

Mutual Neutralization of NO^+ with O^-

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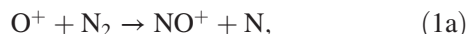
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We have studied the mutual neutralization reaction of vibrationally cold NO^+ with O^- at a collision energy of ≈ 0.1 eV and under single-collision conditions. The reaction is completely dominated by production of three ground-state atomic fragments. We employ product-momentum analysis in the framework of a simple model, which assumes the anion acts only as an electron donor and the product neutral molecule acts as a free rotor, to conclude that the process occurs in a two-step mechanism via an intermediate Rydberg state of NO which subsequently fragments.

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In Earth's upper atmosphere, several exothermic reactions between oxygen and nitrogen produce NO^+ , e.g.,

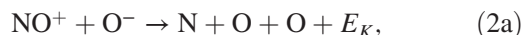


The low ionization potential of NO (9.26 eV) implies that once NO^+ is formed, further charge transfer generally is energetically unfavorable, and, thus it becomes the dominant ion in the *E* region (90–160 km) [1], and possibly the upper *D* region (≈ 90 km) [2], of the daytime atmosphere. The ions produced in these reactions are typically rovibrationally excited, and NO^+ is a significant infrared radiator. For example, during auroral disturbances hot bands from NO^+ ions with at least 1.9 eV of rotational energy have been observed [3]. Though vibrationally hot ions are produced in all three reactions, these are typically quenched in collisions with N_2 due to its near vibrational resonance [4].

The main destruction mechanisms of NO^+ are believed to be through mutual neutralization (MN), the subject of this Letter, and dissociative recombination (DR). In general, and in contrast to DR in particular, MN is a significantly less well-studied reaction from both

experimental and theoretical perspectives. In the ionosphere, MN of atomic oxygen and nitrogen ions is expected to contribute significantly to the observed UV-airglow [5] via the production of excited atomic products [6,7]. *In situ* measurements show that in the *D* region during polar cap absorption events, NO^+ is measured to be the predominant positive ion, and O^- a significant anion [8]. Further afield, studies of the Venusian atmosphere report oxygen as a critical electron acceptor [9] and NO^+ a prominent cation [10].

In the MN of NO^+ with O^- at low collision energies ($E_{\text{c.m.}} < 1$ eV), two different classes of reaction products are energetically available:



where E_K is the kinetic energy released in the reaction, which depends on which products are created. The neutralized NO is formed in an intermediate state (NO^*) which either stabilizes by fragmentation yielding three atomic products (2a) or by photon emission, yielding two neutral products (2b). At low $E_{\text{c.m.}}$, the only open three-body channel (2a) produces ground-state products sharing $E_K = 1.3$ eV of kinetic energy, i.e., $\text{N}(^4S) + \text{O}(^3P) + \text{O}(^3P)$, whereas several molecular pathways (2b) are available with E_K varying from 0.1 to 7.8 eV.

Early merged-beams measurements carried out over a broad range of collision energies (0.15–816 eV) [8,11] suggest that the cross section for the MN of NO^+ and O^- is significant, and larger than that for the MN of O^- with the two other important atmospheric ions, O_2^+ and N^+ . However, only indirect information on the reaction

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dynamics and final-state products were reported. Further indirect information is reported from flowing afterglow (FA) studies on the MN of NO^+ with SF_6^- [12], C_6F_6^- [13], NO_2^- [14], Cl^- and I^- [15], where the detection of fluorescent photons is used to infer that the reaction proceeds through the equivalent to (2b).

There is better understanding of the DR of NO^+ ($\text{NO}^+ + e^- \rightarrow \text{N} + \text{O} + E_K$). Sufficient reaction energy is available that several channels with different electronically excited products can be produced. Detailed experimental [16,17] and theoretical [18] studies are reported and the dynamics are understood. The dominant reaction channel produces $\text{N}(^2D)$, which then further reacts with oxygen to produce NO and excited oxygen atoms, resulting in airglow in the night sky. Furthermore, the kinetic energy released produces energetic O fragments which are partially responsible for the hot oxygen layer surrounding the atmosphere [19]. The role of MN in these environments should not be overlooked, and relevant reactions should be treated in equal detail to those on DR.

For a long time, studies of MN reactions were mainly performed in flowing afterglows for which any information on product neutrals was difficult and ill defined. Storage rings combined with imaging techniques have been proven to be a very effective tool in studying MN [6,7]. Storage of ions in confined trajectories under high-vacuum conditions ensures a well-characterized beam of the reactants of interest, and merged-beams configurations both allow control over the collision energy and ensure single-collision conditions, free from three-body effects. Cryogenic ion-storage gives access to studying effects of ion-cooling and few-quantum-state control [6,7,20]. Coupling all of these properties with coincident new imaging techniques, the final-state products are identified, which is crucial for an understanding of the reaction dynamics [6,7]. As such, and in contrast to past experiments, this allows, for the first time, exact comparisons to theory, and thus helps advance the physical understanding of such reactions.

