



# MULTIPLE IONIZATION DYNAMICS OF MOLECULES IN INTENSE LASER FIELDS

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## Abstract

A classical field-ionization model is developed for sequential multiple ionization of diatomic and linear triatomic molecules exposed to intense ( $\sim 10^{15}\text{W/cm}^2$ ) laser fields. The distance  $R_{\text{ion}}$  of Coulomb explosion is calculated for a *combination* of fragment charges, by considering nonadiabatic excitation followed by field ionization associated with the inner and outer saddle points. For diatomic molecules ( $\text{N}_2$ ,  $\text{NO}$ , and  $\text{I}_2$ ), the model explains behaviors observed in experiments, as  $R_{\text{ion}}(21 \rightarrow 31) < R_{\text{ion}}(21 \rightarrow 22)$  between competing charge-asymmetric and symmetric channels, and even-odd fluctuation along a principal pathway. For a triatomic molecule  $\text{CO}_2$ , a comparison of the model with an experiment suggests that charge-symmetric (or nearly symmetric) channels are dominantly populated.

## 1 Introduction

Interwoven electronic and nuclear dynamics emerges in a molecule when exposed to an intense ( $\sim 10^{15}\text{W/cm}^2$ ) laser field [1, 2]. Since its peak field strength is comparable to an internal field in an atom, a small molecule will be multiply ionized and subsequently dissociated into atomic fragment ions (Coulomb explosion). This process has been extensively and intensively investigated with the recent technique of ion-momentum imaging for a variety of diatomic ( $\text{NO}$ ,  $\text{I}_2$ ,  $\text{N}_2$ , ...) [3–6] and linear triatomic ( $\text{CO}_2$ ,  $\text{CS}_2$ ,  $\text{OCS}$ , ...) [7–9] molecules.

Of particular interest thereby is a phenomena called *enhanced ionization*, *i.e.*, remarkable enhancement of ionization rate in comparison with that for an isolated constituent atom. This phenomena has been basically explained for a homonuclear diatomic molecule with a classical field-ionization model developed by Posthumus *et al* [10]. They take account of the effect of bond stretching as a result of initial excitation and ionization. As the bond length  $R$  is elongated during the laser pulse duration ( $\sim 10^{-13}$  s), the outermost electron remaining will get localized into atomic sites to be Stark shifted. Accordingly, the appearance field strength  $F_{\text{ap}}(R)$  of multiple ionization is lowered until reaching a minimum at a *critical distance*  $R_{\text{cr}}$ , which turns out a few times as large as the equilibrium distance, weakly depending on ionization stages. These behaviors are supported by experimental observations [3 – 7] and also by quantum mechanical calculations carried out for one- and two-electron systems [11 – 13].

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In the formulation by Posthumus *et al.* [10], the active electron is assumed to move around in a diatomic molecular ion  $AB^{(q-1)+}$  with a double-well potential determined by ion core charges  $(q_A, q_B) = (q/2, q/2)$ . Consequently, the model describes *charge-symmetric* evolution with total charge  $q = q_A + q_B$ , actually applicable to a principal pathway as  $(q_A, q_B) = (1, 0) \rightarrow (1, 1) \rightarrow (2, 1) \rightarrow \dots$ . The recent experiments [4–6], however, demonstrate the behaviors associated with the freedom of *charge-asymmetry*  $\Delta = |q_A - q_B|$ . In common to the results for NO [4], I<sub>2</sub> [5], and N<sub>2</sub> [6], asymmetric products ( $\Delta = 2$ ) have been observed along with competing symmetric products ( $\Delta = 0$ ). The distance  $R_{\text{ion}}$  at which multiple ionization occurs is measured to be definitely shorter for  $\Delta = 2$  than for  $\Delta = 0$ , such as  $R_{\text{ion}}(3, 1) < R_{\text{ion}}(2, 2)$  [4–6]. This fact would be a puzzle in a framework of the model [10] because the third outermost electron in one atom is ionized earlier than the second in another atom (*i.e.*, the fifth in the molecule earlier than the fourth). Moreover, the distance  $R_{\text{ion}}$  exhibits slight but systematic even-odd fluctuation with  $q$  superposed on a mean trend along the principal pathway, more elongated for even- $q$  ( $\Delta = 0$ ) than for odd- $q$  ( $\Delta = 1$ ). Automatic application of the model would predict an inverse fluctuation through the even-odd fluctuation in the binding energy of  $q$ -th molecular electron. These observations need to be clarified.

