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Collision-induced dissociation of ∼2-MeV O_3^+ and N_3^+ ions

E. Vigren,[1,*] V. Zhaunerchyk,[1,†] W. D. Geppert,[1] M. Larsson,[1] E. Bahati,[2] C. R. Vane,[2] M. E. Bannister,[2] M. R. Fogle,[2,‡]
M. Hamberg,[1,†] M. Danielsson,[1] M. Kaminska,[3,†] and R. D. Thomas[1]
[1]*Department of Physics, AlbaNova University Center, Stockholm University, SE-10691, Stockholm, Sweden*
[2]*Physics Division, Oak Ridge National Laboratory, PO Box 2008, Oak Ridge, Tennessee 37831, USA*
[3]*Institute of Physics, Jan Kochanowski University, Zeromskiego 5, 25-369 Kielce, Poland*
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We present a study into the collision-induced dissociation (possibly including electron stripping) of O_3^+ and N_3^+ with rest gas molecules (predominantly H_2) in the heavy-ion storage ring CRYRING. The projectile ions had kinetic energies of 1.96 MeV (O_3^+) and 2.25 MeV (N_3^+) and from the experimental data we could derive the relative importance of the channels that produce at least one neutral product fragment. The dominant type of fragmentation for both ions involves the production of a single neutral fragment, namely an individual atom. We also find pronounced dissimilarities when comparing the O_3^+ and N_3^+ results, which we link to the stronger chemical bonds in the nitrogen system.

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I. INTRODUCTION

In the interaction between a fast molecular ion and a neutral target atom or molecule the perturbation of the projectile ion by the target can lead to collisional excitation of the ion. If the (vertical) excitation energy is larger than the ion's dissociation energy, the ion can undergo fragmentation (see, e.g., [1,2]), and this is referred to as collision-induced dissociation (CID). A competing pathway, in particular for cations, involves electron transfer from the target to the ion. Here the resulting species may be created in an excited state lying above the dissociation limit and fragment, and this is referred to either as charge transfer dissociation or electron capture induced dissociation (ECID) (see, e.g., [3]).

Many experimental studies have focused on the CID and ECID involving ions possessing up to keV kinetic energies and following their interactions with various target species. At or near threshold, such studies have proven to be a robust method for determining the thermochemistry of a broad range of molecules (see, e.g., [4] and references therein). The interaction of 50-keV biomolecular ions (e.g., nucleobases, nucleotides, and peptides) with target gases such as Cs, Na (alkali metals are optimal for ECID studies), and Xe (noble gases are optimal for CID studies) have been investigated in detail with the use of electrospray ion sources and tandem mass spectrometry (see, e.g., [3,5–7] and references therein) providing insight into, for example, their fragmentation patterns and the shielding effects of the ions due to solvation.

Studies of CID and/or ECID reactions have also been performed in the keV energy range for a wide range of simpler molecular ions including, e.g., H_2^+ [8], H_3^+ [9–11], H_3O^+ [12], HeH^+ [13,14], O_2^+ [15], CO^+ [1,2], and CO_2^+ [16]. In Ref. [8] the ECID of H_2^+ ions (with energies ranging from 1.5 to 6.5 keV) with a number of target atoms (Ar, Mg, Na, and Cs) were studied and it was shown, for example, that the relative transition probabilities to different electronic states of H_2 primarily depend on the ionization energy of the target. In [9] the $L\alpha$ polarization was measured in coincidence with the H_2^+ ions produced in the CID of 4.83-keV H_3^+ with He, providing insights into what states the H_3^+ ions were excited in the process. The three-body breakup into H + H + H (D + D + D) in the ECID of 12-keV H_3^+ (D_3^+) with Cs was studied in [10] revealing the state-specific three-body dissociation dynamics for the lowest metastable Rydberg states of H_3 (and D_3). In the ECID of H_3^+ and H_3O^+ with Cs, reported in [11,12], respectively, the branching fractions for the different product channels were determined. These data showed significant differences to the branching data determined from dissociative recombination experiments [17,18], although this is not surprising considering the different reaction mechanisms.