In this Letter, we thus report on the first MN study involving a molecular ion in which the final-state products and reaction dynamics have been resolved. We find for the first time that the MN of NO^+ with O^- is completely dominated by dissociation into three ground-state atomic products, and that the process proceeds in a two-step mechanism via a Rydberg state of NO.

The experiment was carried out at the unique double electrostatic ion storage ring, DESIREE, at Stockholm University. A detailed description of the facility is given elsewhere [21,22], and only relevant details are given here. NO^+ was produced in an electron cyclotron resonance ion source using N_2 and O_2 as source gases, while O^- was produced in a Cs sputtering ion source using a SnO_2 cathode. The NO^+ and O^- ion beams were accelerated to their final storage energies of 17 keV and 8 keV, respectively, mass selected, and injected simultaneously into their

respective storage rings. Here the ions were stored for 10–15 s. During this time, the hot NO^+ ions radiatively couple to the ≈ 22 K cryogenic environment [23,24], cooling away their internal energy. The radiative lifetimes of the first ten vibrational levels of NO^+ are on the order of 100 ms [25], and a beam of pure NO^+ ($v = 0$) will be present after less than one second of storage. However, rotational cooling lifetimes are several orders of magnitude longer [17], and the J -state distribution of the ions is expected to not change significantly from that they had at their creation. No rotational manipulation of the ions was undertaken [23,24,26].

During each orbit, the ions are merged, overlapped, and pass collinearly through a common straight section of drift tubes before being demerged back into their respective rings. A voltage of 700 V set on three of the tubes accelerates and decelerates the anions and cations, respectively, such that their relative velocity decreases significantly, and collision energies of $E_{\text{c.m.}} < 100$ meV are achieved. Neutralized particles formed in this biased drift region are not deflected, and travel in straight trajectories to the time-and-position sensitive neutral particle detector.

General details about the data acquisition, subsequent analysis, and Monte Carlo simulations of the reaction outcome, are found in Ref. [6]. The main difference here is that the current experiment makes use of a newly installed time-resolved and event-driven camera with a 256×256 pixel array, where each pixel in the sensor possesses its own signal processing circuit (TPX3CAM, see, e.g., [27,28], and the discussion in Supplemental Material [29] (SM)). As such, multiparticle coincidence events can be detected with much greater efficiency than realizable in the previous system, which relied on combining two different detection systems for position and timing information.

The detection scheme employed at DESIREE allows the positions and arrival-time-differences of the products from reaction (2) to be recorded on an event-by-event basis, and the total kinetic energy released ($E_{\text{tot}} = E_K + E_{\text{c.m.}}$), in each MN event is determined from these data through the relationship

$$E_{\text{tot}} = \frac{v^2}{2L^2} \sum_{i=1}^N m_i \vec{r}_i^2, \quad (3)$$

where $\vec{r}_i = (\Delta x_i, \Delta y_i, v\Delta t_i)$ are the measured displacements of each product, with mass m_i , L is the distance of the event to the detector, v is the average velocity of the two ion beams, and N ($= 2, 3$) is the number of products. The displacements are calculated relative to the center of mass (c.m.) of the three masses, which is obtained assuming the identities of the three individual detected particles such that their center of mass is closest to that of the two beams. Details, and the (surprisingly small) effects of misassignment are described in SM [29]. Events are then filtered

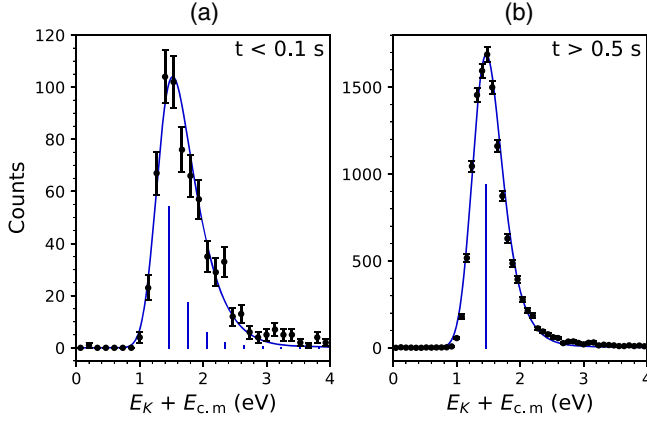


FIG. 1. Kinetic energy release distributions of the $N + O + O$ products at two different storage time intervals. The full lines results from fits assuming a constant rotational distribution ($T_{\text{rot}} = 1500$ K) and a vibrational distribution described by $T_{\text{vib}} = 3000$ K (a), and $T_{\text{vib}} = 22$ K (b). The vibrational state positions and populations are represented by the vertical bars.

based on this center of mass, as well as arrival time differences, in order to remove events arising due to either collisions with residual gas or to neutralizing collisions occurring in the unbiased parts of the merging region.

