

Formation of Negative Ions upon Irradiation of Molecules by Intense Laser Fields

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Time-of-flight experiments reveal a hitherto unsuspected channel leading to negative-ion formation when molecules interact with intense laser fields. Dissociative attachment by low-energy electrons produced in such interactions, and accelerated by the ponderomotive potential, produces anions whose yield depends on laser intensity. The dissociative attachment pattern is dramatically different from that obtained by low-energy electron impact. Angular distribution measurements show that the laser field spatially aligns triatomic precursors (CS_2^- , CO_2^-) along the direction of the polarization vector. [S0031-9007(98)05851-7]

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In the course of multiphoton ionization (MPI) of a molecule by strong, linearly polarized, laser fields, an electron wave packet is formed each time the oscillating light field passes its maximum value. Within the first laser period after initial electron ejection from the molecule, the evolution of the wave packet is such that there is a finite probability of the electron returning to the vicinity of the molecular core and undergoing an inelastic collision [1]. Experiments show that such "rescattering" gives rise to new nonlinear processes and dynamics which have no analog in weak-field, or zero-field, situations: ejection of further electrons from the molecular core at internuclear separations far from equilibrium (multiple ionization), emission of high-energy photons (harmonic generation) and formation of very-high-energy above-threshold ionization electrons are manifestations of such nonlinear effects which can be observed in positive ion, photon and electron channels, respectively. These strong-field-molecule interaction effects continue to attract considerable contemporary interest [2].

The formation of negative ions upon irradiation of molecules by intense laser fields has remained an unexplored facet of the physics of strong-field MPI. It is the purpose of this Letter to report results of experiments which probe the role played by low-energy electrons created in the MPI process on the dynamical evolution of the plasma formed in strong-field-molecule interactions. Do such "prescattered" electrons give rise to negative-ion formation when molecules are subjected to strong light fields? The results of our experiments offer indications that upon acceleration of MPI electrons due to the ponderomotive potential, dissociative attachment readily occurs to molecules such as CO_2 , CS_2 , and O_2 . The laser intensities used in our experiments (7×10^{12} – $1 \times 10^{14} \text{ W cm}^{-2}$) correspond to ponderomotive potentials (U_p) of 0.5–8 V. Electron energies corresponding to this range of U_p have a high propensity for dissociative attachment (DA) to molecules and it is somewhat surprising that the negative-ion formation channel has been hitherto ignored in all considerations of strong-field-

molecule interactions. We have measured negative ion mass spectra at different laser intensities for CO_2 , CS_2 , and O_2 molecules. Negative ions of all these species are formed, which subsequently fragment; the fragmentation patterns differ from those obtained in low-energy electron-impact DA experiments. Angular distributions of negatively charged fragments are also measured and manifest the spatial alignment of triatomic negative-ion precursors along the laser's polarization axis.

Experiments on these hitherto unexplored channels were conducted using 35 ps laser pulses (of peak intensity 10^{12} – $10^{14} \text{ W cm}^{-2}$ and wavelength of 1064 nm) which were focused to a spot size of $\sim 20 \mu\text{m}$ where they interacted with low-density ($\leq 10^9 \text{ cm}^{-3}$) gaseous targets. Negative ion mass spectra were obtained using a linear time-of-flight (TOF) mass spectrometer whose axis was aligned parallel to the laser's polarization vector. Ion detection was by a channel electron multiplier coupled, via fast pulse electronics, to a digital oscilloscope. Angular distributions of the negative ions were measured by rotating the polarization direction of the incident laser field with respect to the TOF axis; a combination of halfwave plate and linear polarizer was used to obtain the desired polarization at constant intensity. The polarization direction was rotated in steps of 10° .

