Role of Non-Coulombic Potential Curves in Intense-Field Dissociative Ionization of Diatomic Molecules

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Dissociative ionization of N_2 induced by intense picosecond radiation has been studied. A two-step multiphoton model, based on ionization of N_2 through vertical transitions and spontaneous dissociation of N_2^{Z+} ($Z \geq 2$) via Coulomb and non-Coulombic potentials curves, is presented to explain the origin of the kinetic energies of atomic ions observed. The model predicts that dissociation occurs near the internuclear separation of the neutral, charge-asymmetric dissociation channels are important, and dissociation via Coulomb curves will only be observed for pulses with extremely short rise times.

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The ability to generate intense, coherent pulses of short duration has ushered in the era of optical manipulation of the electronic environment of matter. Since the electric field strength in these pulses can be a significant fraction of the atomic field strength, the optical field can no longer be treated as a small perturbation in atom-field interactions. Two of the more striking effects that intense fields can cause are a shifting of energy levels and the removal of electrons. In the case where two atoms are bound together as a diatomic molecule, the loss of electrons is ultimately accompanied by an energetic separation of the atomic ions, a phenomenon often referred to as a "Coulomb explosion." This term is used because it is generally believed that the asymptotic kinetic energies of the two departing atomic ions are related solely to the electrostatic Coulomb potential between them. One of the conclusions drawn from this pure Coulomb picture is that ionization of the diatom does not always occur via vertical transitions but can be interlaced with dissociation [1-5]. As a consequence, the kinetic energies of the atomic ions observed indicate that dissociation must originate at an internuclear separation R_{diss} that is larger than R_e, the equilibrium bond length between the two neutral atoms. In this paper, we will argue that this picture is too simplistic because it ignores the fact that many of the potential curves of multiply ionized diatoms are not represented well by Coulomb potential curves especially at short range ($\approx R_e$). In particular, since the non-Coulomb portion of these potentials tends to lie below the corresponding Coulomb part, dissociation subsequent to vertical transitions only appears to have originated from $R_{\text{diss}} > R_e$.

The models that have been suggested to describe the energetic dissociative ionization of a diatom fall into two camps—multiphoton ionization and field ionization. A multiphoton model including only Coulomb curves requires the diatomic molecule to be ionized repeatedly, while promoting it to higher and higher Coulomb potential curves, until either the radiation field is terminated or the Coulomb repulsion is strong enough that dissociation, $AB^{(Z_1+Z_2)+} \rightarrow A^{Z_1+} + B^{Z_2+}$, is more favorable than further ionization. The total energy shared between A^{Z_1+} and B^{Z_2+} is $14.4 Z_1 Z_2 / R_{\text{diss}}$ eV (with Z_i the number of missing electrons and R_{diss} expressed in Å). In Ref. [4], it was reported that R_{diss} depends strongly on the value of Z_1+Z_2 and only weakly on the wavelength and the molecular species. The mean values deduced in Ref. [4] for N_2, CO, and O_2, obtained at 610 and 305 nm, are summarized in Table I. Since simultaneous dissociation and ionization is a many-body process involving the two departing ions and at least one electron, it is perplexing how the dissociation could occur at a specific R from a multiphoton picture. Field-ionization models do predict that R_{diss} increases with the value of Z_1+Z_2 [6,7]. However, in distinction with multiphoton models, field-ionization models have difficulty accounting for the charge-asymmetric dissociation channels ($|Z_1 - Z_2| \geq 2$) that have been reported [2,8,9]. Since the evidence strongly supports the reality of the asymmetric channels, we will use the multiphoton picture to show that $R_{\text{diss}} > R_e$ is only apparent.

To explore this line of reasoning, consider the following two-step mechanism. In the first step, AB is driven to a low-lying metastable (lifetimes $\gg \tau_{\text{pulse}}$) state of AB^{2+} through multiphoton absorption. Metastable features with vibrational structure are quite common for these light doubly ionized diatoms [10]. Figure 1 shows an *ab initio* calculation of several of the field-free states of N_2^{2+} [11]. At short R, these curves deviate substantially from electrostatic Coulomb curves. The metastable feature is due to the fact that for two singly charged atomic ions, the electrostatic forces are repulsive at large range, while the exchange forces and electrostatic screening responsible for bonding two neutral atoms is nearly

TABLE I. R_{diss} from Ref. [4] for Co, N_2, and O_2.