Analysis of these coincidence events then allows separate kinetic energy release spectra to be obtained for the two-body and three-body data. The contribution of the three-body data to the two-body spectrum is then inferred by randomly selecting two out of three events. On comparison of these spectra (Fig. S3 in Supplemental Material [29]), it is concluded that no real two-body MN events are present and that the data are completely dominated ($98 \pm 2\%$) by three-body MN events. Three-body spectra obtained at a collision energy of $E_{\text{c.m.}} \sim 0.1$ eV are shown in each panel of Fig. 1, where the experimental data are the filled circles. The error bars are dominated by the statistical uncertainties. Because of the rovibrational energy of NO^+ , a shift and broadening of the distribution is observed. The data plotted in Fig. 1(a) are obtained for events occurring within the first 0.1 s of storage, while those in Fig. 1(b) are from events occurring after 0.5 s. The difference between the two spectra is ascribed to the cooling of the NO^+ ($v > 0$) ions: the fit to the data (solid line) in Fig. 1(a) is obtained using a vibrational distribution described by $T_{\text{vib}} = 3000$ K, while 1(b) is described by a fit assuming only $v = 0$ is populated ($T_{\text{vib}} = 22$ K, corresponding to the effective temperature in DESIREE). In both cases, a constant rotational distribution described by a temperature $T_{\text{rot}} = 1500$ K is used in the model, based on a fit to the vibrationally cold spectrum. Figure S4 in Supplemental Material [29] gathers together the data sets shown in Fig. 1.

In order to investigate the dynamics of the reaction, energy- and momentum-conserving Dalitz plots were

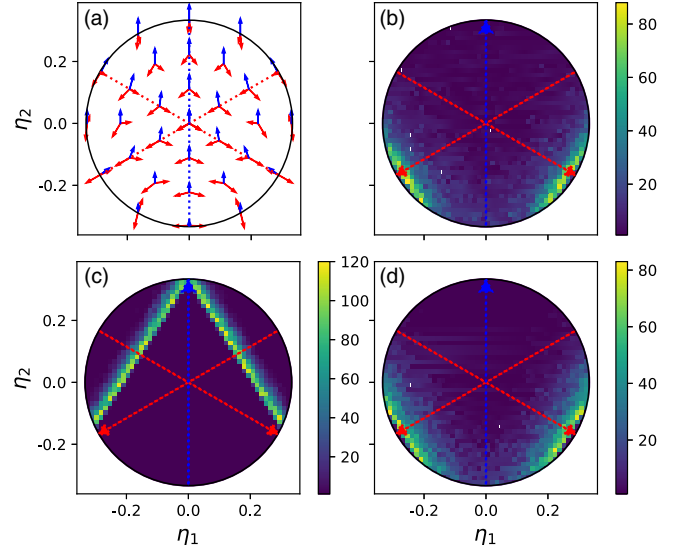


FIG. 2. (a) Breakup geometries in the Dalitz coordinates. The blue and two red arrows at each point correspond to the velocity vectors of the nitrogen and oxygen atoms, respectively. Each dotted line corresponds to the fraction of the total energy that each particle takes, with the vertical blue line corresponding to that of the nitrogen atom. Since the two oxygen atoms cannot be distinguished, the plot is symmetric with respect to the N line. (b) Experimental Dalitz distribution for all MN events after 1 s of storage. (c) Simulated Dalitz distribution using the free rotor model [32] with $\Delta E = 0.95$ eV, corresponding to the $E^2\Sigma^+$ state (d) with $\Delta E = 50$ meV, corresponding to the $D^2\Sigma^+$ state.

constructed [30] according to the standard generalized coordinates for a XY_2 breakup [31]:

$$\eta_1 = \frac{\sqrt{M/m_N}(E_{O1} - E_{O2})}{3E_K}, \quad (4a)$$

$$\eta_2 = \frac{(1 + m_N/m_O)E_N - E_{O1} - E_{O2}}{3E_K}, \quad (4b)$$

where $E_{N,O1,O2}$ are the kinetic energies of the three products. Figure 2(a) indicates the geometry of the $[\text{NO-O}]$ system as it broke up that would give rise to fragments having that set of Dalitz coordinates.