Collisions of keV HeH^+ ions with Cs [13] and Ar [14] have been investigated where, in the latter example, which was performed using an ion-trap technique, the metastable $a\ ^3\Sigma^+$ state of the HeH^+ ion was observed. With the use of translational spectroscopy, it was shown that the ECID of 4-keV $a\ ^4\Pi_u$ O_2^+ ions with Cs and Mg mainly yield Π_u Rydberg states and repulsive states of O_2, respectively [15]. The cross sections for O^+ and C^+ production in the CID of 1.0–9.0-keV CO^+ ions interacting with H_2, N_2, and SF_6 were determined in [1]. Here, García and co-workers reported that the relative yields of O^+ versus C^+ were influenced both by the ion's kinetic energy and by the target molecule. The same group also studied the interaction of 5-keV CO^+ ions with He and showed that the kinetic energy release (KER) distributions of C^+ and O^+ exhibit different features corresponding to the states that participate in the CID processes [2]. As a final example, in the CID of 1.4-, 2.5-, and 50-keV CO_2^+ ions interacting with He the dissociation into CO^+ + O is the preferred channel, despite the O^+ + CO channel being the energetically lowest dissociation pathway [16].

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[*] Present address: Department of Physics, Imperial College, SW7 2AZ London, UK; e.vigren@imperial.ac.uk

[†] Present address: Department of Physics and Astronomy, Ångströmslaboratoriet, Uppsala University, SE-751 20 Uppsala, Sweden.

[‡] Present address: Department of Physics, Auburn University, Auburn, AL 36849, USA.

Fewer experimental studies of ECID and CID reactions have been performed at MeV ion energies. Such studies were first made on light molecular ions of a few atomic mass units. For H_2^+ ions in the range of a few MeV interacting with the noble gases He, Ne, and Ar, it was shown in [19] that the total destruction cross section decreased with increased energy and that the cross sections were highest for Ar and lowest for He, as expected considering the sizes of the targets. The partial collision cross sections for 0.4–1.8-MeV H_3^+ ions in collisions with H_2, N_2, and Li vapor were derived in [20]. The relative importance of the ECID channels was found to decrease with increasing energy, and at 1.8 MeV it was essentially zero. The dominant channel regardless of energy or target was that leading to $H + 2H^+$. The CID of 1.2–3.7-MeV H_3^+ ions interacting with various noble gases was later studied in [21], and it was again found that channels leading to one neutral H atom dominated and that the total destruction rate increased with the size of the target atom. Studies of 0.5–1.04-MeV HeH^+ ions colliding with H_2, He, N_2, and Ne revealed that production of $H^+ + He^+$ dominated [22]. Among the channels producing at least one neutral product, the yield of the ECID channel H + He was 7%–18% at 1.04 MeV depending on the target gas (lowest for H_2, highest for He). In [23] collisions of He_2^+ ions with Ar were studied. Differences in the fragmentation patterns were observed for the two different ion energies considered: 0.4 and 0.8 MeV. The dissociation fractions with higher charges were observed to be larger for the higher collision energy.

As for heavier ions at MeV energies, a few studies [e.g., [24–26]] have been performed on charge stripping reactions, primarily to investigate the lifetime against dissociation of molecular dication states. More recently the fragmentation of ions with MeV energies of the form C_n^+ and C_nH^+ following collisions with He have been studied in great detail at the Tandem facility of the Institute de Physique Nucléaire in Orsay, France [27–29].

In this paper we demonstrate that magnetic storage rings can be used as an additional tool to study fragmentation patterns in CID and ECID reactions in the MeV range for light as well as for moderately heavy molecular ions. The basic idea is to treat the residual gas within the storage ring as the neutral target. As an illustration, we present investigations into the CID of (1) the ozone cation, O_3^+ and (2) the azide radical cation, N_3^+. More specifically, we have investigated the relative importance of channels producing different combinations of neutral products in the CID of 1.96-MeV O_3^+ ions and 2.25-MeV N_3^+ ions in collisions with rest gas molecules, R_g (predominantly H_2), in the heavy-ion storage ring CRYRING at the Manne Siegbahn Laboratory, Stockholm University, Sweden.

