The formation of NO + from the reaction of N 2 2 + with O 2
Claire L. Ricketts, Sarah M. Harper, Sunny W.-P. Hu, and Stephen D. Price

Citation: The Journal of Chemical Physics 123, 134322 (2005); doi: 10.1063/1.2050648
View online: http://dx.doi.org/10.1063/1.2050648
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/123/13?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Ion-molecule reaction dynamics: Velocity map imaging studies of N+ and O+ with CD3OD

Dissociation of internal energy-selected methyl bromide ion revealed from threshold photoelectron-photoion coincidence velocity imaging

Bond-forming reactions of dications: Production of ArO + and ArO 2+ in the reaction of Ar 2+ with O 2

Guided-ion beam study of the O 2 + + C 2 H 2 charge-transfer and chemical reaction channels
J. Chem. Phys. 110, 4291 (1999); 10.1063/1.478312

Collisional reactions of Na n + (n=3–9) with N 2 O
The formation of NO+ from the reaction of N2^2+ with O2

Claire L. Ricketts, Sarah M. Harper, Sunny W.-P. Hu, and Stephen D. Price

Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ, United Kingdom

(Received 12 July 2005; accepted 11 August 2005; published online 6 October 2005)

We have studied the potentially ionospherically significant reaction between N2^2+ with O2 using position-sensitive coincidence spectroscopy. We observe both nondissociative and dissociative electron transfer reactions as well as two channels involving the formation of NO+. The NO+ product is formed together with either N+ and O in one bond-forming channel or O+ and N in the other bond-forming channel. Using the scattering diagrams derived from the coincidence data, it seems clear that both bond-forming reactions proceed via a collision complex [N2O2]^2+. This collision complex then decays by loss of a neutral atom to form a daughter dication (NO2^+ or N2O3^+), which then decays by charge separation to yield the observed products. © 2005 American Institute of Physics. [DOI: 10.1063/1.2050648]

I. INTRODUCTION

Diatomic dications have been known to exist for several decades and are believed to be potentially important components of various energized media. The molecular nitrogen dication (N2^2+) is of particular interest because of the high abundance of nitrogen in the terrestrial atmosphere and, partly because of this, the electronic states of the N2^2+ ion have been widely investigated both experimentally and theoretically. The contribution of molecular dications to the properties of planetary ionospheres has generally been assumed to be insignificant. However, a recent prediction of a CO2^2+ layer in the ionosphere of Mars has implied that dications, and processes involving dications, may have more significance than previously thought in the upper atmospheres of planets. Indeed, very recent studies have also predicted the presence of N2^2+ and O2^2+ in the Earth’s ionosphere and N2^2+ in the ionosphere of Titan.

Detecting N2^2+ in the terrestrial atmosphere is problematic, in part because of the difficulty in distinguishing N2^2+ from N+ by mass spectrometry. However, calculations have modeled the density of N2^2+ at altitudes of 100–500 km in the Earth’s ionosphere, showing a peak between 100 and 200 km. At an altitude of 100–200 km the ionospheric plasma is only partially ionized so ion-neutral reactions make an important contribution to the chemistry. Hence, the N2^2+, O2^2+, and O2+ dications present in the terrestrial ionosphere are thought to be lost both by dissociative recombination and by collisions with the neutrals N2, O2, and O.

Recent experiments have shown molecular dications to have an extensive reactivity with neutrals, commonly producing a pair of monocations, sometimes together with one or more neutral species, via electron transfer or bond-forming processes. Such experiments have recently been reviewed. The mutual Coulombic repulsion between the pair of product monocations gives them high kinetic energies. Hence, the products of dication reactions are markedly more translationally energetic than the ionic products from monocation-neutral reactions and may have significantly different reactivity in subsequent collisions where, for example, their extra translational energy can allow normally endothermic processes to proceed. Thus, both the reactivity of dications and the reactions of the energetic products of dication reactions can potentially influence ionospheric properties.