Dalitz distributions generated from experimental MN data have been obtained. Figure 2(b) plots all MN events analysed after 1s of storage time. From these data, it is concluded that fragmentation only from certain $[\text{NO-O}]$ geometries is favored, and these correspond to events in which the N and O atoms from NO are found in close proximity. This can be explained if the reaction involves a delayed breakup of the NO molecule, i.e., if the initial electron capture by NO^+ forms a predissociative state of NO, which subsequently couples to the dissociative exit state. The timescale for the dissociation must be considerably shorter than the flight time of the products from the interaction point to the detector which, in the current

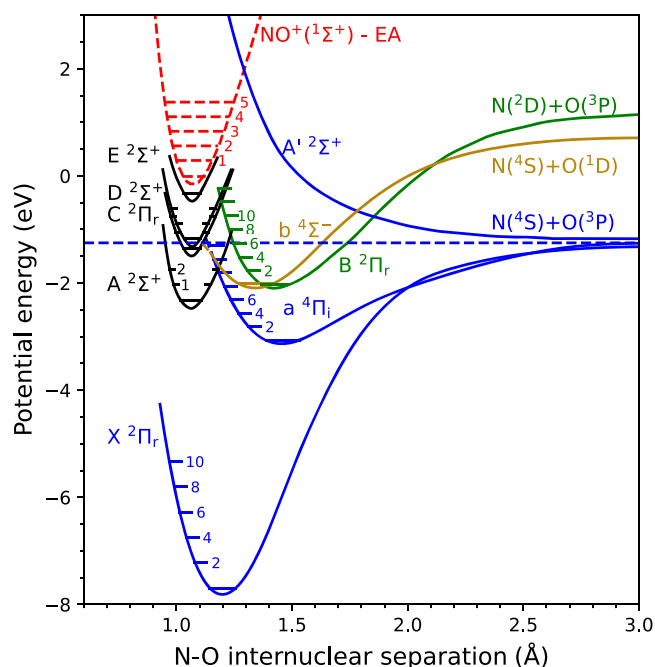


FIG. 3. Selected potential energy curves of NO^+ and NO . Adapted from [18,33–35].

experiment, is $\approx 10 \mu\text{s}$. Additional support for this conclusion is presented in Supplemental Material [29], where further analysis of Dalitz plots is presented.

To assist in interpreting these results, a few selected potential energy curves of relevance are plotted in Fig. 3 (adapted from [18,33–35]). In the model underlying the following discussion, it is assumed that as electron transfer in the MN reactions occurs at sufficiently large $\text{NO}^+\text{-O}^-$ separations that the neutral NO potentials are unperturbed by the anion, and that once the electron has been transferred the O atom is purely a noninteracting spectator. The NO^+ ground-state potential is shown as a dashed line, and has been shifted down by the electron affinity of O^- , such that the difference in energy between the ion and neutral potential curves corresponds to the energies released in the MN reaction.

The nonadiabatic transition probability of the reactants to specific neutral states depends on the electronic and vibrational couplings between the ionic and covalent potentials. However, while the electronic couplings require advanced and expensive calculations, the vibrational couplings only relate to the Franck-Condon overlap between these states. For an efficient transfer, this implies that the required intermediate neutral state is one with an internuclear separation similar to that of the parent ion. Calculations by Tsuji *et al.* show that the Franck-Condon overlap is near unity for $v \rightarrow v'$ transitions from the ionic potential to all Rydberg states [13]. The reaction could therefore initially involve the D or $E\ 2\Sigma^+$ Rydberg states, which lie above the dissociation limit.

To compare with the experimental data plotted in Fig. 2(b), we have performed three-body Monte Carlo simulations of the energy and momentum distribution of the atomic products in the framework of a sequential breakup of a free rotor [32]. This model introduces a parameter ΔE which is the difference between the internal energy of the intermediate molecular state and its dissociation limit. The parametrization is explained in SM [29], and we assume that the relevant reaction energy is transferred from the parent ion into the intermediate state. As a control, momentum vectors were simulated using randomized energy sharing, which for the candidate D and $E\ 2\Sigma^+$ states, yields $\Delta E \sim 50 \text{ meV}$ and 0.95 eV , respectively. Figures 2(c) and 2(d) show Dalitz plots resulting from analysis of the simulated particle vectors according to Eq. (4). The simulated Dalitz data obtained from the E state, Fig. 2(c), is clearly an extremely poor comparison to the experimental data, while the plot obtained for the D state, Fig. 2(d), is in excellent agreement. Both the dense areas and the spread of data points are well reproduced by the simulations, within an uncertainty of 20 meV . This supports the assumption that the reaction proceeds via a two-step mechanism by coupling first to the $D\ 2\Sigma^+$ Rydberg state, lying 50 meV above the dissociation limit, and dissociation occurring via isoenergetic curve crossings between this state and accessible non-Rydberg states of NO .

