Carrier-Envelope-Phase Effects in Ultrafast Strong-Field Ionization Dynamics of Multielectron Systems: Xe and CS_2

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Carrier-envelope-phase- (CEP) stabilized 5 and 22 fs pulses of intense 800 nm light are used to probe the strong-field ionization dynamics of xenon and carbon disulfide. We compare ion yields obtained with and without CEP stabilization. With 8-cycle (22 fs) pulses, Xe^{6+} yields are suppressed (relative to Xe^{+}) by 30%–50%, depending on phase, reflecting the phase dependence of nonsequential ionization and its contribution to the formation of higher charge states. Ion yields for Xe^{q+} ($q = 2$–4) with CEP-stabilized pulses are *enhanced* (by up to 50%) compared to those with CEP-unstabilized pulses. Such enhancement is particularly pronounced with 2-cycle (5 fs) pulses and is distinctly phase dependent. Orbital shape and symmetry affect how CS_2 responds to variations in optical field that are effected as CEP is altered, keeping intensity constant. Molecular fragmentation is found to depend on field strength (not intensity); the relative enhancement of fragmentation when CEP-stabilized 2-cycle pulses are used is found to be at the expense of molecular ionization.

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Experiments with ultrashort pulses of intense laser light interacting with isolated atoms and molecules continue to invigorate strong-field science [1]. In such studies, typical laser intensities generate optical fields whose magnitudes match Coulombic fields. Consequently, the interaction is dominated by multiple ionization and, in the case of molecules, inevitably results in the breaking of one or several bonds. During the last decade, experiments with intense pulses of tens of femtosecond duration have established the main drivers of the laser-molecule dynamics: enhanced ionization (EI), spatial alignment, and rescattering ionization [1]. However, the recent availability of few-cycle pulses [2] indicates that the dynamics may differ significantly with sub-10-fs pulses. Dynamic alignment no longer occurs as molecules experience the optical field for too short a period for the polarization-induced torque to act on the molecular axis [3]. Furthermore, the few-cycle dynamics proceed essentially at equilibrium bond lengths; consequently, EI is effectively ''switched off'' as nuclei do not have sufficient time to move to the critical distance [3] at which the ionization propensity is greatly enhanced. Indeed, Coulomb explosion studies of N_2 with 10 fs pulses confirm that the N-N bond does not significantly stretch [4]. Few-cycle molecular dynamics are, therefore, considerably simplified as only rescattering occurs wherein the ionized electron oscillates in the optical field (on attosecond timescales) and recollides with the parent ion, inducing further ionization. Experiments on H_2 have shown control of the dynamics by tuning pulse intensity and duration [5]. Few-cycle pulses, therefore, offer the prospect of disentangling the different processes that contribute to strong-field molecular dynamics. However, ultrashort dynamics are even richer because they are governed by the instantaneous magnitude of the optical field and not just by the intensity envelope of the laser pulse. The parameter of importance, therefore, becomes the carrier envelope phase (CEP): a measure of the temporal offset between the maximum of the optical cycle and the maximum of the pulse envelope. The very recent availability of few-cycle pulses whose CEP can be selected and stabilized opens new vistas for strong field dynamics. A new class of measurements now becomes possible in which the pulse intensity is kept fixed but the magnitude of the field experienced by the irradiated atom or molecule is controlled via the CEP. Reported here are results of experiments that probe the effect that CEP has on the ultrafast dynamics of CS_2 and Xe; our results will facilitate new insights into strong field atomic and molecular dynamics in the ultrafast regime and highlight the role of nonsequential ionization in the overall dynamics in the few-cycle regime. We also show that orbital shape and symmetry have a bearing on a molecule's response to variations in optical field at constant intensity. Our experiments with CEP-controlled 5 fs pulses show, counterintuitively, that atomic fragmentation is enhanced, and that it depends on the instantaneous strength of the optical field; moreover, the enhancement of fragmentation with phase-stabilized pulses is at the expense of molecular ionization.