Six different combinations of neutral products can be produced in the interaction of 1.96-MeV O_3^+ ions with R_g: (a) O_3, (b) O_2 + O, (c) O + O + O, (d) O_2, (e) O + O, and (f) O. Channels (a)–(c) are ECID channels leading to exclusively neutral products. The neutrals produced in channels (d)–(f) are from CID reactions, possibly including electron stripping, and may be accompanied by different combinations of charged species. Equation (1) shows, for each of the six cases (neglecting channels producing negative ions), the most energetically favorable set of products (with $x = 1$ for CID processes and $x = 2$ for processes involving electron stripping of the ion):

$$O_3^+ + R_g \rightarrow O_3^* + R_g^+ \text{ or } O_3^{x+*} + R_g + (x-1)e^-,$$

$$O_3^* \rightarrow O_3 \quad [-12.5\,\text{eV}], \tag{1a}$$

$$O_3^* \rightarrow O_2 + O \quad [-11.4\,\text{eV}], \tag{1b}$$

$$O_3^* \rightarrow O + O + O \quad [-6.3\,\text{eV}], \tag{1c}$$

$$O_3^{x+*} \rightarrow O_2 + O^+, O_2 + O^{2+} \quad [2.2\,\text{eV}, 37.3\,\text{eV}], \tag{1d}$$

$$O_3^{x+*} \rightarrow O + O + O^+, O + O + O^{2+} \quad [7.4\,\text{eV}, 42.5\,\text{eV}], \tag{1e}$$

$$O_3^{x+*} \rightarrow O + O_2^+, O + O^+ + O^+, O + O_2^{2+} \quad [0.6\,\text{eV}, 21.0\,\text{eV}, 24.7\,\text{eV}]. \tag{1f}$$

The energies given within brackets are the heat of formation of the products relative to the heat of formation of O_3^+. For example, the production of $O_2 + O^+$ [channel (1d)] requires that the O_3^+ ion is excited by at least 2.2 eV in the initial stage of the CID process. The quoted values correspond to the vibronic ground states of all species and are predominantly based on thermochemistry data provided in [30]. The corresponding channels and associated energetics for N_3^+ are shown in Eq. (2):

$$N_3^+ + R_g \rightarrow N_3^* + R_g^+ \text{ or } N_3^{x+*} + R_g + (x-1)e^-,$$

$$N_3^* \rightarrow N_3 \quad [-15.4\,\text{eV}], \tag{2a}$$

$$N_3^* \rightarrow N_2 + N \quad [-10.5\,\text{eV}], \tag{2b}$$

$$N_3^* \rightarrow N + N + N \quad [-0.7\,\text{eV}], \tag{2c}$$

$$N_3^{x+*} \rightarrow N_2 + N^+, N_2 + N^{2+} \quad [4.0\,\text{eV}, 33.6\,\text{eV}], \tag{2d}$$

$$N_3^{x+*} \rightarrow N + N + N^+, N + N + N^{2+} \quad [13.8\,\text{eV}, 43.4\,\text{eV}], \tag{2e}$$

$$N_3^{x+*} \rightarrow N + N_2^+, N + N^+ + N^+, N + N_2^{2+} \quad [5.1\,\text{eV}, 28.4\,\text{eV}, 32.1\,\text{eV}]. \tag{2f}$$

II. EXPERIMENT AND DATA ANALYSIS

In many aspects the present experiment followed similar steps as dissociative recombination experiments at CRYRING. All measurements conducted in the present O_3^+ experiment were in fact needed for the derivation (and validation) of branching fractions in the dissociative recombination (DR) of O_3^+ [31,32]. For the N_3^+ experiment readers are referred to [33] for details on, e.g., ion production. Here we only briefly explain the experimental procedure for the O_3^+ investigation. An experimental cycle with a duration of 6.0 s consisted of: (i) ion production from O_2 in a Nielsen-type ion source [34] (the source was, however, operated in an untraditional way—it was run in a glow-discharge mode with the filament not being used; see [32]), (ii) mass selection of ions by a bending magnet and injection of ions into the storage ring (circumference of ~51.6 m), (iii) acceleration of the ions to 1.96 MeV by a radio frequency cavity system, (iv) storage of the ions in the ring allowing for further relaxation of excited states, (v) data acquisition from CID and ECID events with rest gas molecules (predominantly H_2 with trace amounts of volatiles such as CH_4; see [35]), and (vi) resetting of ring parameters. It is noted that during step (iv) which lasted for 3.7 s, a cold

