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Molecular symmetry effects in the ionization of CS_2 by intense few-cycle laser pulses

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Few-cycle pulses of 800 nm light cause ionization and dissociation of CS_2 in the intensity and temporal regime where, by contemporary wisdom, rescattering is expected to dominate laser-molecule interactions. However, our experiments indicate that in the case of laser-CS_2 interactions in the strong-field regime, the wave packet of the rescattered electron destructively interferes with the antibonding π orbital of CS_2^+ such that rescattering is essentially "switched off." Consequently, dissociation becomes an almost nonexistent channel; long-lived singly, doubly, and triply charged molecular ions dominate the mass spectrum in the few-cycle regime, revealing the importance of molecular symmetry in strong-field ionization. Comparison with CS_2 ionization spectra that we measure in the 700 attosecond domain using fast, highly charged ions corroborates that rescattering is not of importance when CS_2 ionization is caused by intense laser light. Direct signature of enhanced ionization being "switched off" in the few-cycle domain is also obtained in our measurements.

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I. INTRODUCTION

Studies of molecular dynamics in intense fields continue to yield unexpected, often counterintuitive, phenomena and processes that constantly invigorate strong-field science (for a recent compilation of cogent reviews, see [1], and references therein). In such studies, the magnitude of the optical field matches the intramolecular Coulombic field, and the overall laser-molecule interaction is dominated by ionization and the breaking of one or several bonds. Most probes of how molecules behave in strong fields have relied on ion yields measured with infrared pulses that are a few tens to a few hundred femtoseconds long, and it is established that enhanced ionization (EI), spatial alignment, and rescattering ionization are the main drivers of the dynamics [1]. Might the use of few-cycle pulses alter the dynamics? Very recent work [2] seems to indicate so because dynamic alignment of molecules like O_2 and N_2 will not occur as the duration of the optical field is too short for polarization-induced torque to act on the molecular axis. Furthermore, EI is expected to be effectively "switched off" as nuclei do not have enough time to move to the critical distance at which ionization propensity is enhanced [3]. Consequently, one expects few-cycle dynamics to be dominated only by rescattering, wherein the ionized electron oscillates in the optical field and recollides with the molecular ion, inducing further ionization. Few-cycle pulses, therefore, offer the prospect of disentangling the effect of different processes in strong-field molecular dynamics. It may prove to be possible to exercise some measure of control on the molecular dynamics by tuning the intensity and duration of the ultrashort optical field [4].

But what of the quantal structure of the molecule itself? Does it have any role to play? Does the few-cycle, strong-field regime take cognizance of molecular symmetry, a consequence of the quantum-mechanically determined electronic structure? We explore these questions in experiments that we have conducted on irradiation of CS_2 molecules by intense, four-cycle pulses and the results that we report in this paper.

Before rationalizing our choice of CS_2 to probe the possible role of quantal effects in the strong-field, few-cycle regime, we make the following observations on current wisdom pertaining to the importance, or otherwise, of quantal effects on strong-field dynamics. A plethora of data on atoms in strong fields confirms that the ionization rate in multiphoton and tunneling ionization depends only on one atomic property: the ionization energy (V_{ion}). The quantal nature of the molecular orbitals that may be involved in the ionization process does not enter into reckoning. Hence it is established that Ar and N_2 have nearly identical strong-field ionization rates [5] given that the ratio $V_{\text{ion}}(\text{Ar})/V_{\text{ion}}(N_2)$ is 1.01. Unexpectedly, the ionization rate for O_2 is ten times lower than for Xe in spite of $V_{\text{ion}}(\text{Xe})/V_{\text{ion}}(O_2)$ being even closer to unity (1.005). Rationalizations proferred [5] have invoked either multielectron effects or nuclear motion within molecules. Multielectron effects offer unsatisfactory explanation as the resulting ionization yields only match measured ones at laser intensities beyond saturation [6]; calculations [7] show that molecular vibrations also fail to quantitatively rationalize differences between ionization rates for molecules and companion atoms. An entirely different insight has emerged from intense field *S*-matrix calculations [8] that predict suppression of ionization in homonuclear molecules with an antibonding valence orbital, like the outermost π_g orbital in O_2, but not in the case of molecules with a bonding valence orbital, like σ_g in N_2. The shape of the former orbital causes destructive interference by the two nuclei of subwaves of the ionized electron; electron spectroscopy on molecules like N_2 and O_2 irradiated by strong laser fields of 100 fs duration has recently vindicated this projected scenario [9].

