

## Multielectron Dissociative Ionization of Molecules by Intense Laser Radiation

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We solve the hydrodynamic-ballistic equations of motion for a one-dimensional time-dependent Thomas-Fermi model of  $\text{Cl}_2$  exposed to an intense subpicosecond laser field, and observe simultaneous multielectron ionization and molecular dissociation. The fragment kinetic energy defect with respect to the simple Coulomb explosion picture is found to originate in ejected-electron screening of the escaping fragments; its magnitude agrees with that observed in recent experiments. [S0031-9007(96)02059-5]

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Molecules exposed to intense ( $I > 10^{13} \text{ W cm}^{-2}$ ) subpicosecond laser pulses undergo multiple ionization accompanied by dissociation, a process denoted by multielectron dissociative ionization (MEDI) [1–3]. The simplest picture of MEDI is the “Coulomb explosion,” in which the laser field quickly strips electrons off of the molecule, and the charged ionic fragments dissociate under the influence of the repulsive Coulomb potential. In this picture the total kinetic energy of the fragment pair with charges  $q_1e$ ,  $q_2e$  should be equal to  $T = q_1q_2e^2/4\pi\epsilon_0R_e$  (SI units), where  $q_1$  and  $q_2$  are integers,  $e$  is the elementary charge, and  $R_e$  is the equilibrium internuclear separation of the neutral molecule.

In experiments, however, it is found that the fragment kinetic energies are consistently lower than those predicted by the Coulomb explosion model, by an amount called the kinetic energy defect  $\Delta$ . This appears to be true for all observed fragmentation channels, and does not depend much on the laser wavelength or pulse duration. The fragment energies are consistent with a Coulomb explosion at a value of  $R$  some (20–50)% greater than  $R_e$ . However, since the characteristic time scale for molecular internuclear motion (a vibrational period) is long compared to the time scale on which strong-field multiple ionization occurs, it is difficult to see how a simple Coulomb explosion picture could be applicable.

This Letter offers a simple explanation of these MEDI observations and supports it by numerical calculations applied to a model molecule. A Coulomb explosion is initiated at  $R_e$ , when the most loosely bound electrons are stripped from the molecule, but the ejected electron cloud does not expand rapidly. Ionization continues until only a tightly bound electronic core remains, and is then shut off by the strong internal molecular field [although for very intense radiation there may be some post-dissociation ionization (PDI)]. Most electron stripping thus occurs near

$R \approx R_e$ , so one sees a brief interval of acceleration of the ionic fragments by increasing mutual Coulomb repulsion. However, when the ionization shuts off, a countervailing *decelerating* tendency becomes apparent: As the fragments separate through the ejected electron cloud, more electronic charge is encompassed by the increasing internuclear separation  $R(t)$ , and the resultant screening slows the fragments. This post-explosion screening gives a value of  $\Delta$  consistent with that observed in experiments. Charge-symmetric fragmentation is confirmed [4] to be a major channel of dissociation. These conclusions differ from those of other recent models [2,4–6].

To illustrate this picture, we have solved the time-dependent equations of motion for the nuclei and electrons of a model  $\text{Cl}_2$  molecule in a strong laser field. All electrons are treated explicitly, via time-dependent density functional theory. We know of no other treatment of molecules in strong fields that deals explicitly with more than one electron. Our approach is made as follows.

In strong-field laser irradiation of diatomic molecules, it is believed [6] that the molecular axis is quickly aligned with the polarization vector of the radiation field, so the ionization process can be modeled with the molecular axis parallel to the electric field. To simplify the calculations we make the additional approximation of confining all particles in the system to move in one dimension, defined by this axis. This approximation has been used to model strong-field interaction with atoms [7] and with the  $\text{H}_2^+$  molecule [8], and it has replicated much of the essential physics of three-dimensional systems. We utilize time-dependent density functional theory to deal directly with the electron density vs the many-electron Schrödinger wave function. We have previously applied such a theory to treat three-dimensional atoms in strong radiation fields [9] and obtained results for multiple electron ionization that agree well with experiments.