Our target species are both multielectron entities. Xe has, through generation of high harmonics, widespread utility in attosecond science. By measuring ionization spectra of Xe using 5 fs pulses and 22 fs pulses we show how CEP affects the formation of Xe^{q+}, $q = 2$–6. The linear triatomic, CS_2 (and its ions), is known to be an important intermediary in chemical processes in interstellar plasmas, comets, and in planetary and interstellar atmospheres [6,7]. CS_2 is also an efficient ionizing agent in charge-exchange organic mass spectrometry [8] and has

interesting (and important) quantal characteristics in that the four most loosely bound electrons occupy the highest occupied molecular orbital that is antibonding [9]. Removal of up to three electrons effectively enhances the electronic charge density in the internuclear region of CS_2, yielding long-lived molecular dications and trications (their lifetimes are in seconds [10]). Recent work with 4-cycle pulses [9] showed that molecular ionization dominates the ionization spectrum, with hardly any fragmentation.

We used a Ti:sapphire oscillator (75 MHz repetition rate) whose pulses were (i) amplified in a 4-pass amplifier, (ii) stretched to ~200 ps, and (iii) passed through an acousto-optic dispersive filter that controlled pulse shape and duration. The output passed via an electro-optical modulator (which down-converted to 1 kHz repetition rate) to a 5-pass amplifier and compressor. The resulting 22 fs pulse was further compressed to 5 fs using a 1-m-long Ne-filled hollow fiber and chirped dielectric mirrors. CEP stabilization was via a fast-loop in the oscillator and a slow-loop in the amplifier [11]. Typical phase jitter in our measurements is depicted in Fig. 1 which also shows a typical interferometric autocorrelation trace. The jitter (< 60 mrad for 22 fs pulses; <110 mrad for 5 fs pulses over the course of measurements) was determined by an f–$2f$ interferometer at 1 kHz spectrometer acquisition rate with 920 μs integration time and 84 ms loop cycle. Laser energy stability with and without CEP stabilization was 0.4% and 1.7% rms, respectively. Linearly polarized pulses were transmitted to our molecular beam apparatus through a thin (300 μm) fused-silica window [12]; a 5 cm curved mirror focused the beam to 7 μm (width at $1/e^2$) [13]. Ionization was monitored (with unit collection efficiency) using a linear time-of-flight spectrometer; data acquisition at 1 kHz was in list mode using a segmented-mode 2.5 GHz oscilloscope. Figure 1 also depicts the time evolution of the optical field within each 5 fs pulse for different values of CEP. Note that although a π change in phase only reverses the field's direction, the phase flip manifests itself in our ionization spectra. Our setup was recently used to probe time-dependent bond hardening in $Si(CH_3)_4$ at CEP = 0 such that one Si—CH_3 bond is first strengthened and subsequently weakened [14].

In earlier work on Xe with CEP-stabilized pulses [15] of ~10^{13} W cm^{-2} intensity, the dynamics were due to both field-dependent processes and multiphoton ionization (which depends on the intensity of the laser pulse envelope). Our TOF spectra of Xe ions, at 1×10^{16} W cm^{-2} intensity (contrast ratio $>10^5$), were well in the tunneling regime where the dynamics are entirely optical field driven. Typical results with 8-cycle and 2-cycle pulses are shown in Fig. 2. The striking observation is of charge states up to 6+ for 22 fs pulses and only up to 4+ when 5 fs pulses are