$AB^{(Z_1+Z_2)+}$	$R_{\text{diss}}^{610/305\text{ nm}}$ (Å)
$A^{2+}+B^{+}$	2.4
$A^{2+}+B^{2+}$	3.2
$A^{3+}+B^{3+}$	6.5

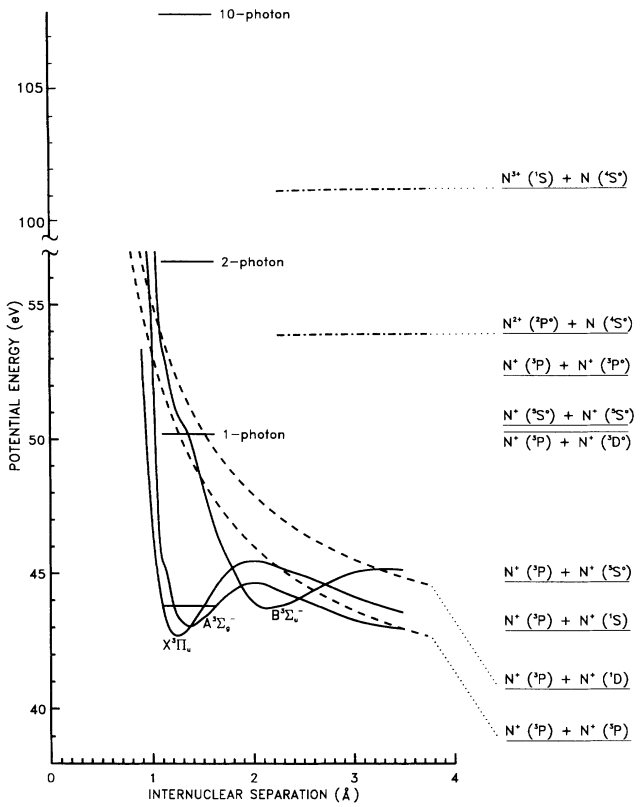

FIG. 1. Three low-lying *ab initio* potential curves of N_2^{2+} from Ref. [11] (solid curves), the Coulomb potential curves converging to the two lowest limits of $N^+ + N^+$ (dashed curves), and the asymptotic portion of the polarization-induced attractive potential curve converging to $N^{2+} + N$ (dot-dashed lines). The X and A states converge to the lowest limit while the B state converges to the next higher limit. The horizontal lines mark the integral number of photon energies from 43.8 eV. The energy scale is relative to the $v = 0$ level of the ground state of N_2.