The electron density of the molecule is described as a fluid of mass density  $\rho(x, t)$ , with an associated velocity field  $v(x, t)$ , which obeys the equations of motion

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}(\rho v) = 0,$$

$$\frac{\partial v}{\partial t} + v \frac{\partial v}{\partial x} = -\frac{1}{\rho} \frac{\partial}{\partial x} P + \frac{e}{m} \frac{\partial}{\partial x} \Phi. \quad (1)$$

The first of Eqs. (1) is the usual continuity equation. The second is the classical equation of motion for an infinitesimal element of fluid subject to forces due to the gradients of an electrostatic potential  $\Phi$  and a pressure  $P = -(\partial U / \partial x)_s$ , where  $U$  is the internal energy density of the fluid. The effects of quantum mechanics in this equation must be expressed by a constitutive relation between  $P$  and  $\rho$ . Such a relation was derived in a semiclassical approximation by Thomas and Fermi (TF) [10]; its variants have been used to investigate the ground state properties of atoms [11,12] and weak-field atomic radiative response [13]. The TF model treats the electrons as a Fermi gas at temperature  $T = 0$  and determines the energy of the gas by filling the available phase-space volume, subject to the Pauli exclusion principle. This gives  $U$  of the three-dimensional electron gas as a local function of the density, of the form  $U(\mathbf{r}) \sim \rho(\mathbf{r})^{5/3}$ .

We have sought a corresponding relationship applicable to the one-dimensional many-electron system. The Hohenberg-Kohn theorem [14] ensures that the energy of a stationary one-dimensional system is a functional of the electron density, but the semiclassical TF arguments may not provide a good approximation to the true energy functional. Experimentation with possible forms of the functional leads us to propose the following expression for the energy density of a one-dimensional electron gas  $U(x) = An^2(x)$ , where  $n(x)$  is the electron density function [ $n(x) = \rho(x)/m$ ], and  $A$  is a universal constant. The value of  $A$  is determined by requiring that it give reasonable physical properties (binding energies, etc.) of the model systems. Such an expression is also obtained by applying the semiclassical method in *two* dimensions [15].

In treating Coulomb interactions in one dimension, it is necessary to eliminate the singularity in the potential at  $x = 0$ . We follow a standard procedure [7,8] and write the electrostatic potential  $\Phi$  of our model diatomic molecule as

$$\Phi = \frac{Ze}{\{b^2 + [x - x_1(t)]^2\}^{1/2}} + \frac{Ze}{\{b^2 + [x - x_2(t)]^2\}^{1/2}} - e \int_{-\infty}^{\infty} \frac{n(x', t)}{[c^2 + (x - x')^2]^{1/2}} dx'. \quad (2)$$

Here  $Z$  is the atomic number and  $x_1(t), x_2(t)$  are positions of the two nuclei. The parameters  $b, c$  serve to smooth the Coulomb interaction at points of coalescence.

By solving the static case of Eq. (1) we obtain the linear relationship  $n(x) = e\Phi(x)/2A$ , which provides an integral equation for the electrostatic potential of the time-independent solution [16]. Its linearity allows us

to construct the solution for a many-atom system by linear combination of appropriately shifted single-atom solutions. It is easy to show that the parameters  $A, b$ , and  $c$  are not independent [16]:  $A = e^2 \ln(c/b)$ . Thus we always have  $c > b$ . Furthermore, our numerical calculations of values of  $R_e$  and  $D$  for various values of  $Z$  indicate that the value of  $A$  must be essentially independent of  $Z$  and that  $A = 0.3$  a.u. [in the usual atomic units (a.u.) in which the numerical values of the electron mass  $m$ , the elementary charge  $e$ , and the reduced Planck's constant  $\hbar$  are equal to unity]. If  $A$  lies outside a narrow band of values around 0.3 a.u., one obtains unreasonable values of  $R_e$  and  $D$ .