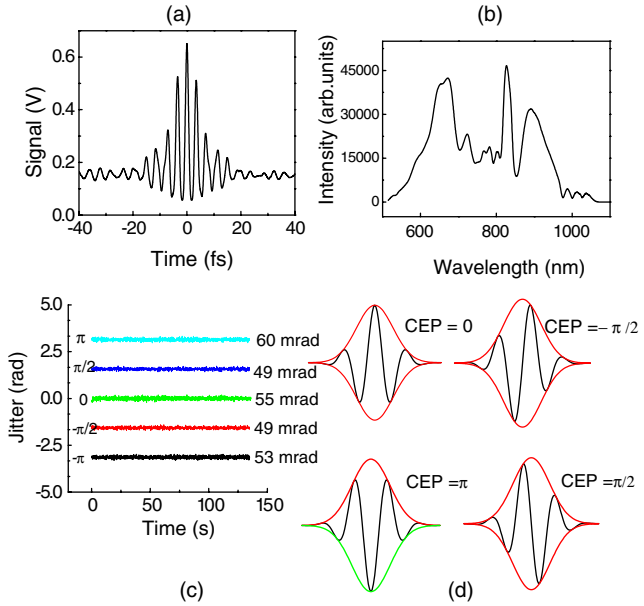

FIG. 1 (color online). Characterization of our 5 fs (2-cycle) laser pulse. (a) Time evolution of the pulse and (b) its spectral profile; (c) jitter in the CEP stabilization (22 fs) on the timescale of measurements; for 5 fs pulses there is an additional jitter of 60 mrad; and (d) time evolution of the optical field within a single pulse at different CEP values.

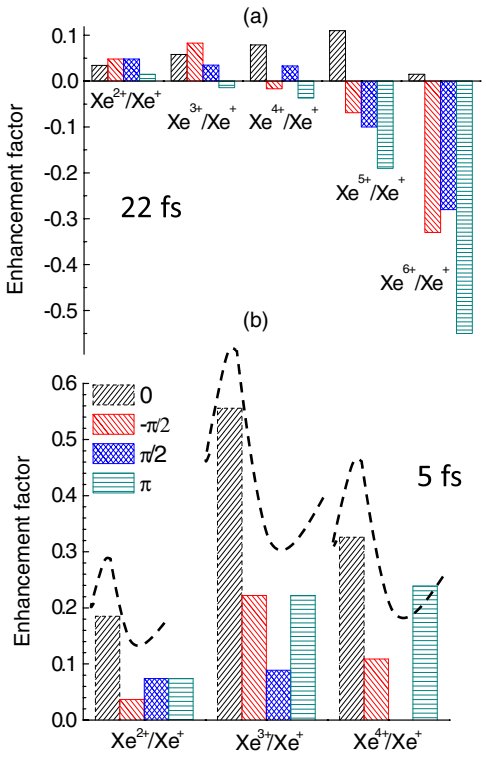

FIG. 2 (color online). Enhancement (with respect to CEP-unstabilized pulses) in the yields of different Xe-ions obtained with different values of CEP-stabilized phase at a peak intensity of 1×10^{16} W cm^{-2} and pulse duration of (a) 22 fs and (b) 5 fs. The ion yield ratios are accurate to within ±2.5%. The dashed lines depicting CEP-dependent modulation in ion yields are a guide to the eye.

used. This reflects suppression of nonsequential ionization as the number of optical cycles becomes very small. In the following, we focus on a comparison of ion yield ratios Xe^{q+}/Xe^{+} ($q = 2$–6) for CEP-stabilized and CEP-unstabilized pulses of the same intensity. That the Xe-ionization spectrum is dominated by field effects is validated in Fig. 2 which follows changes in the Xe^{q+}/Xe^{+} ratio with instantaneous field (as expressed in terms of CE phase for a 2-cycle pulse) for a fixed intensity. Multiple ionization is significantly enhanced (with respect to Xe^{+} yield with CEP-unstabilized pulses). Figure 2 shows that while there is only marginal enhancement of ion yield for charge states up to $4+$, changes in Xe^{q+} ($q = 5$, 6) yields are negative and substantial: the yields reduce relative to those with CEP-unstabilized pulses, possibly because of reduction in nonsequential ionization when CEP-stabilized pulses are used.