We focus here on a linear triatomic, CS_2, in order to probe the possible role of symmetry effects in strong-field dynamics in the few-cycle domain. CS_2 is an important molecule as, in both neutral and ionized form, it is an intermediary in chemical processes in cold interstellar plasmas, cometary environments, and in planetary and interstellar atmospheres

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[10]. The CS_2 molecule also has terrestrial importance from an applications viewpoint, for instance, as a most efficient ionizing agent in charge-exchange organic mass spectrometry [11]. From the perspective of this work, we note that the electronic configuration of the ground state of CS_2 is

$$(\mathrm{core})^{22}(5\sigma_g)^2(4\sigma_u)^2(6\sigma_g)^2(5\sigma_u)^2(2\pi_u)^4(2\pi_g)^4,$$

which yields overall $^1\Sigma_g^+$ symmetry. The outermost $2\pi_g$ orbital is mostly built up of $3p$ orbitals of spatially extended S atoms. Hence the equilibrium C–S bond length is large ($\sim$1.6 Å) and there is little π overlap between the two peripheral atoms. Consequently, the outermost orbital has strong antibonding character and it is this that dominates single, double, and triple ionization that occurs upon removal of one, two, or three electrons. Each such removal effectively *enhances* the electronic charge density in the internuclear region, resulting in long-lived doubly and triply charged ${CS_2}^{2+}$ and ${CS_2}^{3+}$, with lifetimes of the order of seconds [12,13].

II. EXPERIMENTAL METHOD

Work on few-cycle ionization dynamics has been conducted using the hollow-fiber pulse compression technique [14]. Recently, however, few-cycle pulses have also begun to be generated using filamentation in gas-filled tubes [15], and it is this method that we have adopted to generate four-cycle pulses in the present experiments. We used here 0.5 mJ, 50 fs laser pulses centered at 800 nm (1 kHz repetition rate) from a Ti:sapphire amplifier. After passing through an aperture the laser beam was focused with a metal-coated spherical mirror (f=1 m) on to a 1.5-m-long tube containing Ar at 1.2 atm. The central part of the resulting broadband light was compressed by a set of chirped dielectric mirrors (CDM) to produce 15 fs pulse (0.3 mJ energy). These pulses were then passed through another aperture and focused on to a second 1-m-long tube (filled with Ar at 0.9 atm). The broadband light was again compressed using a second pair of CDM to yield 11 fs (four-cycle) pulses with 0.25 mJ energy. Our experimental method has recently been presented in detail elsewhere [16].

These few-cycle pulses were characterized by us by means of spectral phase interferometry for direct electric field reconstruction (SPIDER) and were then directed through a 300 μm fused silica window into an ultrahigh vacuum (UHV) chamber in which the laser-CS_2 interaction occurred at pressures of $\sim 10^{-9}$ Torr. The four-cycle pulses were precompensated for chirp and focused within the UHV chamber by a spherical mirror (f=5 cm). Ion analysis was by conventional, linear time-of-flight (TOF) methods.

