x-ray gain. Nevertheless, specific x-ray laser schemes based on OFI have been proposed in neon [8] and experimental observation of x-ray gain has been reported for the 13.5 nm Lyman-\(\alpha\) transition in Li\(^{3+}\) [9].
On the other hand, in the interaction of short, intense light pulses with dense targets, i.e., condensed matter, incoherent, and broadband (continuum) emission of hard x radiation has been observed [10]. Studies performed so far have demonstrated the production of photons with very high energies, up to the MeV range [11]. These findings immediately indicate a much more efficient coupling of laser energy into the plasma than for gases. Absorption mechanisms in a solid-density plasma favor deposition of significant fractions (10%) of the laser pulse energy into the plasma [12,13]. A further enhancement in the absorption of the laser energy by solid targets has been achieved by using structured targets consisting of gold clusters [12,14]. An absorption of more than 90% of the incident laser energy was found, resulting in a high conversion efficiency of laser energy into x rays, of about 1% in the 1-keV photon-energy range.

For recombination-pumped x-ray laser schemes, solid targets clearly have the advantage of efficient creation of high charge states at relatively low laser intensities, due to collisional ionization in these dense ($\approx 10^{23}$ atoms/cm$^3$) and hot plasmas. However, the extremely high electron temperature of the plasma (exceeding several hundred eV) would lead to a drastic decrease of the three-body recombination rate and thus of the pumping efficiency for any inner-level transition [1].

Based on these facts, it has been realized that atomic clusters may combine the useful aspects of both gaseous and solid targets: Due to the (locally) high, solidlike densities, clusters are likely to absorb laser energy very efficiently, therefore resulting in strong x-ray yields upon illumination with short, intense pulses. A rapid hydrodynamic expansion of the resulting “microplasma” would then lead to efficient cooling, facilitating ion-electron recombination. Since this is required for recombination-driven population inversion of inner-shell transitions, clusters appear to be a promising “starting” material for optically pumped x-ray lasers.

High-pressure gas jets undergoing rapid expansion and, associated with that, adiabatic cooling, result in the formation of clusters in the jet. Illumination of these clusters with high-intensity femtosecond pulses (10 PW/cm$^2$), has been shown to produce rapidly cooling, moderate-density plasmas [15]. Clusters formed in gas jets show an enhanced absorption of laser light as compared to gases. This results in the production of high ion-charge states via collisional ionization and thus in strong x-ray emission from this hot plasma. The charge states produced are much higher than those predicted by OFI of individual atoms. From Kr and Ar clusters irradiated with high intensity laser pulses, copious L and M shell keV x rays were detected [16]. This strong x-ray emission occurs on a time scale determined by hydrodynamic expansion and cooling of the plasma. In the keV range, emission of x rays was speculated to occur on a time scale shorter than 1 ps [17]. Studies based on classical-trajectory Monte Carlo simulations of inner shell ionization and electron dynamics in femtosecond laser-driven clusters also point to efficient K- and L-shell x-ray emission from rare gas (large) clusters [18].

A disadvantage of the noble-gas clusters studied so far is that neither the structure nor the size of the clusters are well defined. An alternative to these noble-gas clusters is the buckminsterfullerene molecule C$_{60}$, that can also be regarded as a small natural “carbon cluster.” Ever since its discovery [19], there has been ongoing interest in the study of the C$_{60}$ molecule, also with respect to its interaction with intense laser light (see Ref. [20], and references therein). In a recent paper, Wülker et al. [21] have already shown that excitation of a vapor of C$_{60}$ clusters with a high-intensity subpicosecond (6 PW/cm$^2$) KrF laser results in efficient highly charged ion production and x-ray line emission, similar to the experimental results with rare gas clusters.

The interaction of short-pulse lasers with clusters formed in gas jets has been studied extensively in a recent paper by Ditmire et al. [5]. Three stages in describing the interaction of femtosecond laser pulses with clusters in general (and C$_{60}$ molecules in particular) can be distinguished, namely, the initial ionization of the cluster, the heating of the electrons still bound to the cluster and the cluster expansion.

In a recent paper [22], ionization of C$_{60}$ with 790 nm light at intensities below 100 TW/cm$^2$ has been shown to occur via multiphoton excitation of the 20 eV plasmon resonance. This mechanism of collective excitation of the plasmon accounts for the ionization of the molecule as the first step in the interaction with femtosecond, infrared laser pulses. Once a few electrons are created, they will be driven by the laser field into a quiver motion, gaining ponderomotive energy from the field. These energetic electrons will then collide with other atoms in the medium, knocking other electrons off. Higher charge states are produced in this hot plasma through collisional ionization, as a result of the high density in the cluster. The third stage is the expansion of the cluster: it will be a Coulomb explosion that occurs when a significant charge has accumulated on the cluster.