Most dication electronic states are purely repulsive and dissociate rapidly, via charge separation, to a pair of monocations. However, most molecules possess at least one “metastable” dicationic electronic state, a state which possesses a barrier to this unimolecular decay. Indeed, from the ready detection of dications in simple mass spectrometric experiments, it is evident that many of these metastable dicaticonic states can survive for more than several microseconds. In fact, storage-ring experiments show that metastable dication states can survive for lifetimes of the order of at least seconds. Of course, for a reaction between a dication and a neutral to be relevant in ionospheric chemistry, the relevant dication must possess at least one metastable electronic state which can be readily populated and can exist for a period of time sufficient to encounter neutral molecules.

In the late 1980s, the first detailed investigations of the bimolecular reactivity of molecular dications, often with the rare gases as collision partners, were made using conventional or adapted mass spectrometers at significant collision energies. These experiments revealed significant cross sections for electron transfer from the neutral to the dication: CF2^2+ + Ar → CF2+ + Ar*,

CF2^2+ + Xe → CF+ + F + Xe*. (2)

Following the extension of these studies of dicationic electron transfer to lower (~10 eV) collision energies, the observation of “bond-forming” chemistry following dication-neutral collisions has stimulated further investigation of the “chemical” reactivity of molecular dications and neutrals. As...
mentioned above, this dication chemistry has been the subject of a number of recent review articles.\textsuperscript{51–54,65} In fact, the first report of a bond-forming reaction of a molecular dication arose from drift-tube experiments in 1989.\textsuperscript{66}

\[ \text{O}_2^+ + \text{NO} \rightarrow \text{NO}_2^+ + \text{O}^+. \]  

(3)

As a result of the above investigations, we now have a general picture of the classes of reactivity exhibited by small molecular dications.\textsuperscript{51–54,65,67–73} Electron transfer, both dissociative and nondissociative, usually dominates the product ion yield in such encounters. When the electron is transferred from the neutral to the dication, a pair of monocations is formed. If these “primary” monocations do not dissociate, the electron transfer reaction is termed “nondissociative” [Eq. (1)]; in contrast, if one or both of these primary monocations dissociate [Eq. (2)], the reaction is termed “dissociative” and neutral species are formed, in addition to the pair of monocations. Double-electron transfer processes have also been observed following dication-neutral collisions, but their cross section is usually smaller than the cross section for single-electron transfer.\textsuperscript{74}

\[ ^{13}\text{CO}_2^+ + \text{Xe} \rightarrow ^{13}\text{CO} + \text{Xe}^2+. \]  

(4)

Energy transfer following collisions between molecular dications and neutrals may promote the dication to an excited vibrational or electronic level. These excited dication states may then decay either by charge separation [Eq. (5)],\textsuperscript{52} where the dication fragments to form two singly-charged ions, or by neutral loss [Eq. (6)]\textsuperscript{75,76} forming a daughter dication:

\[ \text{CO}_2^{2+} + \text{O}_2 \rightarrow \text{CO}^+ + \text{O}^+ + \text{O}_2. \]  

(5)

\[ \text{CF}_3^2+ + \text{H}_2\text{O} \rightarrow \text{CF}_2^2+ + \text{F} + \text{H}_2\text{O}. \]  

(6)

At moderate collision energies (1 keV) and below, single-electron transfer reactions between dications and neutrals can be well explained using the “reaction window” model, which is based on the Landau-Zener theory.\textsuperscript{53,74,77,78} This theory pictures the electron transfer occurring at the intersection of two potential-energy curves: the reactant potential (M\textsuperscript{2+} + N), which is attractive at large interspecies separations, and a repulsive product potential (M\textsuperscript{+} + N\textsuperscript{+}). If the intersection of these two potential-energy curves occurs in the reaction window (3–6 Å), there is a high probability of electron transfer. Curve intersections outside the reaction window result in a considerably lower probability of electron transfer. For a given collision system there are usually many different possible curve crossings corresponding to the formation of different product electronic states. Hence, dissociative [Eq. (2)] and/or nondissociative [Eq. (1)] electron transfer channels are often readily available, explaining why electron transfer is often the dominant reactive channel in dication-neutral collisions.\textsuperscript{51–53}