III. RESULTS AND DISCUSSION

A typical TOF spectrum that we obtain with four-cycle pulses at intensity 5×10^{15} W cm^{-2} is shown in Fig. 1. The two striking features of this spectrum are (i) the dominance of peaks corresponding to different charge states of CS_2, and (ii) the absence of fragment ion peaks that dominate spectra obtained with longer pulses, a typical example of which is presented in Fig. 2(a) for 40 fs pulses of 800 nm light at intensity 7×10^{15} W cm^{-2}. The inset in Fig. 1 quantifies relative ion yields that we measured with 11 and 40 fs pulses. The fragmentation pattern is clearly much richer with 40 fs pulses, with a gamut of energetic atomic fragments being produced up to charge state 4+ (even S^+, S^{2+} are measured to have as much as $\sim$4 eV energy), the precursors being excited electronic states of ${CS_2}^{q+}$ ($q > 1$) that Coulomb-explode. Long-lived ${CS_2}^{2+}$, ${CS_2}^{3+}$ are observed, but with much lower overall yield compared to the fragment ions. The stark difference between spectra in Figs. 1 and 2(a) is obvious and lies in the dramatic suppression of fragmentation channels when few-cycle pulses are used. How do we rationalize this difference? Is the broad spectral bandwidth of few-cycle light a factor that needs to be taken cognizance of? We also made measurements using broadband light, with bandwidth $\sim$500–900 nm [Fig. 2(b)]. This supercontinuum was generated by irradiating 1-cm-thick BK-7 glass with 40 fs pulses of intense 800 nm light; the methodology adopted by us for such white light experiments on molecules, including estimation of the white light intensity, has been described recently [17]. The resulting TOF spectrum also shows prominent fragments S^+ and CS^+, whose yields relative to, say, ${CS_2}^{2+}$ are consistent with single-color 40 fs data [Fig. 2(a)]. We conclude that the broadband nature of our four-cycle pulses is not an important factor in suppressing CS_2 fragmentation.

	11 fs	**40 fs**
$S^+/{CS_2}^+$	0.09	0.66
$CS^+/{CS_2}^+$	0.02	0.23
${CS_2}^{2+}/{CS_2}^+$	0.34	0.17
${CS_2}^{3+}/{CS_2}^+$	0.08	-

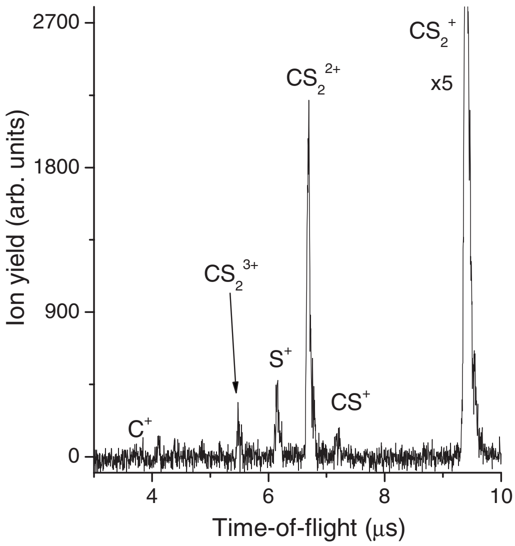

FIG. 1. Typical time-of-flight spectrum of CS_2 measured at 5×10^{15} W cm^{-2} intensity with four-cycle (11 fs) pulses of 800 nm light. Inset indicates ion yield ratios. The ratios remained essentially unaltered over the range of intensities $2\text{–}7 \times 10^{15}$ W cm^{-2}.

One major clue pointing to the importance of the quantal description of the irradiated molecule emanates from observation of fragments like S^+ and CS^+ when we use 40 fs

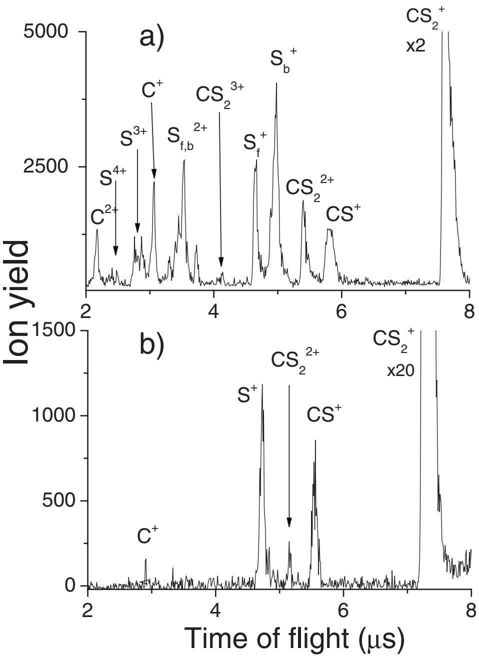

FIG. 2. (a) Time-of-flight spectrum of CS_2 obtained at intensity 7×10^{15} W cm^{-2} using 40 fs pulses of 800 nm light. Note the preponderance of fragment ions. S_f^+, S_b^+ denote S ions that Coulomb-explode toward and away from the detector at the end of our TOF spectrometer. (b) Corresponding spectrum using broadband (500–900 nm) light.