In the present experiment, we study the interaction of C$_{60}$ molecules with a femtosecond Ti:sapphire laser at intensities in the range 10 TW/cm$^2$–1000 TW/cm$^2$. This study is largely motivated by the idea of exploring C$_{60}$ molecules in combination with Ti:sapphire laser radiation as candidates for a recombination-pumped x-ray laser in the water window (2.3–4.4 nm). As a first step, we investigate the production of highly charged carbon ions at the abovementioned intensities. Furthermore, to obtain more insight into the dynamics of highly charged molecules and the characteristics of the hot microplasmas formed upon irradiation with short, intense laser pulses, we investigate the electron temperature of the plasma, the average charge developed on the C$_{60}$ molecule prior to the Coulomb explosion and the kinetic-energy release of the C ions from this explosion, as a direct probe of the ionic potential created by the C ions.

In Sec. II, we present the experimental setup used to investigate the ionization of C$_{60}$ with femtosecond, high-intensity Ti:sapphire laser pulses. Several algorithms used to analyze the data are discussed in Sec. III. Experimental results are presented and discussed in Sec. IV. Conclusions and a comparison with related work is given in Sec. V.

II. EXPERIMENTAL SETUP

Figure 1 shows a schematic view of the experimental setup. For the ionization experiments of C$_{60}$, we used a chirped-pulse amplification (CPA) Ti:sapphire laser system, similar to that described in Ref. [23]. The laser operates at 1 kHz repetition rate, 790 nm central wavelength; the energy
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FIG. 1. Schematic of the experimental setup. A C\textsubscript{60} molecular beam, formed in an oven, crosses at right angles a focused Ti:sapphire laser beam. The carbon ions produced in the laser focus, between the extraction plates of an ion spectrometer, are accelerated by a field of 2 kV/cm in the direction of the ion detector. Time-of-flight spectra of the C ions are collected with a digital scope.

per pulse after stretching, regenerative amplification, and recompression is 600 \(\mu J\). The average pulse duration is adjustable between 45 and 390 fs. The experiments are performed in a time-of-flight (TOF) ion spectrometer. The femtosecond laser beam is focused into the ionization region with an \(f = 40\) cm lens. The pulse duration is varied by adjusting the grating distance in the compressor. The energy of the laser pulses is varied by a combination of a \(\lambda/2\) plate, placed in front of the compressor, and a thin-film polarizer.

A C\textsubscript{60} molecular beam is produced by evaporating purified fullerene powder (99.7%, Hoechst AG) in a small oven at a temperature of about 600 K. The C\textsubscript{60} vapor forms a collimated beam entering the ionization region through an orifice in the oven of 1 mm diameter. The fullerene beam passes between the plates of the TOF setup, where it crosses at right angles with the laser beam. The C\textsubscript{60} density at this point is estimated to be \(10^{10}\) molecules/cm\(^3\). The carbon ions produced in the laser focus are accelerated perpendicularly to both the C\textsubscript{60} and the laser beam, towards an ion detector. The electric field accelerating the ions is typically \(V_{\text{acc}} \approx 2\) kV/cm. The ions pass the upper plate of the extraction region through a narrow slit (1 \(\times\) 30 mm) perpendicular to the laser beam and enter a 17 cm field-free drift region (indicated with \(x_{\text{dir}}\) in Fig. 1). The ion detector is a microsphere plate (MSP) detector (El-Mul Technologies, Ltd.). TOF spectra are collected with a digital oscilloscope and transferred to a personal computer. The intensity dependence of the C-ion yields in the time-of-flight spectra is obtained by binning the data according to the energy of individual laser shots, as measured by a calibrated photodiode.

One of our aims in this paper is to investigate the intensity dependence of the C-ion production. This yield might still change above the ‘‘saturation intensity’’ (the intensity at which 100\% of the clusters disintegrate) because of additional rapid heating. Such a change is likely to be obscured by focal-volume effects if no special precautions are taken. In order to avoid domination of the signal by regions with an intensity much lower than the peak intensity, arising from the large volume before and after the focus, the narrow slit is used, as indicated in Fig. 1. This 1 mm wide slit blocks all ions except those originating from that part of the focal volume which has a nearly homogeneous intensity distribution along the propagation coordinate \(z\).

By focusing the femtosecond laser beam [9 mm full width at half maximum (FWHM) beam diameter] with an \(f = 40\) cm lens, a nearly collimated beam is obtained in the focus, with a confocal parameter \(b = 1.4\) mm. In order to extend the region of maximum on-axis intensity, the lens was tilted by an amount such that the resulting astigmatism reduced the maximum intensity by a factor of 2. In this configuration, the second derivative of the intensity in the \(z\) direction vanishes. This optimizes the homogeneity of the intensity in the region visible through the slit and increases the depth of the focus by a factor \(\frac{1}{12}\) FWHM, to 2.6 mm, causing a theoretical intensity variation in front of the slit of less than 0.1\%. Although this makes the beam cross section elliptical in places, the resulting intensity distribution in the focus is the same as for a cylindrically symmetric Gaussian profile. Although spatial averaging over intensities still takes place in this focus due to the radial intensity profile, it will be shown in Sec. III that such a profile allows ‘‘deconvolution’’ of experimental data in order to obtain yields as a function of the true pulse peak intensity, as opposed to the maximum peak intensity in the focus.