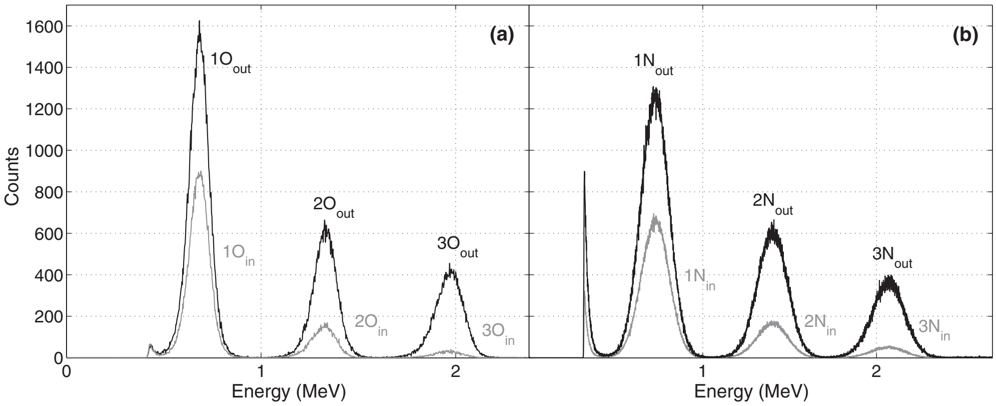

FIG. 1. (a) Normalized energy spectra recorded by the IISD (radius ~3.0 cm) for the neutral products stemming from the CID and ECID events of 1.96-MeV O_3^+ ions with rest gas molecules (predominantly H_2) in CRYRING. The black line shows the spectrum without the grid inserted in front of the IISD and the gray line shows the spectrum recorded with the grid inserted in front of the IISD. The small feature near 0.5 MeV is due to detector noise; (b) same as (a) but for 2.25-MeV N_3^+ ions.

electron beam was merged with the ion beam along a straight section of the ring equipped with an electron cooler. Heat transfer from the ions to the electron beam then helped in reducing the phase space occupied by the ions (for a review of electron cooling, see [36]), though this effect was small for the investigated ion [32]. During step (v) which lasted for 1.3 s, the speed of the electrons was adjusted such that the interaction energy with the ions became ~1 eV. At such interaction energy dissociative recombination (DR), a process leading to exclusively neutral product fragments, is rather inefficient, but the possible contamination from the process to recorded data from ECID events is not ignored in the present study (note that DR events lead to the same products as the ECID events, though possibly with different branching fractions). An $O_3^+ + e^-$ collision at an interaction energy of 1 eV can also produce $O + O_2^+$ (dissociative excitation) as the threshold for this channel is only 0.63 eV. As will be shown, we could correct for signals arising from this type of interaction. The corresponding collisional excitation channel in N_3^+ is not open at such low energies, and so the data do not need correcting.

CRYRING consists of twelve equally long straight sections joined by bending magnets keeping ions of a preset mass-to-charge ratio in appropriate trajectories. A bending magnet situated after the electron cooler kept the parent ions in their appropriate trajectories, while deflecting charged products from collision events and leaving the neutral products of these events unaffected. The neutral products then left the ring tangentially and were detected by an energy-sensitive ion implanted silicon detector (IISD), with a radius ~3.0 cm, situated ~4 m from the center of the straight section of the ring defining our "observable interaction region." The IISD was connected to a multichannel analyzer (MCA) allowing for the recording of pulse height spectra. Following another straight section of the ring, a microchannel plate (MCP) detector was installed and connected to a multichannel scaler. The recorded counting intensity versus time was proportional to the ion current in the ring.

Neutral products from the same CID or ECID (or DR) event reached the IISD within such a short time difference that only the sum of their kinetic energies could be recorded. To enable the extraction of branching fractions an additional pulse height spectrum was recorded with a grid inserted in front of the IISD (for early uses of similar or conceptually similar grid techniques, see, e.g., [20,23,37,38]). The stainless steel grid utilized at CRYRING consists of ~80-μm-diameter closely packed holes giving each product fragment a probability of $P = 0.297 \pm 0.015$ to pass through it and hit the detector [18]. It is stressed that charged product fragments were deflected by the bending magnet situated after the electron cooler and did not hit the detector.

To investigate the relative importance of channels (1a)–(1f) [(2a)–(2f) for N_3^+] in the laboratory environment (wherein signals from ECID channels may have contributions from DR events) we used the pulse height spectra recorded with and without the grid inserted in front of the IISD. Normalizing the data according to the ion beam intensities measured by the MCP resulted in the spectra shown in Fig. 1(a) (O_3^+) and Fig. 1(b) (N_3^+).