In the present report, we reformulate the classical field ionization model for a diatomic molecule so as to derive the distance  $R_{\text{ion}}(q_A, q_B)$  of Coulomb explosion for a *pair* of fragment charges  $(q_A, q_B)$ ; the freedom of charge-asymmetry  $\Delta$  is incorporated as well as total charge  $q$ , while the mechanism responsible for enhanced ionization is retained. This treatment is shown to explain the even-odd fluctuation and the relation as  $R_{\text{ion}}(3, 1) < R_{\text{ion}}(2, 2)$ . Furthermore, we extend the model to a linear triatomic molecule ABC along the same lines for deriving the distance  $R_{\text{ion}}(q_A, q_B, q_C)$  for a *combination* of three fragment charges. Comparison of the model with an experimental result for CO<sub>2</sub> [9] suggests that charge-symmetric (or nearly symmetric) channels are dominantly populated.

## 2 Reformulation and extension of the model

We address the multi-electron dissociative ionization of diatomic and linear triatomic molecules in an intense laser field applied along the molecular axis  $\hat{R}$ . The molecule is assumed to be sequentially ionized; a single active electron is removed in respective steps. In general, electronic motion (velocity  $\sim 1$  au) in a molecule is much faster than dissociating nuclei ( $\sim 10^{-2}$  au), and also than the field oscillation (angular frequency  $\sim 10^{-2}$  au). Hence, the many-electron dynamics is treated as a sequence of the over-the-barrier electron-releasing processes, each described by an appearance laser intensity for a fixed bond distance. Such a treatment is justified when the Keldysh parameter is small enough that the ionization probability is almost unity within half a laser cycle [2].

In the previous treatment by Posthumus *et al.* [10] for a diatomic molecule AB, the active electron is uniquely taken in respective ionization steps to be the outermost (least binding) electron in a *molecular* ion  $AB^{(q-1)+}$ . By contrast, we consider two possible pathways for the production of a pair of ions  $(q_A, q_B)$ , as  $(q_A - 1, q_B) \rightarrow (q_A, q_B)$  and  $(q_A, q_B - 1) \rightarrow (q_A, q_B)$ ; the active electron is taken to be either an outermost electron in an *atomic* ion  $A^{(q_A-1)+}$  or that in  $B^{(q_B-1)+}$ .

Hence, the single electron dynamics is described for both pathways with a two-center

Coulomb potential generated by core charges ( $q_A, q_B$ ) plus the field  $F$  applied, as

$$U(\mathbf{r}; R, F) = -\frac{q_A}{|\mathbf{r} + \mathbf{R}/2|} - \frac{q_B}{|\mathbf{r} - \mathbf{R}/2|} - F\hat{\mathbf{R}} \cdot \mathbf{r}. \quad (1)$$

This potential has two saddle points,  $U_{\text{in}}(R, F)$  inside the molecule, and  $U_{\text{out}}(R, F)$  outside either beyond B or beyond A according to the sign of the field  $F$ . The energy level is given, when the electron is localized in site A, as

$$E_A(R, F) = -I_A - \frac{q_B}{R} + \frac{FR}{2}, \quad (2)$$

with the  $q_A$ -th ionization potential  $I_A$  of an isolated atom A. Hence, a phase diagram is constructed in the  $R$ - $F$  plane, as shown in Fig.1, with boundaries as

$$E_A(R, F) = U_{\text{in}}(R, F), \quad (3)$$

$$U_{\text{out}}(R, F) = U_{\text{in}}(R, F). \quad (4)$$

As shown in the figure, the solution of Eq.(4) has two branches,  $F^{(+)}(R)$  ( $> 0$ ) and  $F^{(-)}(R)$  ( $< 0$ ), both proportional to  $R^{-2}$  because of a character of the Coulomb potential. Eq.(3) has a single branch  $F_A(R)$ , which negatively diverges more rapidly than  $F^{(-)}(R)$  in the limit of  $R \rightarrow 0$ , and converges to the atomic appearance field  $I_A^2/(4q_A)$  in  $R \rightarrow \infty$ . In between, the curve  $F_A(R)$  crosses the axis of  $F = 0$  at a distance  $R_0 = (q_A + 2\sqrt{q_A q_B})/I_A$ , which turns out to be a few times longer than the equilibrium length  $R_{\text{eq}}$  in a covalent molecule. The phase diagram for ionization from site B is constructed in the same way as that from site A, but taking the equation of  $E_B(R, F) = U_{\text{in}}(R, F)$  with the energy of

$$E_B(R, F) = -I_B - \frac{q_A}{R} - \frac{FR}{2}, \quad (5)$$

in stead of Eq.(3) with Eq.(2).

