Production of multiply charged molecular ions (N_2^{12+}–N_2^{14+}) and multiply charged atomic ions (N^{6+}, N^{7+}) in energetic, heavy-ion impact on N_2 molecules

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Multiply charged atomic recoil ions up to N^{6+}, along with a weak trace of N^{7+} ions, have been observed in 1.05-MeV/amu Ar^{12+}-ion impact on molecular targets (N_2). A shift of the peak positions for these multiply charged atomic ions (N^{l+}) toward the high-energy side in charge-energy spectra, compared with those for recoil ions from single-atom targets such as Ar, strongly suggests that these recoil ions (N^{l+}) have fairly large initial kinetic energies due to the Coulomb explosion of multiply charged molecular ions produced in the impact of highly charged projectiles. It is believed, therefore, that those multiply charged atomic ions, for example, N^{6+} ions, originate from multiply charged molecular ions, for example, N_2^{11+}, N_2^{12+}, or N_2^{13+} ions, which dissociate into two atomic ions.

The first detailed observation of multiply charged recoil ions in high-energy proton impact was reported by Wexler, who determined the cross sections for production of ions up to Ar^{5+} and Kr^{5+} from Ar and Kr targets.[1] Recently, Cocke systematically measured the cross sections for the production of multiply charged recoil ions by heavy, highly charged projectile ions and compared them with the calculations based upon some models.[2] Since then, a number of similar investigations have been made in energetic, heavy-ion impact.[3] Some of our results have been reported on the partial cross sections for production of recoil Ar^{l+} ions in 1.05-MeV/amu Ne^{q+} ($q=2$–10)-ion and Ar^{q+} ($q=4$–14)-ion impact.[4] Most of these results indicate that in addition to direct multiple ionization through the strong Coulomb interaction due to the high charge of the projectile ions, electron transfer processes contribute significantly to production of multiply charged recoil ions if projectile ions have inner-shell vacancies.[3,5] Most of these works used rare-gas atoms. Few investigations have been made on molecular gas targets. Therefore, it is not clear whether any meaningful difference in the production of multiply charged recoil ions exists between atomic and molecular targets.

Here is a short summary of the results on the production of multiply charged molecular and atomic ions from molecular targets (N_2). In electron impact, the cross sections for production of singly charged molecular ions (N_2^+) from N_2 targets are similar in magnitude to those of singly charged Ar^+ ions, as expected, because the potentials for single ionization of the outermost electrons in both N_2 and Ar are similar. On the other hand, the ratios of the cross section for the production of doubly charged molecular ions (N_2^{2+}) to that for singly charged molecular ions (N_2^+) are found to be one order of magnitude smaller than those for Ar^{2+} ions to Ar^+ ions, respectively.[6] This phenomenon can be explained, at least qualitatively, using the fact that part of the doubly charged molecular N_2^{2+} ions dissociate into two ions with a finite lifetime before arriving at the detector.[7] The lifetimes of multiply charged molecular ions are expected to become short as the ionic multiplicity of the molecular ions increases. Experimentally, no triply charged molecular ions have been observed up to now.

Similarly, the available information on the production of multiply charged atomic ions from molecular targets is very limited. Daly and Powell determined the cross sections for production of N^{3+} ions by electron impact on N_2 targets, with a maximum value of 2.5×10^{-23} cm^2 at the collision energy of 240 eV, which seems to be much too low compared with those N^{2+} ions[8] (see Table I). In 1-MeV He^+-ion impact upon N_2 targets, the energy distributions of the N^{3+} ions have been observed to extend up to 50 eV by Edwards, Wood, and Steuer.[9] However, both sets of authors did not discuss the detailed production mechanisms for N^{3+} ions in the charged-particle impact. Furthermore, Mann *et al.*[10] observed the broadening of Auger-electron spectra emitted from N^{4+} ions in the metastable $(1s2s2p)\,^4P$ states which were produced in 1.40-MeV/amu Ar^{12+}-ion impact. This significant broadening of Auger-electron spectra from N_2 targets, compared with that from NH_3 targets, indicates that this is due to Doppler broadening caused by the kinetic energies of the emitting ions. These kinetic energies of the electron-emitting ions are provided in the Coulomb explosion where the two dissociating ions share the Coulomb potential energies and are found to be in good agreement with the *ab initio* self-consistent-field calculations of Hartung

TABLE I. A comparison of relative yields of ions produced in 240-eV electron and 1.05-MeV/amu Ar^{12+}-ion impact on N_2 targets.