We have applied this model to describe the  $\text{Cl}_2$  ( $Z = 17$ ) molecule in a strong radiation field. By solving the static equation as a function of internuclear distance, we find the Born-Oppenheimer potential curves for  $\text{Cl}_2$  and  $\text{Cl}_2^{+2}$  displayed in Fig. 1. These results were obtained with the parameter set ( $A = 0.3$  a.u.,  $b = 1.22$  a.u.,  $c = 1.65$  a.u.) which yields  $R_e = 3.8$  a.u. and  $D = 0.11$  a.u., in agreement with the experimental values [17] of  $R_e = 3.76$  a.u. and  $D = 0.091$  a.u., respectively.

We treat the time-dependent system by adding the electric dipole interaction with the radiation field to (2) and solving the hydrodynamic equations for the electronic density simultaneously with the classical equations of motion for the positions of the nuclei. We treat Eqs. (1) as an initial value problem, with the density  $\rho(x, t = 0)$  given by the static solution, and the nuclei initially at rest and separated by  $R_e$ . The first check of the time-dependent method is to verify that it reproduces molecular vibrations when no external field is present. That it does is shown in the inset of Fig. 1, which displays the free oscillation of the internuclear distance in the absence of a radiation field. The period of oscillation of 34 fs is shorter than the experimental value [17] of 59 fs,

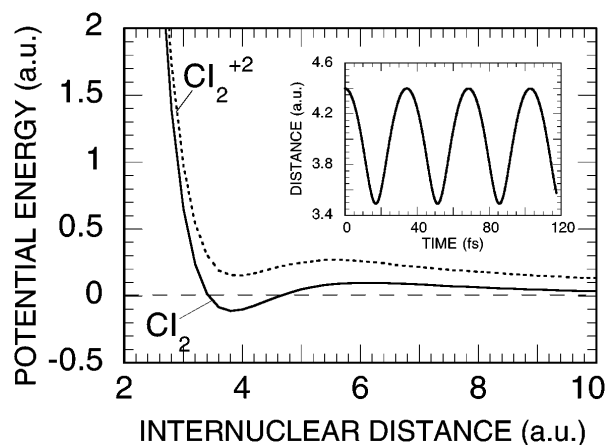


FIG. 1. Potential energy curves for  $\text{Cl}_2$  and  $\text{Cl}_2^{+2}$  as computed with the parameters  $A = 0.3$  a.u.,  $b = 1.22$  a.u.,  $c = 1.65$  a.u. Inset: Internuclear distance as a function of time for free oscillations of  $\text{Cl}_2$  for small internuclear excursions away from  $R_e$ .

so our model overestimates the stiffness of the molecular potential at  $R_e$ .

We now discuss the effects of an intense subpicosecond laser pulse on this system. The laser frequency of  $\omega = 0.0746$  a.u. (wavelength  $\lambda = 610$  nm), is that used in the experiments of Refs. [2,3]. The laser pulse is turned on with a  $\sin^2[\pi t/(2\tau)]$  ramp; we treat short-pulse and long-pulse cases in which the ramp time  $\tau$  is 10 or 70 optical periods  $T$  (20 or 140 fs), respectively.

Figure 2 shows short-pulse results for a peak field strength  $F_p = 0.6$  a.u. (corresponding to a laser intensity  $I = 1.3 \times 10^{16}$  W cm $^{-2}$ ). The inset to Fig. 2(a) shows