pulses. Leaving aside, for the time being, consideration of electron rescattering, it is clear that fragments S^+ and CS^+ cannot be produced by direct ionization of CS_2 since Franck-Condon factors preclude vertical access to the dissociation continua of the X, A, and B electronic states of $CS_2{}^+$. We base this conjecture on the absence of any peak in the CS_2 photoelectron spectrum [18] near the appearance thresholds for S^+ and CS^+ fragments (14.81 and 15.78 eV, respectively), and also from results of photoion-photoelectron coincidence measurements [19] that show the equilibrium structure of $CS_2{}^+$ being close to that of CS_2. However, the next higher ionic state, C, lies above the dissociation limits S^++CS and S+CS^+ and, hence, fully predissociates as has, indeed, been established by photoion-photoelectron coincidence [19]. At intensities of 5×10^{15} W cm^{-2} the nonobservation of S^+ and CS^+ fragments appears to indicate that the optical field is not strong enough to allow direct, vertical access to the C state in our four-cycle experiments. In the case of our longer-pulse (40 fs) experiments, however, the enhanced ionization process sets in, resulting in a lengthening of the C–S bond. This has two consequences. First, there is now an enhanced possibility of transitions to the C state and to higher excited electronic states beyond the C state. Second, the increased bond length opens possibilities for excitations in regions that lie outside the Franck-Condon zone defined by the equilibrium geometry of CS_2. It is the population of higher excited electronic states of $CS_2{}^+$ that becomes likely in the long-pulse regime and it is these states that are precursors of the fragments that are observed in Fig. 2(a). The disappearance of these fragments in four-cycle spectra is clear and a direct signature that EI switches off in the few-cycle domain.

We estimate time scales for dissociation of multiply charged CS_2 by taking the $CS_2{}^{2+}$ and $CS_2{}^{3+}$ potential surfaces to be purely Coulombic. We take S atoms to have reduced mass M at an initial separation of $2\beta a_o$. Following ionization to charge states Z_1 and Z_2, the time, τ, taken for the products of Coulomb explosion to develop a separation of x is [20]

$$\tau \sim \frac{\lambda_C}{2\pi c\alpha_2}\left[\frac{\beta^3 M}{2m_e Z_1 Z_2}\right]^{1/2}\left\{\frac{x(1-2\beta a_0/x)^{1/2}}{2\beta a_0} + \frac{1}{2}\ln\left[\frac{1+(1-2\beta a_0/x)^{1/2}}{1-(1-2\beta a_0/x)^{1/2}}\right]\right\}, \qquad (1)$$

where α is the fine-structure constant, m_e is the electron mass, and λ_C is the Compton wavelength; a_0 and c are the Bohr radius and speed of light, respectively. Following Coulomb explosion of $CS_2{}^{2+}$, it takes as long as ~40 fs for S^+-S^+ ion pairs to separate to 10 Å, far too long for a four-cycle pulse.