	N_2^+	N_2^{2+}	N^+	N^{2+}	N^{3+}	N^{4+}	N^{5+}	N^{6+}	N^{7+}
Electron	1.0	1.7(−2)	2.6(−1)	1.2(−2)	1.3(−7)				
Ar^{12+}	1.0	3.1(−1)		4.4(−2)	9.0(−3)	1.5(−3)	5.3(−4)	1.0(−4)	Weak

et al.[11]

To gain more insight into mechanisms for production of multiply charged ions from molecular targets, we have measured the charge-state distributions of the recoil ions produced in 1.05-MeV/amu Ar^{q+} ($q=4,12$)-ion impact on molecular targets.[12] The experiment has been made with the same apparatus previously described in detail.[4] In short, the recoil ions produced by high-energy ion impact are extracted through a relatively weak extraction field (40 V/cm), accelerated up to 1.5 kV, and, finally, charge-mass analyzed with a double-focusing sector magnet. The weak extraction field used is important to select only ions which are emitted in a proper direction to be accepted into the analyzer magnet and to determine their energy. (If a too-strong extraction field were used, the peaks of ions with initial kinetic energies would become broad and their energy could not be determined accurately, though the ion collection efficiencies would be high.[13]) Typical examples of the charge spectra of ions from N_2 targets are shown in Figs. 1(a) and 1(b), where a number of peaks corresponding to multiply charged nitrogen atomic ions (N^{i+}) as well as a dominant peak of singly charged molecular ions (N_2^+) are seen. The peaks of the doubly charged molecular ions (N_2^{2+}), whose intensities are estimated to be about 6% of the total peak intensities at $M/e=7.00$,[14] are overlapped on the peak of the singly charged atomic ions (N^+). By comparing two charge-distribution spectra in Fig. 1(a), we can see that the production of multiply charged atomic ions, relative to that of singly charged molecular ions, is enhanced when projectile ions have higher incident charge. This behavior has already been observed in a number of atomic-target experiments.[2,3,5]

It should also be noted that no trace of N_2^{3+} ions, corresponding to a peak at $M/e=9.33$ (an arrow), is found in these spectra, indicating that no triply charged molecular ions (N_2^{3+}) could be detected, probably because their lifetimes are so short that they could not arrive at the detector. In Fig. 1(b) an expanded part of the charge spectra is shown, where a peak corresponding to N^{6+} ions is clearly seen. When a mixture of $^{14}N_2$ and $^{15}N_2$ gases is used, a weak trace of $^{15}N^{7+}$ ions is observed, although it is less clear because of H_2^+ background ions.

As the atomic ions, in particular, multiply charged atomic ions produced from molecular targets, often have initial kinetic energies due to the Coulomb explosion which are much larger than the recoil energies obtained in collisions (see later discussion), a complete collection of these atomic ions is very difficult, as discussed by Rapp, Englander-Golden, and Briglia.[13] With the assumption of their isotropic distribution, and based on the present charge spectra, the production cross sections of N^{6+} ions from N_2 targets under 1.05-MeV/amu Ar^{12+}-ion impact are estimated to be of the order of 10^{-18} cm^2.