We first focus attention on the morphological features of the data that have been obtained. Figure 1 shows a typical negative-ion mass spectrum obtained when CS_2 was irradiated with a laser intensity of $3.5 \times 10^{13} \text{ W cm}^{-2}$; also shown is the variation in the fragment ion pattern as a function of laser intensity. We note the following features of the data before discussing the implications:

(i) The relative intensities of the negative ions are very different from those obtained by electron-impact (EI) where the S^- signal dominates the anion mass spectrum for electron energies up to 40 eV [3]; the CS^- ion, whose relative intensity drops very rapidly with increasing electron energy in EI experiments, continues to be the dominant anion over the entire energy range in the present experiments. Such differences may be manifestations of

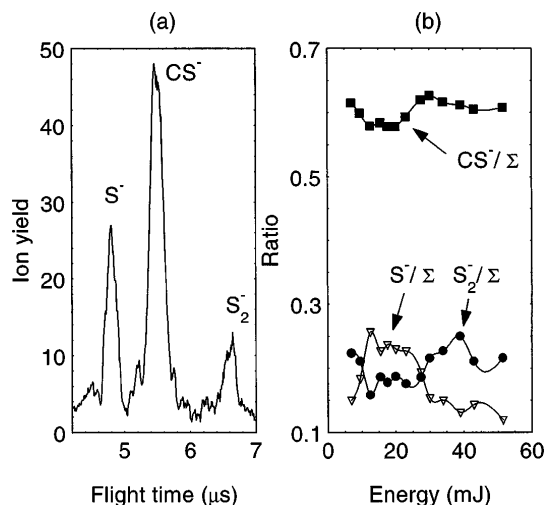


FIG. 1. (a) Anion mass spectrum obtained when CS₂ was irradiated by 1064-nm, 35-ps-wide laser pulses of peak intensity: $3.5 \times 10^{13} \text{ W cm}^{-2}$. (b) Variation of the ratio of specific anion yields to total anion yield (Σ) with laser intensity.

field-induced distortions of the potential energy functions of the precursor CS₂⁻ state. In the absence of quantum-chemical computations of potential surfaces in intense fields, quantitative analysis of such differences is not possible, but it is of interest to note that calculations on positively charged polyatomics have offered tantalizing evidence of gross distortions of electronic charge clouds in the presence of strong external fields [4]. Such electronic distortions would also be expected to deform the CS₂⁻ potential energy surface such that the branching ratios for dissociation into different fragment anions is different to that obtained in zero-field (EI) conditions.

(ii) The variation of anion signal with laser intensity [Fig. 1(b)] reveals that all the fragments have the same threshold, corresponding to $U_p \sim 1 \text{ V}$. This finding is also at variance with EI results where (a) the appearance threshold of each fragment reflects the vertical electron affinity of the electronic state of the precursor anion and (b) the relative intensities vary in consonance with different functional dependences of the DA cross section on electron energy. The common threshold indicates that the same CS₂⁻ potential surface may be the precursor for all three anion fragments, with approximate branching ratios of 0.6, 0.2, and 0.2 for formation of CS⁻, S⁻, and S₂⁻, respectively, over the range of laser intensities employed in the present studies. On the basis of a high degree of reproducibility we draw attention to the intriguing indication offered by data shown in Fig. 1(b) that the variation with laser intensity of the ratio of S⁻ and S₂⁻ to the total anion production might be in “antiphase.”

(iii) EI experiments have established that the variation of CS⁻ and S⁻ signals with electron energy is sharp in the 1–10 eV range [3] with an onset of broad, featureless signals at energies in excess of $\sim 12 \text{ eV}$. The sharp

peaks observed in EI experiments are consistent with the resonant nature of the DA process, whereas the higher-energy signals are attributed to formation of anion-cation pairs. Figure 2 shows the variation of CS⁻ and S⁻ signals with laser intensity in the present experiments, and gross differences with EI data are again noted. EI data [3] in the electron energy range 1–8 eV show sharp S⁻ peaks at 3.6, 6.2, and 7.7 eV, with cross sections (in units of 10^{-20} cm^{-2}) of 35, 23, and 5, respectively. For CS⁻, EI data show a single peak at 6.2 eV, with a cross section which is 30% of that for the S⁻ peak at the same energy. In contrast, four structures were observed in the present experiments for both anions. As noted above, the CS⁻ yield was more than double that of S⁻ almost over the entire range of U_p . Furthermore, *no* signals were obtained at laser intensities corresponding to U_p values higher than 7 V. Coincidence measurements were conducted on formation of CS⁻-S⁻ pairs; no evidence was found for CS₂²⁻ precursors.

