Analysis of charge-asymmetric Coulomb explosion of N$_2$ molecules with slow Kr$^8^+$ ions

Tomoko Ohyama-Yamaguchi$^1$ and Atsushi Ichimura$^2$

$^1$ Tokyo Metropolitan College of Industrial Technology, Shinagawa, Tokyo 140-0011, Japan
$^2$ Institute of Space and Astronautical Science, JAXA, Sagamihara, 229-8510, Japan

E-mail: $^1$yamaguti@tokyo-tmct.ac.jp, $^2$ichimura@isas.jaxa.jp

Abstract. We investigate a nontrivial asymmetric population observed in a triple-coincidence measurement for charge-asymmetric Coulomb explosion of N$_2$ molecules in collisions with a slow (10 — 100 eV/amu) Kr$^8^+$ ions. The three-center over-the-barrier model is developed to describe collision dynamics including many active electrons as the formation of a triatomic quasi-molecule and its decay into three moving atomic ions. The present model predicts an asymmetry effect consistent with the measurement, where molecular bond elongation during a collision is crucial. Electron localization processes in the quasi-molecular decay are examined in detail in relation to two saddle points in the three-center Coulomb potential.

1. Introduction

Much attention has been called to the Coulomb explosion of molecules in a variety of collision processes on a basis of the momentum imaging technique. Of particular interest is a triple coincidence measurement done by Kaneyasu and coworkers [1] for collisions of slow (10 — 200 eV/amu) Kr$^8^+$ ions with N$_2$ molecules; they detected, in a coplanar geometry, the dissociating ion pair (N$^Q^+$, N$^Q^0$) in transverse to the beam axis and the scattered ion in forward left and right directions. A remarkable result thereby was unequal strengths of charge-asymmetric fragmentation between the near and far sites relative to the projectile trajectory. For a given nonequivalent charge pair $Q \neq Q'$, the asymmetry parameter is obtained as $A(Q, Q') = (P_\geq - P_\leq)/(P_\geq + P_\leq)$ through $P_\geq$ and $P_\leq$, where $P_\geq$ ($P_\leq$) denotes a coincident population for $Q_{\text{far}} > Q_{\text{near}}$ ($Q_{\text{far}} < Q_{\text{near}}$), with $Q_{\text{far}}$ and $Q_{\text{near}}$ being the far and near fragment charges. The experiment generally indicated a striking positive asymmetry $A$; the far site is populated more by a higher charge than by a lower charge. This asymmetry was interpreted [1] to come from target electron polarization by the projectile charge during a collision.

We have made some analyses in previous works [2, 3] to get insights into the observations [1] by developing the three-center Coulombic over-the-barrier model. In the first paper [2], we took a conventional but questionable two-step picture, i.e., ‘electron removal followed by Coulomb explosion’. In this picture, residual electrons in the molecule are polarized by a receding projectile and get localized into two atomic sites on the way of fragmentation. Although leading to a correct sign of $A$, the polarization effect was found too small to account for the measurement. Hence, in the second paper [3], we extended the model so as to describe an inseparable process of electron transfer and Coulomb explosion; we treated the formation of a three-center quasi-molecule and its decay into three (one scattering and two dissociating) moving atomic ions. The
large asymmetry observed was suggested to reflect bond elongation during a collision.

In the present paper, we further develop the model to describe the decay of a three-center quasi-molecule including many active electrons. The electron localization probabilities into the near and far sites along with their dependence on the impact-parameter vector are analyzed.

2. Three-center Coulombic over-the-barrier model

We address collisions of a slow (v ≪ 1 au) highly charged ion $A^{q+}$ with a homonuclear diatomic molecule BC. The molecular bond-length is not fixed to be the equilibrium one but allowed to be elongated during a collision.

The many-electron dynamics is treated as formation and decay of a triatomic quasi-molecule,

$$A^{q+} + BC \rightarrow ABC^{q+} \rightarrow A^{(q-r)+} + B^{Q_{B}+} + C^{Q_{C}+},$$

where $r = Q_{B} + Q_{C}$ is the number of removal electrons from the molecule. According to the original over-the-barrier model by Niehaus [4], the dynamics is described by a sequence of quasi-molecule formations of respective electrons in numerical order of ‘rank’ $t$ ($= 1, 2, \ldots$) in the way in of a collision, and by a sequence of their decays in the reverse order in the way out. One electron dynamics in respective steps is described with a three-center Coulomb potential $U(r)$ determined by ion core charges $q_{A}$, $q_{B}$, and $q_{C}$. This potential has two saddle points ($U_{\text{high}}$ and $U_{\text{low}}$) in contrast with the two-center potential containing one saddle point (see Fig. 1).