It is established that the oft-used Ammosov-Delone-Krainov theory [16] underestimates rates for multiple ionization of Xe. In the present context, this discrepancy may be ascribed to Xe^{q+} ($q = 4$–6) ions being mostly due to nonsequential (NS) ionization wherein simultaneous tunneling of more than one electron occurs through xenon's field-distorted radial potential function. Yamakawa *et al.* [17] have shown suppression of NS ionization in the few-cycle regime. Our results indicate that even with 8-cycle pulses, Xe^{6+} yields are suppressed (relative to Xe^{+} yields) by 30%–50%, depending on phase. This reflects the phase dependence of NS ionization and its contribution to the formation of higher charge states. On the other hand, ion yields for Xe^{q+} ($q = 2$–4) with CEP-stabilized pulses are actually *enhanced* compared to those with CEP-unstabilized pulses (Fig. 2). The enhancement is particularly pronounced with 2-cycle pulses and is distinctly phase-dependent, with the largest enhancement being for CEP $= 0$. The relative yields of individual ions exhibit CEP-dependent modulation and clearly highlight the field-dependent (not intensity-dependent) nature of NS ionization in multielectron atoms like Xe. Rescattering is, of course, one of the drivers of NS ionization [18] and it is, therefore, expected that NS-induced enhancements (Fig. 2) exhibit a pronounced CEP dependence (noting that it is the CEP that determines when, in the course of the optical pulse, the ionized electron is "born").

In the case of CS_2, we compare the yields of atomic and molecular ions (with respect to CS_2^+) for CEP-stabilized and CEP-unstabilized pulses of the same intensity (Fig. 3). The ratios are accurate to within $\pm 2.5\%$. As with Xe, we find that CEP-stabilized pulses enhance fragment ion yields; moreover, the relative yields exhibit a CEP-dependent modulation. At CEP $= 0$, the atomic fragment signal is significantly enhanced while the molecular dication and trication yields (with respect to those with CEP-unstabilized pulses) remain essentially unchanged. At CEP $= -\pi/2$, the relative yield of atomic fragments

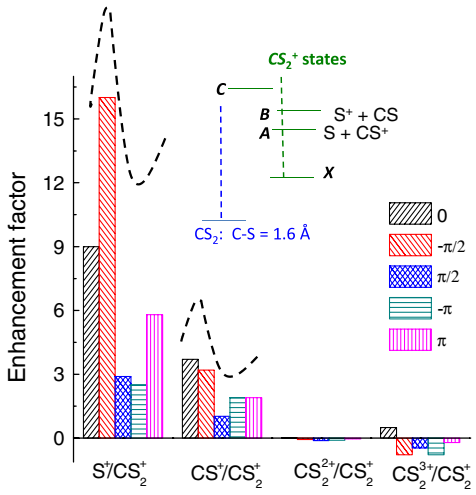

FIG. 3 (color online). Enhancement (with respect to CEP-unstabilized pulses) in the yields of ions obtained from CS_2 obtained with different values of CEP-stabilized phase at a peak intensity of 1×10^{16} W cm^{-2} and pulse duration of 5 fs. Note the enhancement of fragment ions S^+ and CS^+ at the expense of molecular ions CS_2^{2+} and CS_2^{3+}. The dashed lines depicting CEP-dependent modulation in ion yields are a guide to the eye. Some electronic states of CS_2^{q+} ($q = 0$, 1) are also depicted (see text).

become more prominent while that of molecular species is reduced (in fact, CS_2^{3+} is no longer seen at this CEP). Our systematic measurements lead us to conclude that atomic fragmentation depends on the instantaneous optical field as seen in different relative yields for CEP $= \pi/2$ and $-\pi/2$ (Fig. 3). These differences reflect different time evolutions of the optical field for these two phases. Moreover, and significantly, our data indicate that atomic fragments are enhanced at the expense of molecular ionization.

We now consider S^+ and CS^+ fragments whose formation by direct ionization of CS_2 is unlikely as Franck-Condon factors preclude vertical access to the dissociation continua of the ground (X) and excited (A, B) states of CS_2^+. The next ionic state, C, lies above the dissociation limits $S^+ + CS$ and $S + CS^+$ and, hence, fully predissociates. Figure 3 depicts some electronic states of CS_2^{q+} ($q = 0$, 1). In long-pulse experiments, prominent yields of S^+ and CS^+ fragments were rationalized by invoking EI: the C—S bond lengthens so as to allow population of excited CS_2^{+*} states which act as precursors of these fragments. The reported disappearance of these fragments in four-cycle experiments [9] confirms that the EI process is "switched off" in the ultrashort domain. Our observation of enhanced S^+ and CS^+ yields with CEP-stabilized pulses (compared to yields with CEP-unstabilized pulses) indicates access to CS_2^{+*} states lying beyond the C state whose dissociation limits permit formation of S^+ and CS^+ fragments. The electronic configuration of ground-state CS_2 is $(\text{core})^{22}(5\sigma_g)^2(4\sigma_u)^2(6\sigma_g)^2(5\sigma_u)^2(2\pi_u)^4(2\pi_g)^4$, yielding $^1\Sigma_g^+$ symmetry. Ejection of an electron from the $2\pi_u$, $5\sigma_u$, and $6\sigma_g$ orbitals yields excited states A, B, and C,