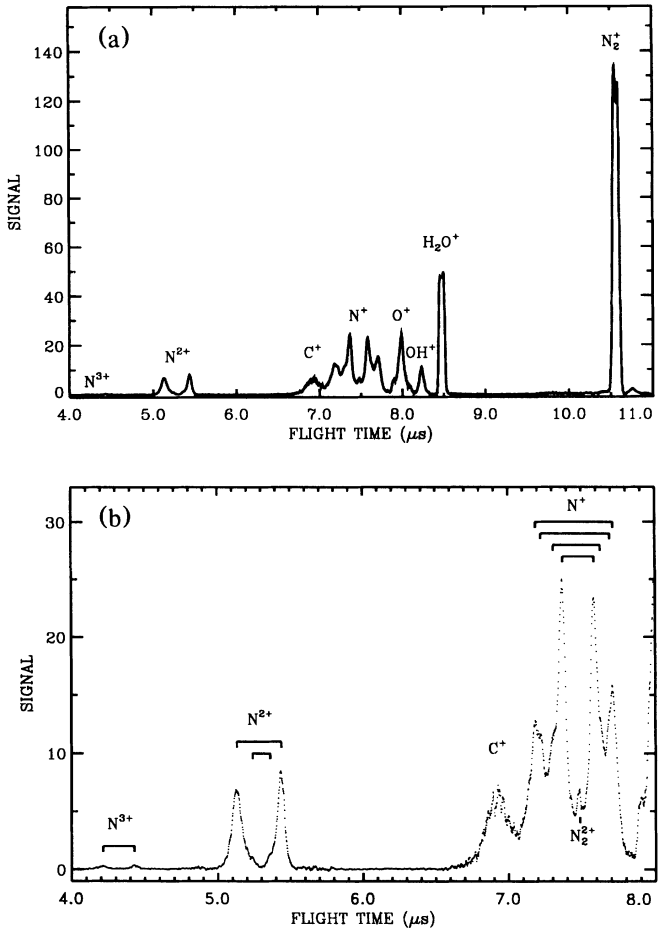

FIG. 2. An average (2688 laser pulses) 193-nm, 12-ps N_2 spectrum with the background (an average of 512 laser pulses) subtracted. Each spectrum was obtained with a temporal resolution of 1 ns and with power densities ranging from 10^{14} to 10^{15} W/cm^2. The doublet in the N_2^{2+} peak is an artifact of an incomplete subtraction due to saturation of the scope.

unchanged at close range [12,13]. To first order, the potential curves will look similar to those of the isoelectronic neutral plus a Coulomb repulsive term with wells that lie above the dissociation thresholds. The second step in our mechanism, which is responsible for the ultimate dissociation, can be as simple as a photodissociation of N_2^{2+}, leading to ground and/or excited ions, or a more complicated multiphoton ionization, with subsequent dissociation leading to nitrogen fragments in higher stages of ionization. Since R_e for N_2, N_2^+, and N_2^{2+} are nearly the same, about 1.1 Å, all the transitions would be nearly vertical.

To test this hypothesis, we performed a series of experiments in N_2 with linearly polarized nearly diffraction-limited 193-nm pulses that were 10–15 ps in duration and focused to an intensity of about 5×10^{14} W/cm^2. (See Ref. [14] for details about the generation of these pulses.) This wavelength was chosen to be as far away from the field-ionization limit as possible without being a harmonic of 610 nm. The experiments were run with N_2 pressures of $(5-8)\times10^{-8}$ Torr. The kinetic energy spectra of ejected atomic ions were obtained by standard time-of-flight (TOF) techniques with a temporal resolution of 1 ns.

A typical spectrum is displayed in Fig. 2. Atomic nitrogen ions with up to three electrons removed appear in the spectrum. The results are summarized in Table II. In column 2, we present the kinetic energies observed for each N^{Z+} ion. The R_{diss}, according to the Coulomb model, are given in column 3 for the ion pairing in column 4. No pairing of atomic ions appears to be due to dissociation at R_e (≈ 1.1 Å) via a Coulomb curve. The pairing of N^{2+} and N^+ ions with a total energy of approximately 10 eV is in reasonable agreement with the data of Table I giving R_{diss} of 2.8 Å. The slow N^{2+} and the N^{3+} components, however, do not follow the pattern

TABLE II. Kinetic energies, Coulomb model R_{diss}, and non-Coulomb model fragment pairing for $R_{diss} \approx R_e$ of N_2, 1.10 Å.

Ion	Energy (eV)	Coulomb model R_{diss} (Å)	Coulomb model Pairing	Non-Coulomb model pairing (at R_e)
N^+	$0.7^{+0.2}_{-0.7}$	N.A.[a]		N/A[a]
	$1.5^{+0.4}_{-0.6}$	N.A.[a]		N/A[a]
	$3.8^{+0.4}_{-1.9}$	1.9	$N^+ + N^+$	$N^+[^3P] + N^+[^1S]$
	$4.5^{+3.0}_{-0.4}$	1.6	$N^+ + N^+$	$N^+[^3P] + N^+[^1D]$
N^{2+}	$1.5^{+0.5}_{-1.4}$	19.2	$N^{2+} + N^{2+}$	$N^{2+}[^2P^\circ] + N[^4S^\circ]$[c]
		9.6	$N^{2+} + N^+$	
	$5.5^{+5.0}_{-3.5}$	5.2	$N^{2+} + N^{2+}$	$N^{2+}[^2P^\circ] + N[^4S^\circ]$[c]
		2.8	$N^{2+} + N^+$[b]	
N^{3+}	7.5 ± 5.0	8.6	$N^{3+} + N^{3+}$	$N^{3+}[^1S] + N[^4S^\circ]$

[a]These ions do not originate from multiply ionized N_2. See text.
[b]The pairing is between the 4.5 N^+ and 5.5 N^{2+} components.
[c]The 1.5- and 5.5-eV components differ by approximately the energy of one photon.

suggested in Table I. As discussed below, the fragment pairing according to our non-Coulomb model is given in column 5.