Until recently, the mechanisms of the bond-forming chemical reactions following dication-neutral collisions had been less well rationalized than their electron transfer counterparts. For example, one of the commonly observed classes of bond-forming reactions [for example, Eq. (7)] involving the formation of a pair of monocations sometimes appears on first examination to involve negative ion transfer from the neutral to the dication:

\[ \text{CF}_2^{2+} + \text{H}_2 \rightarrow \text{HCF}_2^+ + \text{H}^+. \]  

(7)

However, detailed investigations of the dynamics of this class of bond-forming reactions, via angular scattering, isotopic substitution, and position-sensitive coincidence (PSCO) experiments, indicate that these reactions often occur via the formation, rearrangement, and charge separation of a collision complex.\textsuperscript{53,71,73,79–84}

\[ \text{CF}_2^{2+} + \text{H}_2\text{O} \rightarrow [\text{H}_2\text{O}–\text{CF}_2^2+] \rightarrow \text{H}^+ + \text{HO–CF}_2^+ \rightarrow \text{OCF}^+ + \text{H}^+ + \text{H} + \text{F}. \]  

(8)

These experimental observations have been supported by the calculation of the energetics of key stationary points on the relevant dication-neutral potential-energy surfaces.\textsuperscript{80,82–88}

As described above, the majority of the observed bond-forming reactions of dications involve the formation of a pair of monocationic products. However, recently an alternative form of dicationic bond-forming reactivity has been detected involving the formation of doubly charged products:\textsuperscript{89,90,92}

\[ \text{CO}_2^{2+} + \text{Ar} \rightarrow \text{ArC}^2+ + \text{O}. \]  

(9)

The measurement of the angular scattering in ion-neutral collision systems has proven a powerful probe of the associated reaction dynamics and mechanisms. Such angular scattering measurements can be made by rotating a mass spectrometer about the scattering center. However, the fact that dication electron transfer and bond-forming reactions usually produce a pair of monocationic products allows the implementation of a coincidence approach to measure the initial velocities of the monocation products and the mutual correlation of these velocities. This experiment involves detecting the pair of monocation products in coincidence, at a position-sensitive detector, following mass analysis by a time-of-flight mass spectrometer.\textsuperscript{93} The coincidence experiment yields the initial velocity vectors of both the product monocations for each reactive event detected. If the reaction involves the formation of a neutral species, in addition to the pair of monocations [Eq. (2)], a so-called three-body reaction, the PSCO data also allow the velocity of the third body to be determined.\textsuperscript{52,73,87,94} As shown below, the PSCO technique gives a detailed insight into the dynamics and energetics of dication-neutral reactions which produce two monocationic products.

Of course, if a dication reaction produces just two monocations, a two-body reaction, then noncoincidence scattering experiments, which detect just one of these products, can provide detailed information on the associated reaction dynamics. This insight is possible because, for a two-body reaction, the motion of the undetected product can be determined from the data recorded for the detected product via conservation of momentum. However, many dication chemical reactions are three-body processes, forming a neutral species in addition to the pair of monocations; such reactions are often termed dissociative for the study of such dissociative
The reaction of N$_2^+$ with O$_2$ and the proposed routes for loss of ionospheric N$_2$

Simon et al. described the reaction of N$_2$ with O$_2$ via two channels:

$$N_2^+ + O_2 \rightarrow NO^+ + O^+ + N,$$

$$N_2^+ + O_2 \rightarrow NO^+ + N^+ + O.$$ 

The PSCO data show that in both cases NO$^+$ is formed via the formation of an intermediate complex [N$_2$O$_2$]$_2^+$, which decays initially via neutral loss and then by charge separation.

II. EXPERIMENTAL ARRANGEMENT AND DATA PROCESSING

The experimental apparatus, which is shown in Fig. 1, has been previously described in the literature. The apparatus has been developed as a general technique to study the dynamics and energetics of gas-phase dication-molecule reactions. Time-of-flight mass spectrometry coupled with position-sensitive detection is used to collect, in coincidence on an event-by-event basis, the pairs of singly- and doubly-charged product ions formed by dication-neutral reactions. We show below how these data are recorded and how they yield detailed information on the dynamics of dication reactions.