respectively, proper descriptions of which are difficult within a single-electron picture: they necessitate recourse to consideration of multielectron effects [19]. Nevertheless, study of these states are important as they manifest the total breakdown of the Koopman's model of ionization brought about by strong final-state correlations [20].

In invoking highly excited CS_2^{+*} states to validate our observed enhanced formation of S^+ and CS^+ fragments with CEP-stabilized pulses, we note that rescattering is unlikely to contribute. In earlier work with 11 fs CEP-unstabilized pulses, it was established that CS_2^{2+} and CS_2^{3+} molecular ions dominate the four-cycle spectrum, ostensibly at the expense of fragmentation channels [9], a signature of rescattering being "switched off" because of constraints imposed by the symmetry of CS_2's outermost antibonding $2\pi_g$ orbital. The wave packet of the returning electron interferes destructively with the spatial extent of this orbital, leading to effective cancellation of rescattering. The returning electron's energy is, consequently, no longer available for excitation to high-lying CS_2^{+*} states that are quantally allowed to dissociate into S^+ or CS^+. As far as the phase effects are concerned (Fig. 3), they manifest how $2\pi_g$, $2\pi_u$, $5\sigma_u$, and $6\sigma_g$ orbitals respond to field variations experienced under different CEP conditions. Nonperturbative time-dependent density functional theory has been applied to CS_2 at intensities $>10^{14}$ W cm^{-2} [21]; results illustrate how the field affects each orbital differently. We note that the symmetry of individual orbitals will play a role in rationalizing the observations of Fig. 3 [22,23] on how relative ion yields are affected by different CEPs. The π orbitals have a nodal plane containing the molecular axis and, consequently, contribute less to the ionization yield when aligned parallel to the laser's polarization vector, whereas orbitals with σ symmetry ionize most effectively as their density is maximum parallel to the field.

Our experiments on CS_2 with 22 fs CEP-unstabilized pulses yielded data concordant with earlier results using CEP-unstabilized four-cycle pulses [9], where molecular ionization overwhelmingly dominates the dynamics with concomitant reduction in atomic fragments (compared to measurements made with pulses of ≥ 50 fs duration). It is, therefore, the CEP phase in our 5 fs pulses that drives the dynamics depicted in Fig. 3.

Intense few-cycle pulses within which the optical field can be precisely fixed via CEP control will open new opportunities for controlling both the moment when an electron wave packet is "born" and its subsequent motion, providing a fillip to attosecond science. Enhancing the intensity of such CEP-stabilized pulses will permit control of electronic motions in the inner orbitals, enabling new classes of experiments on heavy atoms (like Xe) and molecules containing heavy atoms (like CS_2) in which such electrons are relativistic. Little is known about the possible interplay of electrons in inner and outer orbitals in multielectron entities. There has been inconclusive debate on how effectively external fields may be shielded from electrons in inner orbitals [24]. Screening in Xe and CS_2 makes it difficult to estimate the local field experienced by inner valence electrons; systematic descriptions of the dynamics in multielectron systems remain intractable. Our experiments should aid in testing the efficacies of future theoretical developments in this direction. From the perspective of molecules, those that comprise heavy atoms require dipole and polarizability corrections to be incorporated into existing strong-field theories; such corrections need to be CEP dependent and, as with heavy atoms, we anticipate that our results will stimulate further theoretical work.

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