The maximum intensity reached in the experiment is estimated from calibration measurements performed on xenon. At the maximum intensity, ions up to Xe\textsuperscript{5+} were detected. The barrier-suppression model, as applied to Xe, predicts a threshold intensity required to reach the fourth ionization stage of about 1000 TW/cm\(^2\). The threshold intensity needed to ionize Xe to the fifth ionization stage is about 1700 TW/cm\(^2\). Apparently this intensity was not reached in our experiment, since no Xe\textsuperscript{5+} ions were detected. The maximum intensity deduced from calibration measurements is at least 33\% lower than what would be estimated from beam diameter, pulse energy and pulse duration. This difference is probably due to an imperfect beam mode.

Time-of-flight measurements are performed for two different pulse durations, namely, 45 fs, the shortest obtainable pulses, and ‘‘long’’ pulses of 390 fs. The pulse duration is varied by adjusting the grating distance in the laser compressor. Assuming that the profile of the pulses will be unaffected by chirping them, the maximum intensity reached in the ‘‘long’’ pulse case is about 9 times lower than in the case of the short pulses of the same energy.

III. DATA ANALYSIS

In order to extract ion kinetic-energy distributions and intensity dependences of the ion yields from the ion TOF spectra, careful analysis is required. A typical TOF spectrum is shown in Fig. 2. The pulse duration used for this measurement is \(\tau_p = 45\) fs. The extraction field accelerating the carbon ions is 2.9 kV/cm, resulting in flight times of the order 1 \(\mu s\) for the singly charged carbon ion. As seen from Fig. 2, carbon ions up to C\textsuperscript{4+} are detected. The inset in the figure shows a blow-up of that part of the spectrum corresponding to ions having a low mass-over-charge \((m/q)\) ratio, namely, the peaks corresponding to the H\textsuperscript{2+} and the C\textsuperscript{4+} ions.

An important feature (as can also be seen from the inset)
in Fig. 2 is the large width of the C-ion peaks, as compared to the narrow peaks corresponding to doubly ionized oxygen and singly ionized molecular hydrogen. The peaks that do not arise from ionization of C_{60} have a width of about 5 ns FWHM, resulting from the finite focal size and from the detector response. The broad peaks corresponding to the C ions suggest that these ions result from the Coulomb explosion of the C_{60} molecule, having a large kinetic energy distribution and therefore giving a broad peak in the TOF spectrum.

In the TOF experiment, we record the flight time to the ion detector of C ions produced upon irradiation of the C_{60} molecules with fs laser pulses. The time-of-flight \( t \) for ions having nonzero kinetic energy \( E_{\text{kin}} \) is given by the expression

\[
 t = \frac{x_{\text{drift}}}{\sqrt{2m/\left(qU_{\text{ext}} + E_{\text{kin}}\right)}} + \delta t,
\]

where \( x_{\text{drift}} \) is the length of the field-free drift region (indicated in Fig. 1), \( U_{\text{ext}} \) is the potential energy the ions are extracted with, \( m \) is the mass of the ions, and \( q \) their charge. The second term in Eq. (1) describes the time spent between the acceleration plates. Neglecting this small term, ions having zero-kinetic energy have a flight time proportional to the square root of the ratio \( m/q \) (mass-over-charge). These ions are identified on the basis of their \( m/q \) ratio, given a certain extraction potential.

In order to analyze the data from the TOF spectra, the acceptance angle of the detector in the TOF section has to be taken into account. Only a fraction of the C ions generated from the Coulomb explosion of the C_{60} cluster will be detected by the ion detector. The maximum accepted transverse velocity of the C ions is \( (d/2x_{\text{drift}})v_0 \), \( d = 2.5 \) cm being the diameter of the ion detector, \( v_0 \) the velocity acquired due to the acceleration potential, and \( x_{\text{drift}} = 17 \) cm is the length of the field-free drift region in the TOF section. The solid angle (in units of \( 4\pi \) sr) in which ions created through the Coulomb explosion of the C_{60} are detected is then given by

\[
\eta = 1/2 \left( 1 - \sqrt{1 - \frac{d^2v_0^2}{2x_{\text{drift}}^2a^2}} \right),
\]

\( v \) being the initial velocity of the ions.