The quasi-molecule is formed at a critical distance $R_{t}$ determined by a classical over-the-barrier criterion, $E = U_{\text{high}}$, with the electron diabatic energy $E$ and the barrier height $U_{\text{high}}$. Here the $t$-th electron is assumed initially bound in the target with its $t$-th ionization potential.

The quasi-molecule decays via two-step electron localization into three atomic sites associated with the two saddle points. This decay may occur in three processes (labeled by I, II, and III in Fig. 1) according to the nuclear configuration formed by three ion cores A, B, and C; the configuration space is divided into three domains labeled by $D_{A-BC}$, $D_{C-AB}$, and $D_{B-CA}$ in view of classical electron motion when $U_{\text{high}} > E > U_{\text{low}}$. For the three processes, one-electron localization probabilities into three atomic sites are respectively given by

$$\text{process I} : p_{A} = p_{A}^{\text{high}}, \quad p_{B} = p_{B}^{\text{high}} \times p_{\text{low}}, \quad p_{C} = p_{C}^{\text{high}} \times p_{\text{low}},$$

![Figure 1](image1.png)  
**Figure 1.** Formation (upward arrows) and decay (downward arrows) of a quasi-molecule. In the decay of a three-center quasi-molecule, an electron is localized into three atomic sites via two steps associated with higher and lower saddle points.

![Figure 2](image2.png)  
**Figure 2.** Network of the charge state ($q_{B}, q_{C}$) evolution in the decay of a three-center quasi-molecule with 10 active electrons.
process II : \( p_A = p_{A}^{AB} \times p_{low}^{A}, \ p_B = p_{high}^{AB} \times p_{low}^{B}, \ p_C = p_{high}^{A} \) \( \) (3)

process III : \( p_A = p_{A}^{CA} \times p_{low}^{A}, \ p_B = p_{high}^{A} \times p_{low}^{C}, \ p_C = p_{high}^{CA} \times p_{low}^{C} \) \( \) (4)

through the branching probabilities calculated with phase-space volumes at \( U_{\text{high}} \) and \( U_{\text{low}} \),

\[
p_{s}^{\Gamma} = \frac{p_{s}^{\Gamma}}{p_{s}^{\Gamma} + p_{s}^{\Delta}}, \quad p_{s}^{\Gamma, \Delta} = \int_{\Gamma, \Delta} d\rho d\tau (U_{s} - p^{2}/2 - U(r,q_{A},q_{B},q_{C})). \] \( \) (5)

Here a suffix ‘s’ labels higher or lower saddle point, which divides the available phase space into two separable regions denoted by \( \Gamma \) and \( \Delta \).

Considering all the electrons, we obtain the probability distribution for dissociating ion-pair,

\[
P(Q_B, Q_C) = \sum_{\text{string}} \prod_{t=1}^{t_{\text{max}}} p_{j(t)}(q_{A}(t), q_{B}(t), q_{C}(t); \text{string}), \] \( \) (6)

where \( t_{\text{max}} \) denotes the number of active electrons determined by the impact parameter \( b \) and the critical distances \( R_{c} \). In Eq. (6) \( p_{j} \) indicates one-electron localization probability given by Eqs. (2—5). The suffix \( j \) \((= 0, 1, 2)\) labels A, B or C according to a ‘string’ \([4], \{j(t); \ t = 1, 2, \ldots , t_{\text{max}}\}\), representing evolution of ion-core charges \((q_{A}, q_{B}, q_{C})\) due to successive electron localization in descending order of \( t \). The evolution starts at \( t = t_{\text{max}} \), where we take \( q_{A} = q \) (incident ion charge) and \((q_{B}, q_{C}) = (t_{\text{max}}/2, t_{\text{max}}/2)\) for even \( t_{\text{max}} \). For odd \( t_{\text{max}} \), we consider two kinds of evolution starting from \((t_{\text{max}} + 1)/2, (t_{\text{max}} - 1)/2)\) and from \((t_{\text{max}} - 1)/2, (t_{\text{max}} + 1)/2)\), and take their average in Eq. (6). The summation in Eq. (6) is taken over all possible ‘strings’ leading to ion pair \((Q_B, Q_C)\). Figure 2 shows a network of the charge-state evolution projected onto \((q_{B}, q_{C})\) plane starting from \((5,5)\).