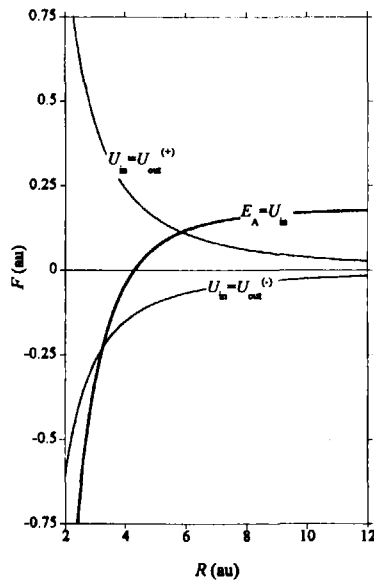


Fig.1. Phase diagram relevant to ionization  $(2, 1) \rightarrow (3, 1)$  with  $I_A = 0.5 \times q_A$  au.

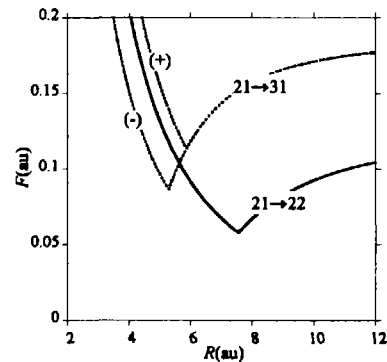


Fig.2. Appearance field curves for  $(2, 1) \rightarrow (3, 1)$  and  $(2, 1) \rightarrow (2, 2)$ .

We suppose that the bond distance is stretched near to  $R_0$  during the laser pulse duration. For a given laser strength  $F_0 (> 0)$ , the field  $F$  is oscillated over a range of  $-F_0 \leq F \leq +F_0$ , which will cover the localized ( $F < F_A(R)$ ) and delocalized ( $F > F_A(R)$ ) domains. Hence the field oscillation is expected to induce nonadiabatic excitation to an energy around the inner saddle, and subsequently causes field ionization over the outer saddle if  $U_{in}(F, R) \geq U_{out}(F, R)$  is satisfied either at  $F = +F_0$  or at  $F = -F_0$ . This mechanism derives the appearance strength curve  $F_{ap}(R) (> 0)$  as shown in Fig.2. It is seen that the negative phase ( $F = -F_0$ ) is favored when  $q_A > q_B$ , and that the charge asymmetric ( $\Delta = 2$ ) channel has smaller appearance strength than the competing symmetric ( $\Delta = 0$ ) channel. We note that this ionization mechanism requires a two-step process in two half cycles of field oscillation, as illustrated in Fig.3.

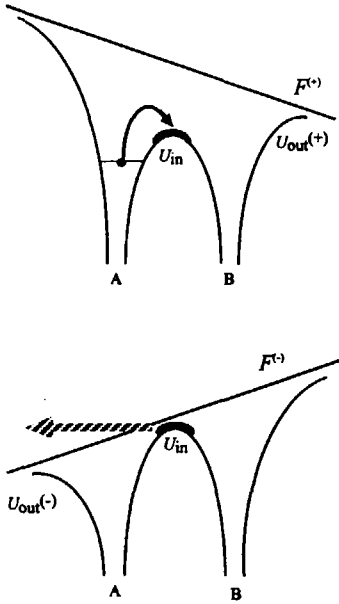


Fig.3. Optimum two-step ionization mechanism in a diatomic molecule AB from site A.

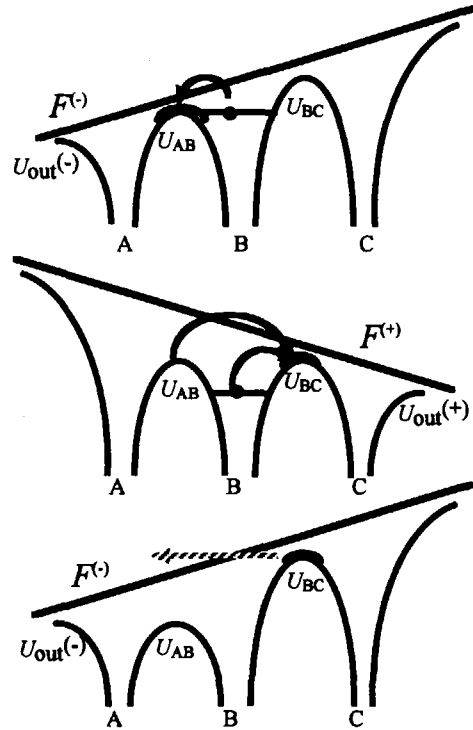


Fig.4. Optimum three-step ionization mechanism in a linear triatomic molecule ABC from site B.