We have already noted that the negative-ion fragments produced from CS₂ have a common threshold as far as laser intensity is concerned. The same CS₂⁻ state is evidently responsible for the subsequent dynamics as the common threshold precludes the possibility of anion-cation pair formation. Such formation is also inconsistent with the variation we measured of anion signals with laser intensity and gas pressure. We conducted measurements on diatomic O₂ and our results show the formation of O⁻ with *no* concomitant formation of O⁺ ions, at least over the range of laser intensities available in the present study. This is the most explicit evidence that cation-anion

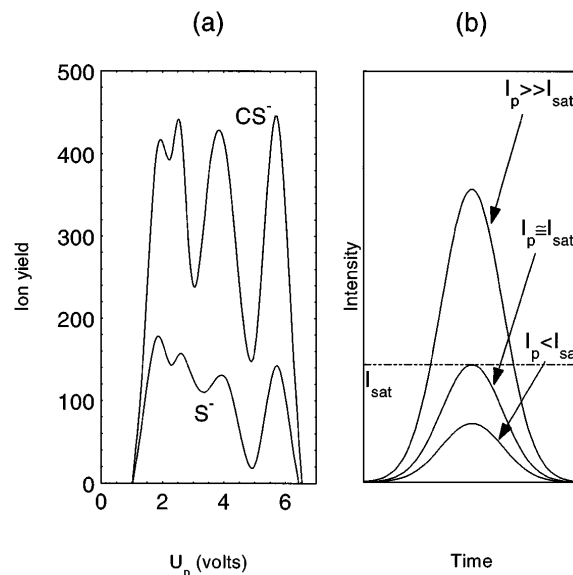


FIG. 2. (a) Variation of anion yields with the ponderomotive potential, U_p . In these experiments, 1 mJ of laser intensity was equivalent to a value of U_p of 0.146 V. (b) Schematic depiction of laser pulses with different values of peak intensity (I_p). I_{sat} denotes the saturation intensity of CS₂⁺ (see text).

pairs are not formed. Field-induced fragmentation of the neutral molecules followed by electron attachment to fragment species is a scenario which is also inconsistent with the common threshold. So, how is the CS_2^- precursor formed? In our experiments anions were formed at laser intensities which lay both below as well as above the saturation intensity (I_{sat}) of CS_2 . We recall that I_{sat} is that intensity at which *all* molecules exposed to the intense laser field become ionized. Consequently, at intensities greater than I_{sat} ($9 \times 10^{12} \text{ W cm}^{-2}$ for CS_2^+) the laser field interacts exclusively with ionized species. Under such circumstances, anion formation can occur only if one postulates a double electron attachment process of the type: field + $\text{CS}_2^+ \rightarrow \text{CS}_2^- \rightarrow$ anion fragments. Simple energetic considerations rule out such processes; we suggest the following mechanism for anion formation: Ionization of neutral molecules is induced by the laser field, at intensities above as well as below I_{sat} . The slow, ejected electrons are accelerated by the ponderomotive potential (U_p) whose magnitude depends upon the time-dependent laser intensity. Values of U_p shown in Fig. 2(a) pertain to the peak laser pulse intensity (I_p). For $I_p < I_{\text{sat}}$, low-energy electrons interact with neutral molecules and dissociative attachment, in view of large cross sections, occurs with high probability. As depicted in Fig. 2(b), when $I_p \sim I_{\text{sat}}$, the rising edge of the laser pulse will still produce low-energy electrons, and there will still be less than 100% ionization of the target species. Dissociative attachment to neutral CS_2 will still be possible. Once the parent anion species is formed, it dissociates along the field-distorted potential energy surface, giving rise to different fragment anions whose apparent threshold (in terms of laser intensity) is determined solely by the threshold for formation of the precursor anion. For $I_p \gg I_{\text{sat}}$, although electrons may still be ejected at the rising edge of the laser pulse, I_{sat} values are also attained much earlier in the time evolution of the laser pulse. Consequently, by the time the MPI electrons are accelerated to sufficient energy there are no neutral molecules left to be attached to. In this scenario, anion formation is expected to have a maximum probability only at intermediate values of I_p , consistent with data depicted in Fig. 2(a).