There are four major N^+ components that appear in our spectrum. The two lower-energy components are uninteresting for this discussion because they can be associated with the dissociation of N_2^+ [15]. The two higher-energy components are consistent with a seven-photon (44.8 eV) vertical excitation of N_2 that leaves N_2^{2+} in the A state. This would be followed by a one-photon (6.4 eV) transition to the B state. As shown in Fig. 1, a vertical one-photon transition from the middle of the A well (43.8 eV) would result in N^+ fragments in the ^3P and ^1D states each with 4.7 eV of kinetic energy. This would account for the fastest N^+ component. The full picture of the potential curves is complicated by a plethora of curve crossings [11]. Consequently, as the ions separate on the B state, some of the ^1D ions will be excited to the ^1S state. The energy of each fragment would be reduced to about 3.6 eV, close to what we observe. One must remember that the energies determined from the field-free curves are only approximate because the intense field will perturb the curves.

The energy level diagram in Fig. 1 suggests that a charge-asymmetric dissociation via a curve leading to $N^{2+} + N$ could contribute to the production of N^{2+}. The threshold to generate $N^{2+} + N$ at R_e could be as low as 54 eV. This is because the force between N^{2+} and N will be attractive at long range, varying as $1/R^4$ due to the polarization induced in N by N^{2+}. At some point, roughly when the electrons' clouds begin to interact, bonding (or antibonding) features will begin to appear. In contrast, the asymptotic behavior of a potential curve leading to $N^{2+} + N^+$, which is necessary for the Coulomb-model explanation of N^{2+}, will be repulsive as $1/R$. The lowest threshold to generate N_2^{3+}, at R_e, will be 95 eV if the potential curves remain Coulombic and somewhat less if there is some residual bonding. In general, it is more favorable to reach asymmetric non-Coulombic curves than quasi-Coulomb curves. Our two N^{2+} components are consistent with a two- and three-photon dissociation via the asymmetric curve shown Fig. 1. It is interesting to note that the 1.5- and 5.5-eV components are separated by nearly $h\nu/2 = 3.2$ eV and are thus possible examples of above-threshold dissociation of N_2^{2+}.

As additional electrons are removed, the non-Coulombic curves will always be reached before the corresponding quasi-Coulomb curve leading to the same stage of atomic ionization. In the case of N^{3+}, the threshold to generate $N^{3+} + N$ at R_e (threshold ≈ 101 eV at $R = \infty$) will be substantially lower than that of $N^{3+} + N^+$ (threshold ≈ 156 eV at R_e), $N^{3+} + N^{2+}$ (threshold ≈ 224 eV at R_e), or $N^{3+} + N^{3+}$ (threshold ≈ 311 eV at R_e). As few as ten, eleven, or twelve photons could generate N^{3+} with 3.3, 6.6, and 9.8 eV, again depending on the bonding characteristics and energy of the ejected electron. The broad feature we observe is consistent with this postulation.

The validity of our model rests in part on the reality of asymmetric dissociations, which have been controversial [1,5,7]. The controversy has been fueled by the near null observation of asymmetric channels when the spectra are analyzed by ion-ion covariance, which allow ionic dissociation partners to be associated with each other unambiguously [16]. The recent observation of asymmetric channels in an I_2 experiment using 30- and 80-fs pulses [9] provides the resolution of this controversy. When relatively long-pulsed lasers ($T_{pulse} > 500$ fs) are used, the intensity will still be high enough after dissociation that multiple ionization of the atomic fragments will occur, as they will require fewer photons to reach the multiple ionization stage than did the diatomic molecule. Ion-ion covariance cannot distinguish nascent ions from postdissociation ions.

In conclusion, we have shown that the non-Coulombic potential curves can trap the doubly ionized diatom near

R_e and cause the final kinetic energies of the ions to be lower than what would be expected for a Coulomb curve dissociation. True Coulomb explosions, which have been observed when intense pulses with extremely fast rise times are employed [8,9], will only occur for AB^{Z+} when $Z \geq 4$ where the Coulomb term dominates. These curves are apparently not reached in long-pulsed experiments.

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