3. Results and Discussion

We apply the present model to collisions of \( \text{Kr}^{8+} + \text{N}_2 \) at a velocity of \( v = 0.04 \) au \((i.e., 40 \) eV/amu) and consider 10 covalent electrons in the \( \text{N}_2 \) molecule as active electrons. We assume linear trajectories of incidence and of dissociation retaining the beam axis \((\hat{v})\) and the initial molecular orientation \((\hat{d})\), satisfying \( \hat{d} \perp \hat{v} \).

**Figure 3.** Time \( \tau \) evolution of half the bond length \( d \) at \( v = 0.04 \) au for impact parameters \( b = 0, 2, 4, 6 \) and 8 au.

**Figure 4.** Probability distributions over charge-asymmetry \( Q_B - Q_C \) when \( r \) electrons are removed at \( v = 0.04 \) au, \( b = 3 \) au and \( \phi = 0 \) deg.
Time $\tau$ evolution of half the bond length, $d$, is calculated and shown in Fig. 3, where the horizontal scale is taken $z = v\tau$ representing the projectile position along the incident trajectory. In this calculation, we have solved Newton equation by taking a sum of empirical N—N interatomic potential and Coulomb repulsion between dissociating ions with charges of $q_B = q_C = t/2$ after passing the $t$-th critical distance. It is seen from the figure that the molecule dissociates more rapidly as the impact parameter $b$ decreases, because the number, $t_{\text{max}}$, of active electrons increases. In particular, the dissociation velocity changes strikingly in a region of $6 > b > 4$, where $t_{\text{max}}$ increases from 4 to 10.

With these trajectories, we calculate the probability distribution $P(Q_B, Q_C)$ through Eqs. (2—6) by assuming that the quasi-molecule decays at $\tau = 500$ au ($z = 20$ au). Figure 4 shows the result when $r = 3 - 5$ electrons are removed from the target BC. As the figure indicates, the distributions are asymmetric with respect to the sign of $Q_B - Q_C$, leading to an asymmetry parameter of $A > 0$ consistent with the measurement [1]. Note here that B (C) is defined as the near (far) site relative to the incident trajectory of A.

To clarify a mechanism causing this asymmetry effect, we examine the sum and the difference, $p_B \pm p_C$, of one-electron localization probabilities into sites B and C. They are plotted in Fig. 5 for ion-cores of $(q_B, q_C) = (2, 2), (2, 1)$ and $(1, 2)$. It is seen from the figure that an inequality, $p_B \geq p_C$, holds universally if one simultaneously considers a contribution from ‘ion-core exchange’, such as one from $(q_B, q_C) = (1, 2)$ in addition to one from (2, 1). It is also seen that the localization probabilities are discontinuous with respect to the impact parameter $b$, i.e., with respect to the nuclear configuration at the time of quasi-molecular decay. This behavior is due to alternation of the decay process (see Fig. 1). A discontinuity labelled by $\alpha$ in Fig. 5 arises from alternation as process III $\rightarrow$ II, while $\beta, \gamma$ and $\delta$ from I $\rightarrow$ II. As the figure indicates, process I (i.e., nuclear domain $D_{A-BC}$) is only responsible for large impact parameters ($b > 5$); it gives vanishingly small values of $p_B - p_C$, which comes from electron polarization in the target molecule by the projectile ion. Hence, process II ($D_{C-AB}$) gives a dominant contribution to the asymmetry effect. Note that the process III ($D_{B-CA}$) is only responsible for $(q_B, q_C) = (1, 2)$ in the figure. It gives negative values of $p_B - p_C$ as a result of rapid bond-elongation at small impact parameters such as leading to $d \gg b$ (see Fig. 3). This negative contribution from process III for $(q_B, q_C) = (1, 2)$ cancels a positive contribution from process II for $(2, 1)$ at $b < 3.5$.

We have found through the analysis that the present three-center model is explainable for the tendencies of measured charge-asymmetry [1]. The asymmetry effect reflects all the three localization processes illustrated in Fig. 1, among which process II is dominant.

References

[1] Ehrich M, Werner U, Lutz H O, Kaneyasu T, Ishii K, Okuno K and Saalmann U 2002 Phys. Rev. A 65 030702(R); Kaneyasu T, Azuma T and Okuno K 2005 J. Phys. B: At. Mol. Opt. Phys. 38 1341
[2] Ohyama-Yamaguchi T and Ichimura A 2005 Nucl. Instr. and Meth. B 235 382
[3] Ohyama-Yamaguchi T and Ichimura A 2007 J. Phys.: Conf. Series 58 247
[4] Niehaus A 1986 J. Phys. B: At. Mol. Opt. Phys. 19 2925