The pattern of anion formation when CO_2 is irradiated with strong laser fields was also found to be dramatically different from the EI case; Fig. 3 shows a typical mass spectrum measured at a laser intensity of $4 \times 10^{13} \text{ W cm}^{-2}$. The O^- anion dominates but a distinct and highly reproducible signal was obtained which corresponded, unexpectedly, to CO^- . It is well established that CO^- has a negative electron affinity and, as such, is not expected to be long lived enough to be observed in a spectrometer in which ion transit times are as long as microseconds. The observation of this anion prompted an extensive series of careful measurements of mass-to-charge ratios in our TOF spectrometer, details of which will be presented elsewhere. Suffice it to state that

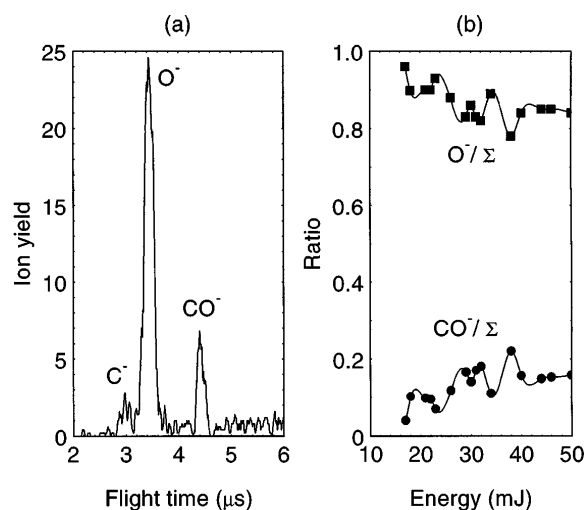


FIG. 3. (a) Anion mass spectrum obtained when CO_2 was irradiated by 1064-nm, 35-ps-wide laser pulses of peak intensity: $4 \times 10^{13} \text{ W cm}^{-2}$. (b) Variation of the ratio of specific anion yields to total anion yield (Σ) with laser intensity.

all tests which we performed confirmed our designation of the second-most intense peak in the anion spectrum as CO^- . Figure 3 also depicts how the ratios of O^- and CO^- to the total anion signal vary with laser intensity; as in the case of CS_2^- , both anions formed from CO_2 possess the same threshold. However, the most significant difference is the observation of a small fraction of C^- ions (note that C^- was not observed at all in measurements on CS_2 ; the C atom is geometrically central in both molecules).

Angular distributions of anions were also measured in the present study. By way of example, polar plots for O^- ions obtained from CO_2 and O_2 are shown in Fig. 4 where the radial distance from the origin of each data point is a measure of ion yield in a given angular direction. The light pulses were elliptically polarized in these measurements; the degree of ellipticity is indicated in the figure. A number of angular distribution measurements were made which, taken together, covered all four quadrants in the angular range 0° – 360° around the TOF axis. As in other recent work reported from our laboratory [5], no difference was found in the shapes of the distributions obtained in the different quadrants when the alignment of the focused laser beam with the molecular target and the TOF axis was perfect. The angular distribution data depicted in Fig. 4 pertain to measurements made in the 0° – 90° quadrant; for clarity of presentation, we have chosen to reflect such single quadrant data over the 90° – 360° range. The anisotropy of the O^- signal from CO_2 is dependent on the vector properties of field-induced transition moments associated with intermediate excited states of the precursor and their relation to the direction of the major and minor laser polarization vectors. Distributions of the form $\cos^n \theta$ and $\sin^n \theta$ result from n -photon excitations, producing major lobes at 0° , 180° and minor ones