The direction of ejection of the C ions released through Coulomb explosion is experimentally established by recording two TOF spectra, one for the laser polarization in the horizontal direction and the other for the polarization rotated by 90°. The two TOF spectra were identical, confirming the hypothesis of an isotropic Coulomb explosion. For an isotropic explosion, the detected fraction of ions is proportional to the detector acceptance angle \( \eta \). From Eq. (2), it follows that this fraction decreases with the kinetic energy of the C ions. To correct for this, the energy spectrum will be built up by multiplying with \( 1/\eta \). Of all the ions ejected isotropically with significant energy in the interaction region, only two groups will reach the detector: those ejected toward and others ejected away from the detector. This gives rise to different arrival times at the detector for ion species emerging from the Coulomb explosion with the same kinetic energy, but in different directions. Ions launched away from the detector will be turned around by the extraction field towards the detector, making thus a detour as compared to the ions ejected directly towards the detector. This time delay between ions ejected towards and ions ejected away from the detector is given by the expression

\[
\Delta t = \frac{2v}{a},
\]

where \( a \) is the acceleration due to the extraction field \( a = qU_{\text{ext}}/m \). For zero kinetic energy C ions, the nominal arrival time corresponds to a peak in the yield of each of the C ions in Fig. 2. The longest flight time corresponds to ions having a very slow initial velocity away from the detector and is only a few nanoseconds longer than the nominal arrival time: if the initial velocity is significant, it takes a little longer to turn the ion around, but this is more than offset by the larger kinetic energy with which the ion traverses the field-free flight tube. The observed asymmetry of the C-ion lines in the TOF spectra can be explained by the fact that ions ejected away from the detector will be turned around by the extraction field and will arrive later at the detector than the forward ions, but still early as compared to the nominal flight time. However, a detailed interpretation requires a thorough data analysis, as will be discussed below.

The kinetic energies of the ions were determined from the TOF spectra by “unfolding” the peaks in there according to Eq. (1) for every C-ion species. As pointed out above, the total measured ion yield consists of two contributions: ions that are initially created with velocities in the direction of the detector and ions that are created with a velocity in the opposite direction. Obviously, these two signal contributions are shifted with respect to each other by the time interval that is required to revert the backward ions and accelerate them back into the direction of the detector.

Kinetic-energy distribution of the C ions are determined as follows: starting with the fastest ions, the unfolding algo-
rithm converts the time channels in the time windows corresponding to each ion species in the raw TOF spectra into a dissociation velocity, assuming these ions went in the forward direction. From the extraction field strength, the arrival time of ions ejected with the same energy in the backward direction can be calculated. Subsequently, the contribution to the signal from the ions ejected in the backward direction (supposed equal to that in the forward direction) is subtracted from the total yield at this arrival time, making the purely forward contribution of ions of lower energy available to the unfolding algorithm once processing has advanced to this flight time.

Measured ion yields, after unfolding and correcting them for the energy-dependent fraction of ions reaching the detector, are still a result of spatial averaging over intensities in the focal volume. In order to obtain yields as a function of the true intensity, as opposed to maximum peak intensity in the focus, we retrieve the true intensity dependence \( S(I) \) of the signal. The measured signal depends on \( S(I) \) as

\[
M(I_0) = \int_0^{I_0} dV(I_0) S(I),
\]

\( dV(I_0) \) being the focal volume in which an intensity between \( I \) and \( I + dI \) is present for a pulse peak intensity \( I_0 \). In our experimental setup, the focal volume is restricted in the axial direction \( z \) to a length much smaller than the Rayleigh length. Assuming a Gaussian laser beam profile, the focal intensity distribution can be approximated by a \( z \)-independent cylindrically symmetric Gaussian with waist \( w_0 \):

\[
I(r,z) = I_0 \exp\left(-\frac{r^2}{w_0^2}\right).
\]

The volume element is \( dV = 2\pi r dr dz \). The derivative of the intensity distribution [Eq. (5)] can be expressed in terms of the volume element \( dV, dI \approx dV/I \) thus resulting in an expression for the focal volume element, \( dV(I_0) \approx dI/I \), independent of \( I_0 \). This formula in combination with Eq. (4) results in a simple expression for the true signal \( S(I) \), namely,

\[
S(I) = I_0 \frac{d}{dI_0} M(I_0).
\]

In other words, for this particular intensity profile, recovering the true dependence from the measured one requires the derivative of the measured yield and multiplication by the intensity.

To test the validity of this procedure, we analyzed the total yields measured for \( \text{Xe}^+ \) and \( \text{Xe}^{2+} \), under the focusing conditions of the \( \text{C}_{60} \) experiment, as a function of intensity. The result of the deconvolution method used on \( \text{Xe} \) is presented in Fig. 3. The curve for \( \text{Xe}^+ \) shows saturation due to depletion of the ground state at an intensity of 200 TW/cm\(^2\), and from there to 550 TW/cm\(^2\) the yield indeed stays approximately flat. The signal then drops again in favor of the production of \( \text{Xe}^{2+} \). Since we do not know the exact dependence of the ion-detector efficiency on the charge state, we multiplied the yield for the \( \text{Xe}^+ \) ion by a factor of 2.15, such that the sum of the two yields, \( \text{Xe}^+ \) and \( \text{Xe}^{2+} \), in the saturated part is constant as a function of intensity.

The increase of the \( \text{Xe}^+ \) signal above an intensity of 800 TW/cm\(^2\), must be an artifact of the procedure used to retrieve the real intensity dependence of the signal, probably due to the presence of a diffraction ring or a secondary maximum around the focal volume, which starts to contribute to the \( \text{Xe}^+ \) yield when the central focal intensity reaches 800 TW/cm\(^2\). However, in the range up to 10 times the appearance intensity of \( \text{Xe}^+ \), the applied procedure works quite satisfactorily.