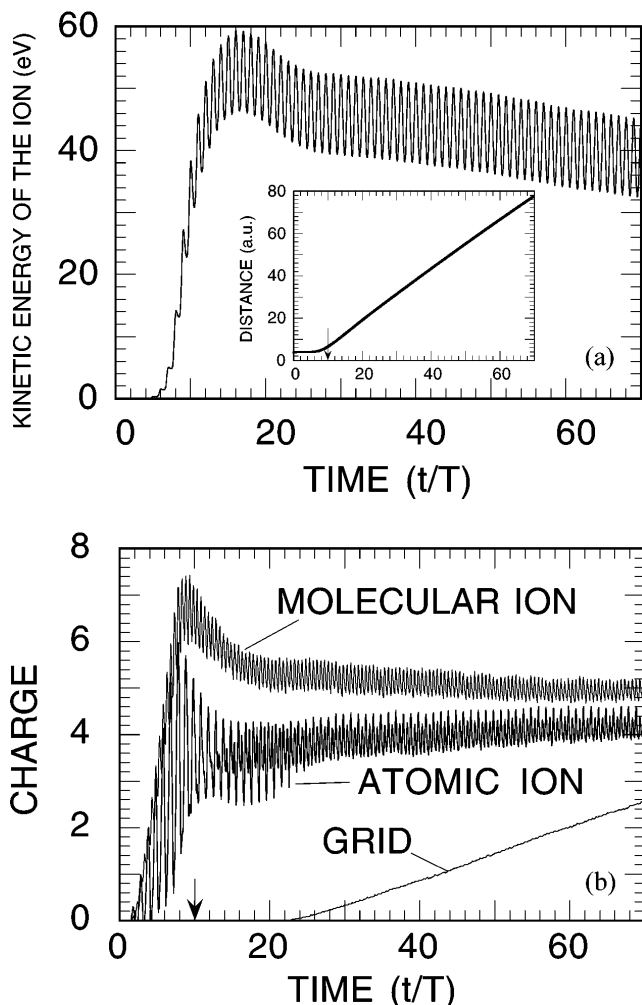


FIG. 2. Evolution of the molecular features for  $F_p = 0.6$  a.u. and  $\omega = 0.0746$  a.u. with the field ramped to maximum intensity in 10 optical periods  $T$ , as marked by the arrow. (a) Kinetic energy of the atomic ion fragments vs time; inset shows internuclear distance vs time. Note that Coulomb explosion begins near the peak intensity; deceleration of the fragments sets in around  $t = 20T$ . (b) Distribution of net electrical charge (includes both nuclear and electronic components). Grid: net charge of the system on our spatial grid, which is contained in a box of length 200 a.u.; increase around  $t = 20T$  comes from ejected electrons leaving the box, as simulated by absorbing boundary conditions. Atomic ions and molecular ions: see text.

the Coulomb explosion: The nuclei remain essentially at rest until a time just before  $F_p$  is reached; then there is rapid acceleration (increase in cycle-averaged kinetic energy) during an interval of about  $10 T$ ; and then a gradual deceleration. The dynamics of this system can be readily understood in terms of the time dependence of the charge distribution, which is summarized in Fig. 2(b). The lowest, nearly straight line, labeled “grid,” displays the total electric charge on our grid, and thus represents the number of electrons that have been absorbed at the boundaries; the “atomic ion” value consists of the charge within 3 a.u. of either of the ionic fragments, which is seen to be a good long-time indicator of the charge localized on that fragment; and “molecular ion” indicates the sum of the two atomic ion charges, plus all charge in between. We can see that by the time the molecular and atomic ions have settled into steady behavior, at  $t \approx 20T$ , no charge has been absorbed at the walls of our box; the gradual departure of charge from the system at later times does not significantly affect them. Note that the final charge state of each atom is  $+4$ , whereas that of the “molecule” is  $+5$ . Thus there are three units of negative charge (electrons) left in the space between the two fragments, which screen their mutual Coulomb repulsion.

The molecular charge is seen to show a sudden decrease at  $t \approx 10T$ , which corresponds to an increase in the enclosed number of electrons. This results from two