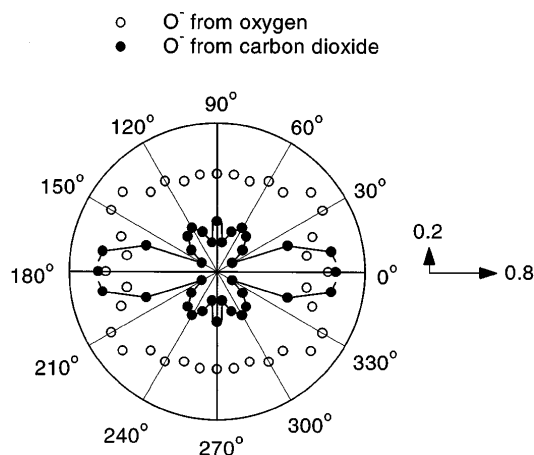


FIG. 4. Polar plot of the angular distributions of O^- from CO_2 and O_2 using elliptically polarized laser pulses of peak intensity: $4 \times 10^{13} \text{ W cm}^{-2}$. The degree of ellipticity is indicated.

at 90° , 270° ; contributions from a $\cos \theta \sin \theta$ type of angular function result in lobes at $\sim 60^\circ$, 120° , 240° , and 300° (for a detailed discussion of such vector correlations, see [6,7]). Qualitatively, the data shown in Fig. 4 indicate that the strong laser field induces dipole moments in CO_2 and that a torque is exerted on the initially randomly oriented molecules such that the internuclear axes tend to spatially align along the laser's field direction. Dissociative attachment to such spatially aligned CO_2 gives rise to the anisotropic angular distribution of O^- fragments. Figure 4 also shows the angular distribution of O^- anions from O_2 . A high degree of isotropy is obtained. This indicates that, in contrast to the CO_2 case, the strong field induces fragmentation of O_2 prior to electron attachment to each O atom.

We now consider the unusually long-lived CO^- fragment observed in our experiments on CO_2 . It is pertinent to note that formation of long-lived CO^- anions has also been recently discovered in a series of carefully conducted experiments [8] on sputtering of $TiAlN(C,O)$ surfaces using 14.5 keV Cs^+ ions. Production of highly excited molecules in the transient, hot plasma formed in the course of sputtering has been proposed as the prerequisite for the formation of CO^- ions. Production of a transient, hot plasma also occurs in intense field experiments of the type we have conducted, and, by analogy, formation of highly excited states of either CO_2 or of CO_2^- might possibly be a precursor to the long-lived CO^- anion. The high degree of electronic excitation of the precursor would, as far as energetic considerations go, make the CO^- state bound with respect to it, notwithstanding the negative electron affinity value (-2.4 eV) ascribed to this anion [9]. It is also possible that such an

excited state possesses nearly linear geometry although, intriguingly, our preliminary *ab initio* computations of the geometry of low-lying doublet, quartet, and sextet states of CO_2^- and CS_2^- indicate nonlinear equilibrium structures [10]. Recent calculations on isoelectronic N_2^- [11] have shown that a quartet state of this anion also possesses a long lifetime. Energetic considerations rule out the possibility of CO^- being formed by two-electron attachment to CO^+ , and it would be of interest to explore whether three "equivalent" electrons around a positive-ion core constitute a relatively stable configuration.

In summary, our experiments have revealed the existence of a hitherto unsuspected channel leading to formation of negative ions in the interaction of intense laser fields with molecules. Dissociative attachment by low-energy electrons produced in the field-molecule interaction is postulated to be responsible for such anion formation. The anions are formed from a common precursor in each case; their yield is dependent on the laser intensity and the overall fragmentation pattern is dramatically different from that obtained in EI experiments. The former is due to variations in ponderomotive potential which accelerates the low-energy electrons, and the latter is likely to be a reflection of the extent of field-induced distortions of anion potential energy surfaces. The laser field also spatially aligns the precursor triatomic anions along the direction of the polarization vector. There are grounds to suggest that the precursor anions are formed in highly excited electronic states. The unusual DA pattern we measure may also result from electron scattering from field-excited neutral molecules.

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