### IV. RESULTS AND DISCUSSION

The \( C^+ \)-ion yields measured as a function of intensity are shown in Fig. 4. In both cases, the yields result from unfolding and correcting the raw TOF spectra for the acceptance of the ion detector, as discussed in Sec. III. They represent the total integrated area of each of the \( C^+ \)-ion peaks in these corrected TOF spectra.

The ion yields shown in Figs. 4(a) and 4(b) result from excitation of the \( \text{C}_{60} \) molecules with laser pulses having different durations. In Fig. 4(a), the pulse duration is \( \tau_p = 390 \text{ fs} \), while for the yields in Fig. 4(b), \( \text{C}_{60} \) is excited with the shortest obtainable pulses, \( \tau_p = 45 \text{ fs} \). The intensity ranges of the two plots correspond to the same pulse fluence. For both measurements, with long and short pulses, the dominant ion formed at all except the low intensities is \( \text{C}^{2+} \), as can be seen from the total ion yields.

A qualitative difference between the two sets of measurements seems to be the saturation of the ion yields: In the long-pulse case, this seems to occur for all the ion species, and quite clearly for the highly charged ions \( \text{C}^{3+} \) and \( \text{C}^{4+} \), while this is different for ionization with short pulses. In this case, for all the charge states except \( \text{C}^+ \), no obvious saturation occurs. Note that the vertical scales in Figs. 4(a) and 4(b) cannot be compared, due to a difference of the \( \text{C}_{60} \) density between these measurements.

The measured ion yields presented in Fig. 4 result from
the spatial average of the intensity-dependent signal over the focal volume. Since we want to investigate the exact fluence/intensity dependence of the ion production, we use the procedure discussed in Sec. III to retrieve the true intensity dependence of the measured yields of the C ions. The result of this procedure for the short-pulse and the long-pulse measurements is shown in Fig. 5. As can be seen from both plots, at all but the lowest intensities, the dominant ion species is the $\text{C}^{2+}$ ion. For intensities ranging from 30 TW/cm$^2$ to 1000 TW/cm$^2$, all the ion species $\text{C}^{n+}$, $n = 1 – 4$ are present. Furthermore, from Fig. 5 the appearance intensity of the $\text{C}^{4+}$ ion can be estimated to be about 30 TW/cm$^2$, more than an order of magnitude lower than the appearance intensity for this ion species based on OFI of isolated carbon atoms.

From the corrected data in Fig. 5, we can extract parameters relevant for the various stages of the disintegration process. In our idealized model, we suppose that the process starts after enough valence electrons are excited to antibonding states to break up the molecule. Once this has happened, the atoms are no longer chemically bonded, and the eventual fate of the cluster (total disintegration) is sealed. At this point, saturation of the total yield occurs.

The unbound plasma of ions and valence electrons will expand and during this expansion, additional heating of the electrons will take place due to the laser field. This stage can be characterized by the electron temperature reached before the molecule disintegrates into individual electrons and ions. This final temperature, that determines to which extent the ions can retain electrons, continues to increase with laser intensity, even after saturation of the total yield occurs.

The heating stage lasts for a short time only, since electrons evaporate from the plasma leading to an excess positive charge that causes rapid explosion of the molecule. This explosion continues even after all electrons have escaped from the plasma, irrespective of the laser. The kinetic-energy distributions of the different charge states can be used to obtain information on the details of this stage. Because the pulse duration potentially plays an important role in the various stages, we now discuss total yields, electron temperature and kinetic-energy distributions and their dependence on pulse duration.

In the long-pulse case, the ion yields seem to saturate at 30 TW/cm$^2$; for higher intensities, no more changes occur in the curves. The singly ionized carbon yield shows a somewhat different behavior as compared to those of other charge states: the yield has a dip for intensities beyond the saturation value, and then increases again. We have no explanation for this effect, but are inclined to see it as a real effect rather than an artifact of the deconvolution method, since it did not appear in the Xe data.

In the short-pulse case, the ion yields for the different charge states seem to saturate at an intensity around 300 TW/cm$^2$. Furthermore, the curves show a different behavior than in the long-pulse case: they saturate more gradually. Since we are interested in the disintegration of the cluster during the laser pulse and also in the possible additional heating of the electron plasma after disintegration of the cluster, we calculate the “total yield” and the “total

**FIG. 4.** Ion yields for $\text{C}^{n+}$, $n = 1 – 4$ as a function of intensity when ionizing the cluster with (a) long pulses $\tau_p = 390$ fs and (b) short pulses $\tau_p = 45$ fs. The yields are plotted on a log-log scale. The intensity ranges correspond to the same pulse fluence, but different pulse durations.