But what of rescattering? This occurs on ultrafast time scales and, as we show in the following, is another area where quantal considerations cannot be ignored as has hitherto been the case in most contemporary strong-field literature. We note that in double ionization of H_2 [4] induced by intense pulses (~15 fs), the first return recollision essentially dominates the rescattering dynamics whereas for longer pulses, the third return recollision could assume importance. Experiments on methane [2] also highlight the importance of the first return recollision when 8 fs pulses are used: no dications were observed with 8 fs pulses but they began to appear when longer pulses were used. In the present work on CS_2, even with enhanced ionization being switched off in the few-cycle regime, if rescattering were to come into play, electron excitation from the ground state of neutral CS_2 to the C state and higher excited states would be energetically possible at intensities of 5×10^{15} W cm^{-2} and, consequently, S^+ and CS^+ fragments would be observed even in spectra measured using four-cycle pulses. However, what is actually observed is that formation of long-lived dication and trication parent ions in the intensity range 10^{15} W cm^{-2} dominates the four-cycle spectrum, ostensibly at the expense of fragmentation channels. This is a signature of rescattering also being "switched off" in our experiments not because of temporal constraints but those imposed by the quantum-mechanical nature of CS_2's outermost $2\pi_g$ orbital. The wave packet of the returning electron interferes destructively with the large spatial extent of this orbital, leading to effective cancellation of the rescattering process. The returning electron's energy is no longer available for electronic excitation to highly excited $CS_2{}^{+*}$ states that are quantally allowed to dissociate into S^++CS or S+CS^+.

There is another, totally different scenario in which strong field effects occur for ultrashort durations *without the possibility of rescattering*. This occurs in large impact-parameter collisions of fast, highly charged ions with molecules [21]. The high charge states of the projectile ions create the strong field and the high kinetic energy of projectiles ensures that the ion-molecule interaction time is very short. We have studied 100 MeV collisions of CS_2 molecules with Si^{8+} ions

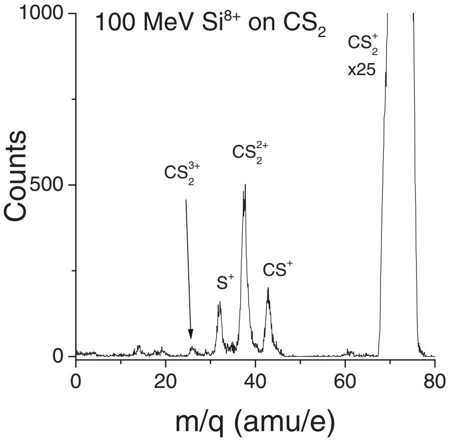

FIG. 3. Mass spectrum of CS_2 in collision with 100 MeV Si^{8+} ions.

produced in a tandem accelerator and measured ion spectra for impact parameters larger than 3 Å. The methodology has been described in detail elsewhere (see [21], and references therein) but we note here that the chosen Si-ion charge state and impact parameter ensure that CS_2 experiences fields of comparable magnitude to those in our four-cycle laser experiments. The collision energy ensures that the interaction time is of the order of 700 as. The resulting ion spectrum that we measure (Fig. 3) is remarkable in its similarity to the four-cycle spectrum (Fig. 1) and further confirms that rescattering plays little or no role in the strong-field dynamics of CS_2 when four-cycle pulses are used.

Our CS_2 results offer unambiguous vindication of the strong-field *S*-matrix theory developed for diatomic molecules [8] and allows us to predict that destructive interference brought about by the antibonding π_g orbital of $CS_2{}^+$ will suppress the plateau region in electron spectra. Such suppression would not be observed in the case of bonding σ_g orbitals. We note that our results pertain to quantal interference affecting the *rescattered* electron wave packet while the *S*-matrix theory [8] treats interferences in the ejected electron channel. Theory predicts that such effects would be effective for short molecular bonds [8] while our measurements on CS_2 seem to indicate some measure of persistence of interference even for long bonds.

From a basic perspective, our few-cycle results bring to the fore a hitherto-hidden facet of strong-field physics: the necessity of properly incorporating quantal molecular structure effects in descriptions of ionization and fragmentation dynamics in strong fields. We note that electron density profiles in N_2, O_2 HOMOs have been mimicked by Alnaser *et al.* [4] using 8 fs pulses and, more recently, Coulomb explosion studies of N_2 with 10 fs pulses have confirmed that there is no significant stretching of the N–N bond on such time scales [22]. Taken together with our results, we believe that intense few-cycle pulses may offer a new route to Coulomb explosion imaging of neutral molecules in their equilibrium (unstretched) geometry.

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