The following equation system applies for the intensities of the peaks in Fig. 1(a):

$$\begin{bmatrix} I(1\mathrm{O}_{in}) \\ I(2\mathrm{O}_{in}) \\ I(3\mathrm{O}_{in}) \\ I(1\mathrm{O}_{out}) \\ I(2\mathrm{O}_{out}) \\ I(3\mathrm{O}_{out}) \end{bmatrix} = \begin{bmatrix} 0 & P(1-P) & 3P(1-P)^2 & 0 & 2P(1-P) & P \\ 0 & P(1-P) & 3P^2(1-P) & P & P^2 & 0 \\ P & P^2 & P^3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 1 & 0 \\ 1 & 1 & 1 & 0 & 0 & 0 \end{bmatrix} \times \begin{bmatrix} \mathrm{C(1a)} \\ \mathrm{C(1b)} \\ \mathrm{C(1c)} \\ \mathrm{C(1d)} \\ \mathrm{C(1e)} \\ \mathrm{C(1f)} \end{bmatrix}. \qquad (3)$$

Here, e.g., C(1e) denotes the number of reactions leading to the neutral products in (1e), while, e.g., $I(1\mathrm{O}_{in})$ is the intensity of the $1\mathrm{O}_{in}$ peak seen in Fig. 1(a). As an example channel (1e) produces two O atoms and contributes both to the $1\mathrm{O}_{in}$ peak with a probability of $2P(1–P)$, as it requires that one of the O atoms passes the grid whereas the other one is stopped, and to the $2\mathrm{O}_{in}$ peak with a probability of P^2 as this requires that both O atoms pass through the grid. Finally, with the grid removed, this channel contributes to the $2\mathrm{O}_{out}$ peak with a probability of 1.

Before solving Eq. (3) we needed to take into account the possible contamination from the electron-impact channel leading to $\mathrm{O} + \mathrm{O}_2^+$. To investigate whether this channel was of any significance we subtracted, from a grid-out pulse height spectrum recorded at an ion-electron interaction energy of ~0 eV, the (normalized) grid-out spectrum recorded at an interaction energy of 1 eV. In the spectrum obtained at 0 eV ion-electron collisions the signals from dissociative recombination reactions were only recorded at the full mass peak. The other peaks were due to reactions between the ions and the residual gas. The intensities of the $2\mathrm{O}_{out}$ peaks were similar in the spectra, but the intensity of the $1\mathrm{O}_{out}$ peak was larger in the 1 eV spectrum than in the 0 eV spectrum, which indicated the contribution from the electron-impact excitation channel leading to $\mathrm{O} + \mathrm{O}_2^+$. The ratio between the intensities of the $1\mathrm{O}_{out}$ peaks (the one from the 0 eV spectrum and the one from the 1 eV spectrum) was found to be ~0.92. Therefore $I(1\mathrm{O}_{out})$ of Eq. (3) was corrected to $0.92I(1\mathrm{O}_{out})$, and $I(1\mathrm{O}_{in})$ of Eq. (3) was updated to $I(1\mathrm{O}_{in})–0.08I(1\mathrm{O}_{out})P$, before solving the equation system. For N_3^+ an equation system similar to Eq. (3) (but with “O” replaced by “N”) was solved to determine branching fractions. No correction due to electron-impact dissociative excitation channels was needed in this case.

III. RESULTS AND DISCUSSIONS

In Table I we list the measured probabilities that collision events in the observable interaction region lead to specific sets of neutral products (we emphasize again that the ECID channels may have been contaminated by DR events). A combination of poor statistics and high sensitivity to the transmission probability of the grid made it impossible to determine with certainty the relative importance of the individual channels leading to exclusively neutral product fragments in the N_3^+ experiment. For O_3^+ we could at least exclude significant flux into the (1a) channel and establish that the (1b) channel has a branching fraction exceeding 7%.

In Table II we list the relative importance of the different CID (including electron stripping) channels and show also the similar data from the investigation of collisions between 1.80-MeV H_3^+ ions with H_2 [20]. For clarification the branching ratios presented for, e.g., O_3^+ in Table II are those obtained when dividing C(1d), C(1e), and C(1f), respectively, with the sum C(1d) + C(1e) + C(1f).