In the DR of NO^+ with electrons, coupling to the $B\ 2\Pi_r$ state is identified as one of the major reaction pathways resulting in the formation of the dominant $\text{N}(^2D) + \text{O}(^3P)$ pair of neutral products [18]. However, this exit channel is energetically closed in low-energy MN, and the $B\ 2\Pi$ state may instead couple to the $A'\ 2\Sigma^+$ state in order to result in the observed dissociation. Fluorescence studies shows that radiative transitions are only observed up to $v = 9$ in the $B\ 2\Pi_r$ state [36], implying that this coupling is significant. While this state only crosses with the higher vibrational states of the $D\ 2\Sigma^+$ states, the $b\ 4\Sigma^-$ state can serve as bridge for the lower vibrational levels. This mechanism was proposed to explain the emission of the $B\ 2\Pi$ state from the $\text{N}(^4S) + \text{O}(^3P)$ pair combination [37]. Coupling via the $a\ 4\Pi_i$ state cannot also be ruled out.

The absence of any intact molecular product is, however, intriguing. As noted earlier, FA studies on MN reactions of NO^+ with different anions (SF_6^- [12], C_6F_6^- [13], NO_2^- [14], Cl^- and I^- [15]) report the observation of fluorescence from Rydberg states, which would then stabilize the two-body channel. In the reactions with Cl^- and I^- , the electron affinity of the parent atom; 3.61 and 3.06 eV , respectively, ensures that the three-body channel is energetically closed by ≈ 0.9 and $\approx 0.4 \text{ eV}$, respectively, for low energy collisions, and that only two-body product channels are open. Both two- and three-body product channels are open for the reactions with the polyatomic anions. There are several possible explanations to the observations of fluorescence in

these reactions. It has been shown that the buffer gas in FA studies can affect the dynamics of the reaction. For example, collisions of NO with helium induces the transitions $D(v=0) \rightarrow C(v=0) \rightarrow A(v=3)$, from which fluorescence is emitted [36]. A simple calculation indicates that there are up to ten helium atoms in the relevant reaction volume of a typical FA apparatus, which would be sufficient to allow such collisional interference. Another possibility could be related to the fact that these studies involve molecular anions. Here, reaction energy could be taken up by structural rearrangement and/or fragmentation of the neutralized anion, i.e., the anion does not just serve as a passive electron donor but actively participates in the reaction, influencing the potential energy landscape. This could effectively stabilize the intermediate Rydberg state, e.g., by reducing the coupling to the dissociative state(s) and so providing enough time for the Rydberg states to radiatively decay. As such, it is of interest to study those particular MN experiments in DESIREE in order to investigate these possibilities.

We have investigated the mutual neutralization of NO^+ with O^- at low collision energies, and, for the first time, observed and determined the reaction products. By measuring the kinetic energy released to the fragments in the reaction we find that the reaction is completely dominated by dissociation into three ground-state atoms. From momentum and energy partitioning into these products, we conclude that the reactions dynamics involves first coupling to an intermediate state in NO which lies energetically very close to the dissociation limit, where the internal energy is transferred from the NO^+ to this NO excited state. Within a simple model framework involving a free rotor, and using relevant potential energy curves in NO, we identify that the very likely candidate is the $D^2\Sigma^+$ Rydberg state of NO, which is accessed just 50 meV above the dissociation limit, and which possesses multiple dissociation pathways.

Unlike DR of NO^+ which leads to significant yields of electronically excited atoms [16,17], eventually resulting in airglow in the night sky, MN only produces ground-state atomic products, and would not contribute to such phenomena. In stark contrast to previous studies into the MN of NO^+ , that inferred from fluorescence that the reaction forms intact molecular NO [12–15], we do not observe any such reaction channel. We conclude that this could be due to the experimental conditions present in flowing afterglows and/or the choice of molecular anion partners in those studies. As such, it is planned to study these particular MN experiments in DESIREE in order to test these possibilities. However, the current results indicate that the outcome of the MN reaction is different than assumed so far, and so we expect a significant effect in relevant atmospheric models.

All resulting data shown in the figures are available electronically under a Creative Commons license [38].

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There are no conflicts of interest to declare.

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