**FIG. 5.** True intensity dependence of the ion yields $\text{C}^{n+}$, $n = 1 – 4$ when ionizing the cluster with (a) long pulses, $\tau_p = 390$ fs and (b) short pulses, $\tau_p = 45$ fs.
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charge'' from the ion yields shown in Fig. 5. The results are plotted as a function of intensity in Fig. 6 for both the long-pulse (a) and the short-pulse (b) case. The total yield is defined as the sum of the yields of all the C ions, \(\Sigma_{n=1}^{\infty} N_{C^n}\), and is a measure for the amount of disintegrated cluster. In the total yield as defined above, neutral carbon atoms have not been taken into account since they could not be detected. Furthermore, the yield for the \(C^+\) ion has been corrected by a factor of 2.15, accounting for the ion-detector efficiency. The total cluster charge, defined as \(\Sigma_{n=1}^{\infty} q_{C^n} N_{C^n}\), where \(q\) is the charge of each of the C ions, is a measure for the extent to which the cluster can be heated during the laser-pulse, even after disintegration.

For the long-pulse measurement, it can be seen from Fig. 6(a) that saturation of the total yield occurs at an intensity of about 30 TW/cm\(^2\). At this intensity, the cluster is completely disintegrated. Saturation of the heating of the cluster (curve labeled ‘‘total charge’’) sets in at the same intensity as does the total yield. We can therefore conclude, that in the long-pulse case, increasing the intensity above 30 TW/cm\(^2\) will not contribute any further to the heating of the cluster.

In the short-pulse case, beyond 250 TW/cm\(^2\), the total yield remains approximately constant. Thus, saturation seems to occur at an intensity about 9 times higher than in the long-pulse case. From this, we can conclude that saturation of the total yield is a function of fluence rather than of intensity, since the fluence of the pulse needed to reach saturation is the same in both cases. To make this conclusion more quantitative, the amount of neutral carbon atoms as a function of intensity should be known. This would then un-ambiguously determine the intensity at which 100% cluster disintegration occurs in the short-pulse case.

In the case of ionization of \(C_60\) with short pulses, Fig. 6(b), the heating of the cluster appears to saturate at an intensity around 400 TW/cm\(^2\), higher than the intensity where complete disintegration of the cluster occurs. Qualitatively, it can be seen that the curve labeled ‘‘total charge’’ still increases beyond the point where the curve labeled ‘‘total yield’’ stays approximately constant. That suggests, that in the short-pulse case, there is still additional heating of the electron plasma during the pulse, even at intensities exceeding the saturation of the cluster disintegration yield.

A. Estimate of the electron temperature

In the previous section, we discussed the additional heating of the clusters occurring during the pulse, and concluded that in the short-pulse case, the saturation of this heating sets in at a higher intensity than the cluster disintegration does. Therefore, an obvious parameter giving more insight into plasma heating during ionization is the electron temperature.

We estimate the electron temperature using the Saha equation [24]. This equation is an extension of the Boltzmann distribution formula to ionized atoms. For a plasma in (local) thermal equilibrium, it gives the ratio of ion densities \(n_{z-1}/n_z\) for consecutive charge states \(z-1, z\):

\[
n_{z-1}/n_z = \frac{2}{U_{z-1}(T)} \frac{U_z(T)}{U_z(T)} \frac{(2\pi m_i kT)^{3/2}}{h^3} \exp\left(-\frac{I_{z-1}}{kT}\right),
\]

where \(n_e\) is the total electron density, \(m_o\) is the electron rest mass, \(T\) is the plasma temperature, \(k\) the Boltzmann constant, and \(I_{z-1}\) the ionization energy. The partition functions \(U_z(T)\) and \(U_{z-1}(T)\) for the ions involved are defined as

\[
U(T) = \sum g_i \exp(-E_i/kT),
\]

Experimentally, we determine from the deconvoluted total yields in the short-pulse case, at the highest intensity, the ratio’s of the charge state abundances \(N_{C^{z-1}}/N_{C^z}\), \(N_{C^{z+}}/N_{C^{z+}}\), and \(N_{C^{z+}}/N_{C^{z+}}\). These ratios are fitted to those obtained from the Saha equation using the plasma temperature \(T\) and the electron density \(n_e\) as fitting parameters. The energy values \(E_i\) for the levels entering the summation in equation (8) are obtained from spectroscopic data [25]. We limit the summation in Eq. (8) to energy levels of all \(C^+\) ions with a maximum principal quantum number of \(n=2\). This constraint is justified, since in a high-density plasma, as is the case for the \(C_60\) molecule, quantum orbits of excited energy states with principal quantum numbers above \(n=2\) are delocalized and cannot be described as belonging to any particular ion.
The best fit to the experimental data is found for an electron density \( n_e = 8.9 \times 10^{23} \text{ cm}^{-3} \) and an electron temperature \( T = 72.5 \text{ eV} \). The electron density corresponds to 240 \( \pi \) electrons in a sphere with a radius of 4 Å. We used these parameters and the experimentally determined number of ions in the first ionization stage to calculate the number of neutral carbon atoms via Eq. (7). In the short-pulse case, at the highest intensity, the partition of neutrals and ions in the various charge states is 3% neutrals, 32% \( C^+ \), 40% \( C^{2+} \), 22.9\% \( C^{3+} \), and 2.1\% \( C^{4+} \). From these charge-state abundances and the number of neutrals, at all but the lowest intensities, the resulting average total cluster charge is found to be 114.