In the production of multiply charged atomic ions from molecular targets a number of mechanisms could be responsible, which may be different from those in atomic targets. Among them the following processes are most likely to occur: (1) ionization produces multiply charged molecular ions first, which then dissociate into multiply charged atomic ions; (2) dissociation of molecules into constituent atoms in the first part of the collision is followed by the ionization of each constituent atom in the last part, resulting in the production of multiply charged atomic ions; and (3) one (or some) of the constituent atoms in the molecules is ionized,

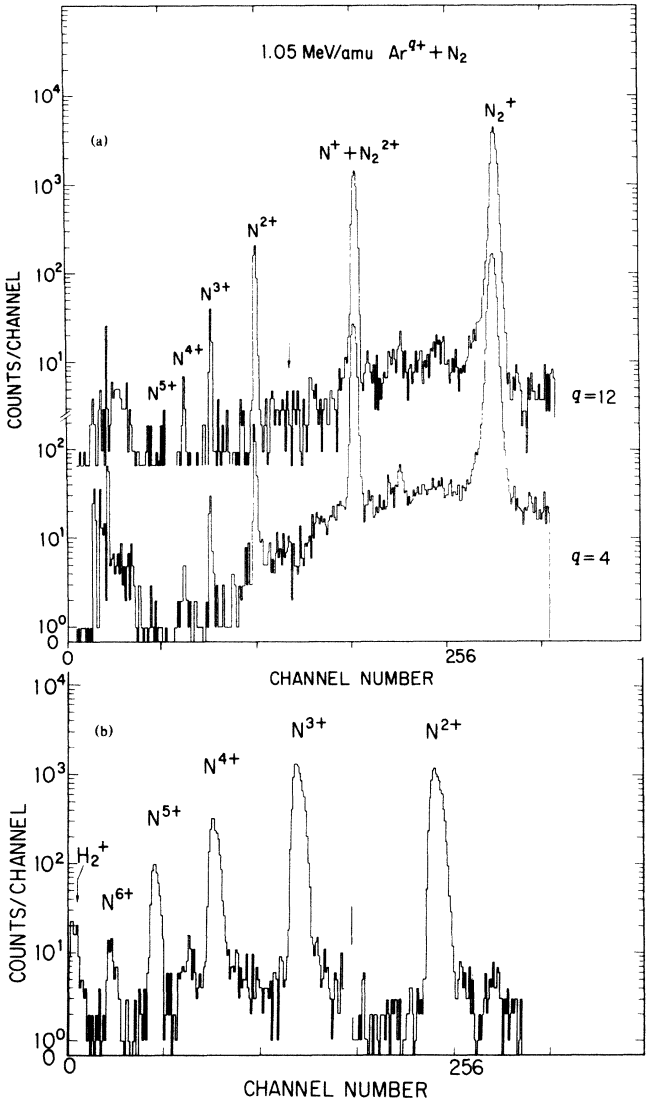

FIG. 1. (a) Charge-mass spectra of ions produced in 1.05-MeV/amu Ar^{q+} ($q=4,12$)-ion impact on nitrogen molecules. An arrow indicates the position corresponding to N_2^{3+} ions ($M/e=9.33$). (b) Expanded charge spectrum of atomic nitrogen ions (N^{i+}) ranging from $i=2$ to 6. Note the vertical scales change between $i=2$ and 3.

resulting in multiply charged atomic ions, the other(s) being only a spectator without any interaction with the projectile ions. In process (1), known as Coulomb explosion, the resulting multiply charged atomic ions are provided with kinetic energies through the Coulomb potential energy acting between the dissociation ions, which can be much larger than the recoil energy of the projectile-ion impact and increases with the ionic charge of the recoil ions. On the other hand, the multiply charged atomic ions produced in processes (2) and (3) get only the recoil energies with the addition of the small dissociating energies of neutral molecules, which are independent of the charge state of the atomic ions. To compare which processes mentioned above are dominant in the production of multiply charged atomic ions, the collision time, dissociation time, and electron-rearrangement time should be the key factors. The collision time in the present work (1-MeV/amu projectile ions) is of

the order of 10^{-17} s; meanwhile, the dissociation time for the molecules is $\sim 10^{-14}$–10^{-15} s (the bond length is 1 Å). Clearly these numbers indicate that the ionization process is much faster than the dissociation process, suggesting that process (2) is less dominant in the production of multiply charged ions from molecular targets.