The model is extended to a linear triatomic molecule ABC by assuming symmetric stretching (equal bond length). The active electron is taken to be an outermost electron at one of the three atomic sites and described with a three-center Coulomb potential. The field oscillation induces nonadiabatic excitation followed by field ionization in a similar way to that for a diatomic molecule, but in more complicated manner associated with two inner and one outer saddle points in the potential. The appearance field curve is determined through comparison among many different curves corresponding to possible mechanisms. The optimum ionization mechanism from the central site B requires three half cycles of field oscillation, as illustrated in Fig.4.

### 3 Results and Discussion

The appearance field curves  $F_{ap}(R)$  is given in the model as proportional to  $R^{-2}$  for diatomic and linear triatomic molecules. From  $F_{ap}(R)$  obtained, the distance  $R_{ion}$  of Coulomb explosion is calculated at a given laser intensity.

In a diatomic molecule, the distances obtained for different fragment pairs are plotted and compared with experimental result [4] for NO molecule in Fig. 5. As indicated in Fig.5, the model explains the experimental observations of even-odd fluctuation with  $q$  along a symmetric pathway ( $\Delta \leq 1$ ) and of a relation as  $R_{ion}(3, 1) < R_{ion}(2, 2)$  between competing symmetric ( $\Delta = 0$ ) and asymmetric ( $\Delta = 2$ ) pathways. These behaviors are related to a general rule derived from the model that, the larger the charge asymmetry  $\Delta$ , the smaller the distance  $R_{ion}$ , for a given total charge  $q$ .

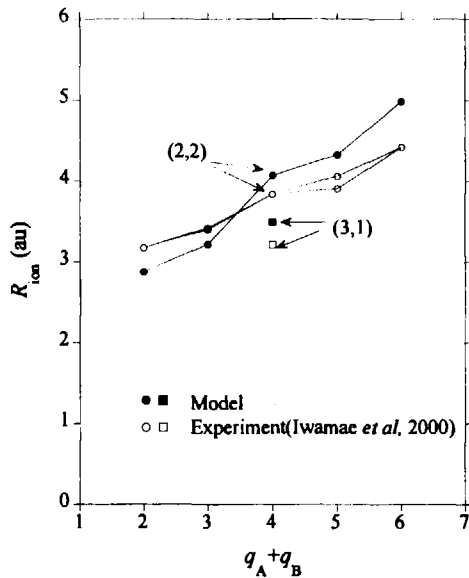


Fig.5. Comparison of the present model with an experiment [4] for the distances of ionization of NO molecule at a laser intensity of  $1.4 \text{ PW/cm}^2$ .

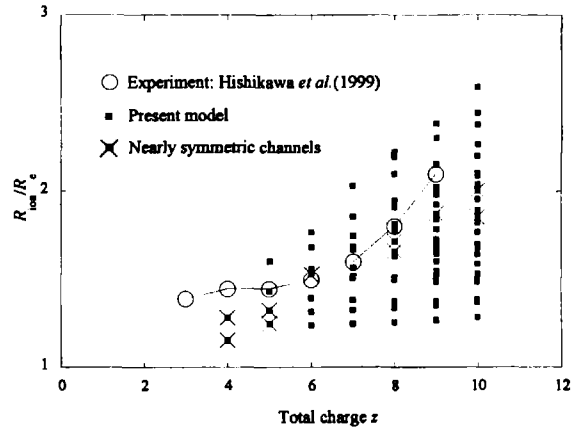


Fig.6. Comparison of the present model with an experiment [7] for the distances of ionization of  $\text{CO}_2$  molecule at a laser intensity of  $1.4 \text{ PW/cm}^2$ .

In a linear triatomic molecule, the effect of enhanced ionization manifests itself more prominently than in a diatomic molecule through more complicated mechanisms involving more saddle points. Comparison of  $F_{ap}(R)$  among ionization pathways permits us to predict which fragmentation channel is produced at a smallest bond length from a common initial channel. A propensity rule is found that the central site B is ionized earliest from left-right asymmetric ( $q_A \neq q_C$ ) channels, while the terminal sites A and C are earliest from symmetric ( $q_A = q_C$ ) channels.

Distances  $R_{ion}$  obtained for different channels are plotted and compared with an experiment [7] for  $\text{CO}_2$  molecule in Fig.6. It is seen from the comparison in the figure that, although fragmentation channels are not clearly resolved in the experiment, its result is consistent with dominant population in charge symmetric or nearly symmetric channels ( $\Delta \leq 1$  for any pair among the three fragment charges). It is also noted in the figure that

the distance increases linearly with the total charge in the model, while nonlinearly in the experiment. This observation may be due to a defect of the model ignoring the bending freedoms of nuclear motion.

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