Note that our description of the disintegration does not exclude the possibility that some of the neutral atoms stay attached to each other or to singly charged ions, since the dominant force driving the separation of fragments is their Coulomb repulsion. Experimentally we could not study this question further; our detector is blind to neutral polyatomic fragments, and a possible yield of \( C^+_2 \) from the disintegration is completely masked by the production of this fragment in the low-intensity fringes of the focus, where it is a major decay product [26] of vibrationally excited \( C^{60} \). Multiply charged polyatomic fragments are not expected under conditions where the electron temperature is high enough to distribute electrons more or less equally over bonding and antibonding orbitals. The small fraction of neutrals predicted by the Saha equation makes one suspect that production of polyatomic fragments is not very significant anyway.

We want to remark that the Saha equation is deduced for a tenuous plasma in local thermal equilibrium. Since this is not the case for the \( C^{60} \) plasma, we do not expect this description to give more than an estimate of the electron plasma temperature, nor do we expect the electron densities to have a real significance.

**B. Kinetic-energy distribution of C Ions**

Through ionization of the \( C^{60} \) cluster, a certain cluster charge is developed, giving rise to an ionic potential well. This potential can sustain electrons with a certain kinetic energy (temperature). If the charge buildup becomes sufficiently large, the cluster will undergo a Coulomb explosion. By studying the kinetic-energy release of the C ions released through this explosion, the depth of the ionic potential well from where these ions generate, is directly probed. From this potential, the charge distribution within the \( C^{60} \) molecule prior to the Coulomb explosion event is also deduced. From the ionic potential created during the laser pulse, the maximum temperature of the electrons bound to this potential can be deduced and compared to the values obtained from the Saha equation and the experimentally determined charge-state abundances.

Using the unfolding algorithm described in Sec. III, kinetic-energy distributions (KED’s) for all the \( C^{n+} \) ions \( (n = 1–4) \) are obtained from the TOF spectra. For the shortest pulse duration \( \tau_p = 45 \text{ fs} \), these energy distributions are presented in Fig. 7. Furthermore, the intensity dependence of the kinetic-energy distribution for all the C ions is investigated. The different traces presented in Fig. 7 for each of the \( C^{n+} \) ions, \( n = 1–4 \) correspond to intensities in the range 100 TW/cm\(^2\) to 1300 TW/cm\(^2\) from bottom to top.

A first feature that can be observed from the plots is that the higher the charge state, the broader the KED becomes. For \( C^{4+} \), the maximum of the distribution occurs at a value of the kinetic energy of 430 eV at all the intensities investigated. The kinetic energy distribution extends to a value of 800 eV. From these values, we conclude that the ions originate from a distribution of potentials from zero to \( \approx 200 \text{ V} \). (Note that the kinetic-energy distributions still contain the effect of spatial averaging over the focus; their signal to noise ratio did not allow deconvolution.) From the average value of the potential (108 V) and the average cluster charge of 114, resulting from the charge-state abundances, the radius of the cluster can be deduced. A value of 15 Å is found, more than a factor of 4 larger than the initial size of the cluster of 3.6 Å.

The kinetic-energy distribution for the \( C^{3+} \) ions peaks at a kinetic energy of 300 eV, at the highest intensities. This value of the kinetic energy indicates that these ions result from an average potential of 100 V, in agreement with the value of the potential deduced from the KED of the \( C^{4+} \) charge state. The width of the KED for the \( C^{3+} \) charge state of 600 eV also points out to the fact that the maximum value of the ionic potential created in the \( C^{60} \) molecule is of 200 V. Another aspect of interest is the increasing width of the KED with intensity. This effect is more obvious for the \( C^{3+} \) ion than for \( C^{4+} \), as the yield of \( C^{3+} \) ions is higher than for the higher charge state. The width of the KED increases from a value of 200 eV at the lowest intensities investigated, to the
value of 600 eV at the highest intensity. The higher the laser intensity, the deeper the ionic potential created.

The KED for the C$^{2+}$ ion is about 300 eV wide and peaks at a value of $\approx$ 90 eV at the highest intensity. We explain the lower value of the ionic potential that results from the peak value of the KED and its width by the fact that lower charge states do not feel the repulsion from the full charge but only from the charge inside the spherical shell they are on. Once the Coulomb explosion of the “plasma ball” sets in, the higher charge states move outwards more rapidly than the lower charge states. The charge in the lower charge states then continues accelerating the higher ones but do not feel any accelerating force in return. This remark holds even to a larger extent for the KED of the singly charged ions. Only few of these ions seem to have energies exceeding 50 eV, most of the ions having a quite narrow energy distribution. This suggests that singly charged C ions do not necessarily originate from the violent Coulomb explosion of the cluster.