Also, the electron-rearrangement (relaxation) time in the product ions $(A \cdot A^{i+})$ in process (3) is estimated to be of the order of 10^{-16} s, though no accurate information is available for multiply ionized ions, and is much shorter than the dissociation time for the molecular ions. The collision product then relaxes to $(A \cdot A)^{i+}$ ions before it dissociates into a multiply charged atomic ion (A^{i+}) and a neutral atom (A) and, finally, breaks into two charged ions. Therefore, process (3) is less likely to produce atomic ions with a high charge as the initial charge of the product is shared between two ions.

It may be concluded from a comparison of the times relevant to the above processes that process (1), namely, the production of multiply charged molecular ions through ionization followed by dissociation, is most likely to be dominant in the production of multiply charged atomic ions. As expected, these multiply charged molecular ions become less stable with increasing ionicity and quickly dissociate into multiply charged atomic ions. As may be expected from the short electron-rearrangement time (see discussion above) and confirmed by Mann *et al.*,[10] those multiply charged molecular ions consisting of two atoms with similar masses tend to dissociate into atomic ions with relatively symmetric charge.

Therefore, the multiply charged atomic ions (for example, N^{6+}) observed in energetic, heavy-ion impact, as shown in Fig. 1, are thought to be produced through the following dissociation processes of multiply charged molecular ions:

$$N_2^{10+} \rightarrow N^{5+} + (N^{5+})^* \rightarrow N^{5+} + N^{6+} + e \ ,$$

$$N_2^{11+} \rightarrow N^{5+} + N^{6+} \ ,$$

$$N_2^{12+} \rightarrow N^{6+} + N^{6+} \ ,$$

$$N_2^{13+} \rightarrow N^{7+} + N^{6+} \ .$$

Here the first process corresponds to dissociation where one of multiply charged atomic ions is in a highly excited state, followed by electron emission, and the other processes correspond to simple dissociation processes.

As mentioned already, if these multiply charged atomic ions are assumed to originate from dissociation of multiply charged molecular ions, they should have the initial kinetic energies provided through the Coulomb potential between the dissociating atomic ions. This potential energy for two dissociating ions can be calculated through $V(r) = i_1 i_2 e^2/r$, where i_1 and i_2 are the ionic charges of the two ions, respectively, and r is taken to be the bond length of the molecular ions when these ions dissociate. If the bond length is 1.0 Å, each ions with charge of 6+ (for example, the N^{6+} ion) should have a kinetic energy of about 115 eV. In fact, the atomic nitrogen (N^{i+}) ions from N_2 targets have been experimentally observed even when the retarding field in the extraction region was relatively large. On the other hand, no molecular ions (for example, N_2^+), which have only small recoil energies, could be detected with a very weak retarding field.

Though our experimental setup is not intended to measure accurate energies of ions, we have tried to determine whether the atomic ions produced from molecular targets have any difference in their energies, compared with those from ions from atomic targets. In Fig. 2 are shown some results of measurements of the charge-mass spectra produced in 1.05-MeV/amu Ar^{12+}-ion impact on different targets and the peak positions of ions with the charge-mass ratios ranging from 2 to 6 are compared. Clearly the peak position of $^{15}N^{3+}$ $(M/e = 5.00)$ ions is found to be shifted toward the higher-energy side, compared with that of $^{40}Ar^{8+}$ ions $(M/e = 5.00)$, which get small recoil energies. Similarly, that of $^{15}N^{5+}$ $(M/e = 3.00)$ ions is shifted toward the higher-energy side from that of $^{12}C^{4+}$ ions (also $M/e = 3.00$). It should be noted that the peak position of $^{12}C^{3+}$ $(M/e = 4.00)$ ions is the same as that of $^{40}Ar^{10+}$ ions within the uncertainties of the present analyzing system. This suggests that C^{i+} ions produced from molecular CH_4 targets have relatively small kinetic energies, possibly comparable