The dominant channels for the three systems (O_3^+, N_3^+, and H_3^+), namely those leading to an individual neutral atomic fragment (O, N, and H), show remarkably similar branching fractions, all being near 65%. On the other hand the three systems have different branching fractions for the CID channels producing a neutral molecule (O_2, N_2, and H_2) or two neutral atomic fragments (O + O, N + N, and H + H). The propensity for molecule formation is highest for N_3^+ and lowest for O_3^+, with the ratios $\mathrm{C}(X_2)/[\mathrm{C}(X_2) + \mathrm{C}(X + X)]$ being approximately 0.07, 0.44, and 0.34 for O_3^+, N_3^+, and H_3^+, respectively. To understand in depth the differences in the relative yields of X_2 and $X + X$ formation in the CID of these ions requires insights into, e.g., the electronic states and the associated potential energy surfaces involved in the reactions. Here it is not surprising, however, that the N_3^+ system shows the highest propensity for molecule formation given its chemical bond strengths. The $X + X + X^+$ channel requires an energy transfer to the projectile ion of (at least) 13.8 eV in the case of N_3^+, while only 7.4 eV is required to be transferred to O_3^+. Interestingly, the $\mathrm{H} + \mathrm{H} + \mathrm{H}^+$ channel requires an energy transfer of 8.8 eV in the CID of H_3^+, the threshold being in between those for the corresponding channels in O_3^+ and N_3^+.

The presence of stronger chemical bonds in the N_3^+ ion was indeed also suggested to be the reason for the significant difference in the importance of the three-body breakup channels for the DR reactions of N_3^+ and O_3^+ with free electrons at ~0 eV interaction energy [33]. While for O_3^+ the branching ratio of the O + O + O channel (exoergic by 6.3 eV) was determined to be 94% ± 3%, the corresponding N + N + N channel in the DR of N_3^+ (exoergic by just 0.7 eV) was only populated by 8% ± 3%. It is noted that the three-body breakup channel in the DR of H_3^+ at ~0 eV interaction energy is exoergic by 4.8 eV and has a branching fraction of ~65%–70% [17,38].

Many experiments have been conducted earlier on the fragmentation of neutral and ionized ozone following photo- or electron impact (see, e.g., [31,32,39–46]). Despite the fact that the 40–500-eV electron impact on O_3 [40] and the 3–100-eV electron impact on O_3^+ [46] produce O_2^+ in significantly higher yields than O^+ we refrain from speculating on whether the O atom in the dominant (1f) channel in the present experiment mainly is accompanied by O_2^+, $2\mathrm{O}^+$, or

TABLE I. Branching ratios obtained by solving Eq. (3) (corrected version in the case of O_3^+, “O” replaced by “N” in the case of N_3^+) and by normalizing the results. The error bars are dominated by the uncertainty in the transmission probability of the grid.

Channel [see Eqs. (1) and (2)]	Products (X = O or N)	Branching fraction O_3^+ (%)	Branching fraction N_3^+ (%)
(1a)–(1c): (2a)–(2c)	X_3 and $X_2 + X$ and $3X$	20 ± 1	18 ± 2
(1d): (2d)	$X_2 + X^+$ and $X_2 + X^{2+}$	2 ± 1	12 ± 2
(1e): (2e)	$2X + X^+$ and $2X + X^{2+}$	25 ± 1	15 ± 2
(1f): (2f)	$X + X_2^+$ and $X + 2X^+$ and $X + X_2^{2+}$	53 ± 1	55 ± 1

TABLE II. Relative importance (%) of channels producing X, $X + X$, and X_2 in the CID (including electron stripping) of O_3^+ and N_3^+ with the H_2 dominated CRYRING residual gas (present experiment) and 1.8-MeV H_3^+ ions with H_2 (Berkner *et al.*, Ref. [20]).

Neutral product(s)	1.96-MeV O_3^+	2.25-MeV N_3^+	1.80-MeV H_3^+
X_2	2.5 ± 1	15 ± 1	∼12.5
$X + X$	31.5 ± 2	18 ± 3	∼24
X	66 ± 2	67 ± 3	∼63.5

O_2^{2+}. Though the production of two O^+ ions requires at least 20.97 eV energy transfer, it is noted that the experiment on 0.4–1.8-MeV H_3^+ ions colliding with H_2 showed that the yield of $H + 2H^+$ (requiring an energy transfer to the projectile ion of >22.4 eV) was a factor of 2–3 higher than the yield of $H + H_2^+$ [20].