The kinetic-energy distributions of all C ions, when the C$_{60}$ clusters are ionized with long (390 fs) pulses, are shown in Fig. 8. In this case versus ionization with short pulses, two main differences in the kinetic-energy distributions occur: (i) the overall width of the distributions is lower and (ii) the maxima of each of the KED’s for the various C ions are shifted towards lower values of the kinetic energy. As can be seen from Fig. 8, for the C$^{4+}$ ion, the KED extends to 500 eV as compared to 800 eV for the same charge state in the short-pulse measurement. The maximum of the KED is found at 250 eV, lower than in the short-pulse case. The ionic potential resulting from ionizing the cluster with longer pulses seems to be more shallow than what is deduced for the short-pulse case. From the KED’s for C$^{4+}$ and C$^{3+}$ a value of the ionic potential of 125 V follows, the kinetic energy corresponding to the maximum of the distribution resulting in a potential of 60 V.

The values we found for the kinetic-energy distributions of the C ions of a few hundred electron volts are comparable to those found by Purnell et al. [27], when investigating the kinetic-energy releases of excited HI and HIAr$^m$ clusters with intense, femtosecond pulses. Similar results have been obtained by Snyder et al. [28] when investigating the laser-induced explosion of ammonia clusters. In both cases, the explanation given for the high kinetic energies of multi-charged species was based on the Coulomb explosion of the clusters.

V. CONCLUSIONS

Through irradiation of C$_{60}$ molecules with laser pulses at intensities ranging from 10 to 1000 TW/cm$^2$, charge states up to C$^{4+}$ have been observed. These charge states have been observed at intensities much lower than predicted on the basis of optical field ionization of isolated carbon atoms. No charge states higher than C$^{4+}$ have been observed in this intensity range and at the wavelength of 790 nm.

The estimated electron-plasma temperature of 72 eV from charge-state abundances implies that the electrons have sufficient energy to collisionally ionize C ions up to C$^{4+}$ ions. The ionization potential of the latter is 64.5 eV. The ionization energies for C$^{5+}$ and C$^{6+}$ are 392 and 490 eV, respectively, both much higher than the electron temperature. The electron plasma is thus too cold to collisionally ionize carbon to more than C$^{4+}$.

We now address the question, why the electron temperature cannot be increased enough to produce higher charges than C$^{4+}$, even by the use of shorter pulses. The ionic potential needed to retain electrons energetic enough to cause K-shell impact ionization is 392 V. To create such a potential, in the initial configuration at least 100 electrons have to be removed from the cluster. However, Coulomb explosion of such a highly charged molecule takes place on a time scale of femtoseconds. It will take for instance 7 fs for such a cluster to double its size. Since the ionic potential is inversely proportional to the cluster radius, it will also drop on this time scale. Even if additional ionization compensates for this, the potential well cannot be deep enough even for a cluster fully stripped of its valence electrons (C$_{60}^{240+}$) after it reaches 2.4 times its initial size. Production of C$^{5+}$ would only be possible if the laserpulse could heat the cluster to more than 392 eV in less than 7 fs.

Efficient laser heating takes place only while the plasma frequency is resonant with the laser frequency. At the wavelength of 790 nm, the laser frequency is 380 THz. The plasma frequency can be approximated by $\nu_p = 9000 \sqrt{n_e}$, where $n_e$ is the electron density in the plasma. Imposing the condition to the laser frequency to equal the plasma frequency, results in a certain electron density. Taking 120 electrons as participating to the plasma heating and the plasma frequency to equal 380 THz, then the required radius of the cluster is $\approx 25$ Å, seven times the value of the initial cluster size. In other words, only when the cluster size
has increased by a factor of 7, will the heating process start to work efficiently. From this result, we can conclude that by using the popular Ti:sapphire laser and given our experimental parameters, no higher charge states than $C^{4+}$ can be produced: by the time the cluster reaches the size corresponding to the laser frequency being resonant with the plasma frequency, the ionic potential gets so shallow, that it is not able to retain hot electrons needed for the $K$-shell ionization, as shown above.

The results of Wülker et al. can be interpreted in terms of this model of plasma heating: at their laser wavelength of 248 nm (KrF laser), the laser frequency is 1200 THz. The plasma frequency equals this value when the cluster size is $\approx 11.6 \, \text{Å}$, on the order of 3 times the initial cluster size. This value is closer to the value of 2.4 times the initial cluster size, such that the ionic potential might still be deep enough to retain the hot electrons needed to collisionally ionize $C^{5+}$ and even $C^{6+}$.

From the total ion yield as a function of intensity, we observe saturation of the disintegration yield at an intensity of 250 TW/cm² in the case of the short pulses. At 9 times lower intensities, when using long pulses, saturation of the cluster disintegration is also observed. From these total ion yield measurements with short and long pulses, it can be concluded that this saturation depends on the pulse fluence rather than on the peak intensity. Furthermore, for intensities above saturation, all molecules explode on the leading edge of the pulse.

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