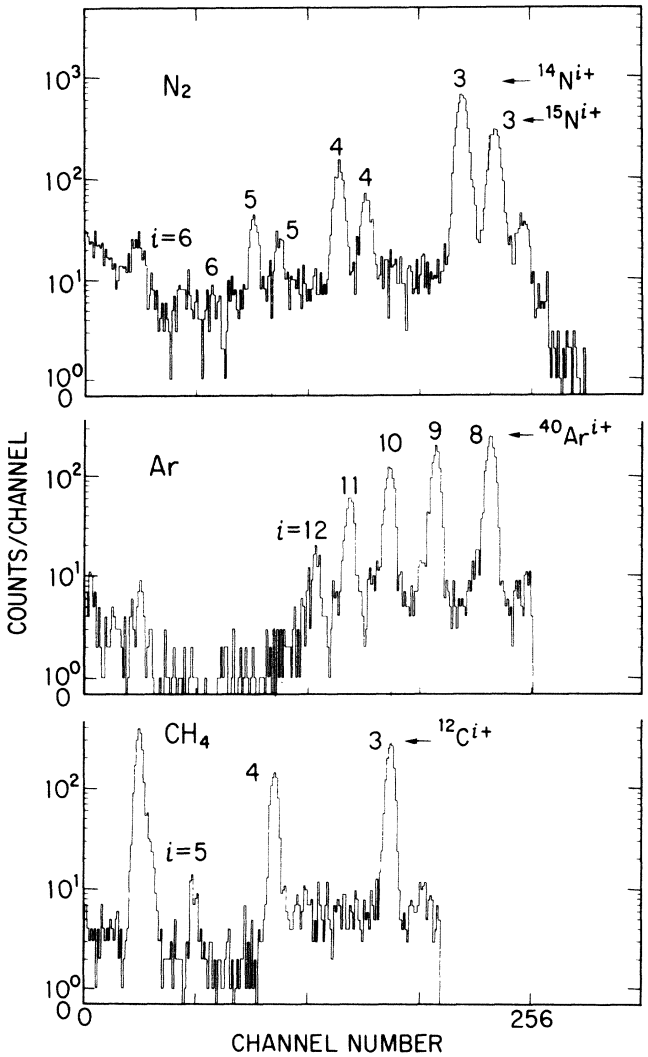

FIG. 2. A comparison of charge-mass-energy spectra of nitrogen ions (N^{i+}) from N_2 targets, argon ions (Ar^{i+}) from Ar targets, and carbon ions (C^{i+}) from CH_4 targets. Note the shift of the peak positions of $^{15}N^{3+}$ ions over $^{40}Ar^{8+}$ ions (both having $M/e = 5.00$) and of $^{15}N^{5+}$ ions over $^{12}C^{4+}$ ions $(M/e = 3.00)$, respectively. Also note no shift of that of $^{12}C^{3+}$ ions over $^{40}Ar^{10+}$ ions $(M/e = 4.00)$ (see the text).

to the recoil energies, indicating that most of the kinetic energies provided through the Coulomb explosion in $(CH_4)^{l+}$ ions are partitioned to the resulting protons and then C^{l+} ions get only a small part of the Coulomb potential energies. Through analysis of these peak positions, it is found that the initial kinetic energies of $^{15}N^{3+}$ and $^{15}N^{5+}$ ions are 42 ± 10 and 88 ± 20 eV, respectively. These energies can be compared with those calculated from the Coulomb potentials mentioned above (57 and 160 eV, respectively). Though the present experimental values are not in complete agreement with the calculated values, a trend is clearly seen that the peak shifts in energies increase with the ionic charge of the produced ions, indicating that these initial kinetic energies have been provided through the Coulomb potentials between the dissociated atomic ions.

Thus, the present results of the peak shifts of atomic ions from molecular targets support our discussion that multiply charged atomic ions observed in high-energy ion-molecule collisions are produced through dissociation of multiply charged molecular ions with short lifetimes.

The present experiments have shown that the energetic, heavy-ion collisions can provide numerous multiply charged molecular ions and can be a good tool for studying the properties of the multiply charged molecular ions, such as their dissociating mechanisms.

To investigate in more detail the production mechanisms of multiply charged atomic ions from molecular targets, precise measurements of the kinetic energies and their distributions among these atomic ions, of the charge correlation, and of the angular distribution of the dissociating ions are under way at our laboratory. Theoretical as well as experimental information on multiply charged molecular ions such as their lifetimes would surely be useful.

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