The presence of long-lived (μs regime) intermediate states may have influenced the derived branching fractions in the present experiment. If a state is sufficiently long-lived against dissociation the fragmentation of the complex can occur after having passed the deflecting bending magnet, with the neutral products not hitting the IISD. CID processes with long-lived ${O_3}^{+*}$ or ${N_3}^{+*}$ states are not expected to cause such problems due to the closed-loop nature of the experiment. The *nondetection* of CID products from long-lived intermediate ${O_3}^{+*}$ (${N_3}^{+*}$) ions formed in the observable interaction region but dissociating after the deflecting bending magnet would be largely compensated by the *detection* of CID products from intermediate ${O_3}^{+*}$ ions (${N_3}^{+*}$ ions) formed elsewhere in CRYRING but dissociating within the observable interaction region. There is still the risk that electron stripping processes or sequential breakup processes may involve long-lived intermediate ionic states, with mass-to-charge ratios different from the ions in the parent beam. To this end it is noted that formation of long-lived dication states (e.g., CD_m^{2+} with $m = 2, 4, 5$ [24] and $HeAr^{2+}$ [25]) have been observed earlier in charge stripping collisions between various ions near MeV energies and Ar. Note, however, that the presence of long-lived intermediate dication states would not affect the derived branching fractions should these complexes dissociate into exclusively charged fragments.

Finally, we need also to assess the risk that some reactions may be associated with a high kinetic energy release (KER), such that product fragments may receive enough transversal velocity to miss the IISD. An O atom can receive up to 2/3 of the total KER in a CID event and the detection efficiency, f(KER), of such atoms can be mathematically evaluated as a function of the total KER from the speed of the parent O_3^+ ions, and by assuming that the O atoms are ejected in random directions from CID events occurring uniformly over a distance 2.5–5.5 m from the detector with radius 3.0 cm. To evaluate f(KER) we assume for simplicity that the parent ion beam was coaxial with the center of the detector and we neglect the fact that the ion beam had a cross-sectional diameter of a few mm. Under these assumptions f(KER) values of 1 are obtained for KER < 30 eV, while f(KER) values of 0.96, 0.90, and 0.83 are found for KER values of 40, 50, and 60 eV, respectively. KER values in excess of 40 eV seem improbable both from intuition and from KER distributions observed in CID processes at keV energies (e.g., [2,16]), though to the best of our knowledge KER distributions for CID processes at MeV energies have never been reported.

IV. CONCLUSIONS

Using the heavy-ion storage ring CRYRING we have investigated the production of neutral products in the CID (possibly including electron stripping) of 1.96-MeV O_3^+ ions and 2.25-MeV N_3^+ ions, with rest gas molecules (predominantly H_2 but with trace amounts of volatiles such as CH_4). The main focus has been to determine the relative importance of channels leading to the neutral products X, $X + X$, and X_2 with $X =$ O or N. The results for O_3^+ and N_3^+ are similar in the aspect that the dominant channels are the ones leading to a single neutral atomic fragment. A similar dominance of H production was observed earlier in the CID of 1.8-MeV H_3^+ ions colliding with H_2 [20]. The most notable difference when comparing the N_3^+ results with the O_3^+ results is that the propensity for X_2 formation is much higher for N_3^+ than for O_3^+, which we believe reflects the stronger chemical bonds in the N_3^+ ion.

We have demonstrated that magnetic storage rings can be used as a tool to investigate fragmentation patterns in CID reactions and we encourage similar investigations into such processes in other storage rings. Several improvements can be made to the experimental protocol used in the present study, which would allow gaining deeper insights into the CID process and also allow determining branching fractions for ECID processes: (1) In case an electron cooler is installed the electron beam should ideally be switched off during data acquisition to completely exclude any contamination from electron-impact processes. (2) The reactions can be studied over a range of ion energies to investigate whether the branching fractions are sensitive to the kinetic energy of the ions. (3) In order to investigate whether high kinetic energy release causes some neutral products to pass by the active area of the detector an iris aperture can be installed in front of the detector to allow monitoring the yield as a function of open area (see, e.g., [47]). (4) The use of grids with different transmission probabilities (see, e.g., [48]) can help to assess more detailed branching fraction information. (5) An experimental setup that allows for the detection of charged product species would help in assessing the nature of the charged species accompanying the neutrals in the CID processes (see [49] for a setup used to detect charged fragments exiting CRYRING, and see [27] for an experimental setup utilizing multiple and movable energy-sensitive detectors that enable coincident detection of neutral and charged CID products). (6) The use of a position-sensitive imaging detector (or ideally energy- *and* position-sensitive detector; see, e.g., [50]) can potentially add insights into the internal states of the reaction products.

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