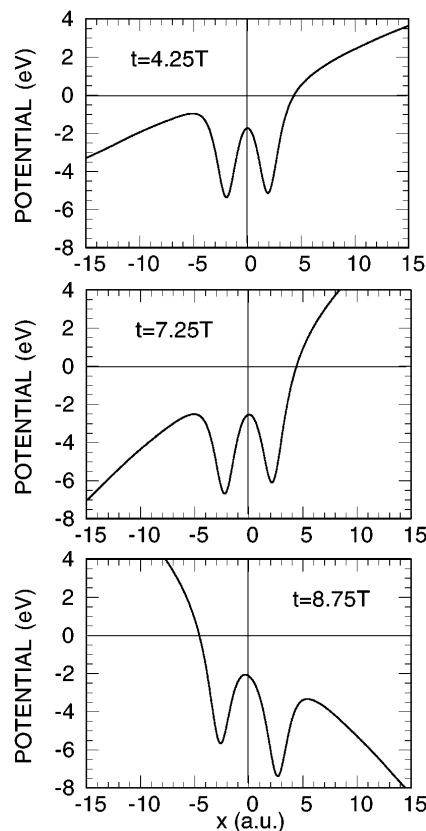


FIG. 3. Self-consistent potential curves for the case of Fig. 2 at  $t = 4.25, 7.25,$  and  $8.75 T$ , as indicated.

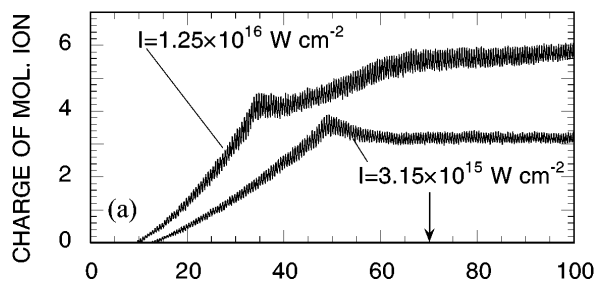


FIG. 4. Molecular charge vs time  $\omega = 0.0746$  a.u. in the case of a long pulse ramp, at two values of peak intensity as labeled:  $F_p$  is attained at 140 fs as marked by arrow. The effects of ionization shutoff and ejected-electron enclosure are similar to those seen in the short-pulse case of Fig. 2. The knee occurs at roughly the same instantaneous field strength in the two cases, corresponding to the shutoff condition displayed in the bottom frame of Fig. 3. PDI is seen at the higher intensity.

effects: the shutoff of molecular ionization; and the increasing distance between the fragments, so that more of the ejected electron cloud lies between them. It is not due to a rescattering mechanism, which would occur on the time scale of one field period. The mechanism of ionization shutoff is shown in Fig. 3, which displays snapshots of the self-consistent molecular potential  $e\Phi(x, t)$  early in the pulse. The two atomic potential wells are superposed on the linear potential of the electric field, which oscillates in time. Electronic charge on the sides of the atomic wells or in the interstitial region will be stripped off early in the pulse since there is no barrier to its escape. However, by  $t = 8.75T$  the loosely bound charge is gone, and the remaining charge is stuck in the atomic wells (tunneling does not occur in our model; it would be slow in real systems under these conditions). The shutoff of the ionization thus stops the molecular charge from increasing; the actual decrease of charge that follows is due to the enclosure of previously ejected electronic charge between the separating ion fragments. Comparison of frames (a) and (b) of Fig. 2 shows that roughly two units of electronic charge are added to the molecule in this way within about 20 fs ( $10T$ ) after ionization shutoff, at which time the deceleration begins. This results in  $\Delta \approx 20$  eV, in agreement with the experiments of Ref. [2,3].

For completeness we comment on the long-pulse case. If the ramp of the pulse is increased, we see the same deceleration mechanism as in the short-pulse case, although PDI occurs at high intensities. Figure 4 shows molecular charges for two intensities, at the same frequency as in Fig. 2, but with a ramp time of 140 fs. At both intensities we see a knee in the curve similar to that in Fig. 2, occurring at about the same value of instantaneous field strength. At the higher intensity, the knee represents only

a pause in ionization, and PDI occurs as the field rises to its peak strength.

In conclusion, we have presented the first dynamical model of MEDI. The model reproduces the main features of the experimental data, but it does not support the idea of stabilization [2], nor does it attribute much importance to enhanced ionization at some critical distance [6]. We predict some post-dissociation ionization for longer, picosecond pulses with peak intensities above  $10^{16}$  W cm $^{-2}$ . This could be tested experimentally.

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