The N$_2^+$ reactant ions are generated, via 150-eV electron ionization of N$_2$, in the ion source. These reactant ions, as well as other singly- and doubly-charged ions, are extracted and pass through a hemispherical energy analyzer. Here the ions are energy selected to give an ion beam with a restricted energy spread of approximately 0.3 eV. After leaving the hemispherical energy analyzer the ion beam is pulsed by applying oscillating triangular voltage wave forms, 180° out of phase, to a pair of deflectors following the analyzer’s exit slit. Using a pulsed ion beam minimizes the spread in the flight times recorded by the time-of-flight mass spectrometer (TOF-MS) by reducing the positional spread of the reactant dications in the mass spectrometer’s source region. The constrained velocity spread of the ion beam, resulting from the hemispherical energy analyzer, facilitates the formation of spatially well-defined reactive ion pulses.

After exiting the pulsing region, the packets of ions pass through a series of focusing and accelerating lenses, which are tuned to maximize the quality of the beam. A commercial velocity filter then selects the dications from the packets of ions and the resulting dication pulses are then decelerated to an appropriate collision energy, a few electron volts in the

...
laboratory frame, using a commercial decelerator. Following deceleration the dication pulses interact with an effusive jet of the neutral gas, O₂ in this case, in the source region of the TOF-MS and bimolecular reactions occur. The gas pressure of O₂ in the source region is kept low (below $4 \times 10^{-6}$ Torr) in order to operate under single-collision conditions. The source region of the TOF-MS is initially maintained in a field-free state to ensure the dication neutral reactions occur at the required low-collision energies. After the reactant ion pulse has reached the center of the source region, we record a TOF mass spectrum by applying a positive voltage (300 or 100 V) to the repeller plate. Mass spectra recorded with a 300 V pulse on the repeller plate result in short enough ionic times of flight to gather the full angular scattering from the dication reactions, despite the considerable kinetic energies of some of the product ions transverse to the axis of the TOF-MS. The longer ionic flight times in mass spectra recorded with a 100 V pulse on the repeller plate result in better energy resolution. However, with a 100 V repeller plate pulse ions with significant transverse velocities are not detected as they fly beyond the detector radius and thus incomplete angular distributions are recorded. Thus, to gather data with both full angular acceptance and optimum energy resolution, we record the spectra at both 100 and 300 V repeller plate voltages.

The TOF-MS is constructed to achieve second-order space focusing. Such focusing minimizes the contribution of the positional spread of the location of the reactive events in the TOF-MS source region to the temporal width of the peaks in the mass spectrum. Note that, as described above, this positional spread is also minimized by employing a pulsed reactant ion beam. The minimization of the contribution to the temporal widths of the mass spectral peak is important because, as described below, we evaluate the z velocity component of each ion’s laboratory velocity from the deviation of the ion’s flight time from the flight time of a zero-kinetic-energy ion. Thus, to maximize the resolution in the velocities, extraneous contributions to the spread in the ionic times of flight must be minimized.

About 400 ns after the voltage pulse is applied to the repeller plate, a “start” pulse is sent to the multihit timing electronics. The timing electronics receives stop signals from the position-sensitive detector (PSD) at the end of the TOF-MS. The PSD is a commercial device in which the electron pulse from a pair of multichannel plates (MCP) impacts on two, perpendicularly wound, wire anodes of known lengths. The position of the ion arrival in the plane of the detector $(x, y)$ can then be derived from the time of arrival of the charge pulse at the end of each anode wire. The charge pulse from the MCP propagates along each wire to its ends and the signals from both ends of the two wires are passed as stop pulses to the timing circuitry, resulting in four times $\{t_{x0}(i), t_{y0}(i), t_{x0}(i), t_{y0}(i)\}$ for each ion in the pair $(i = 1, 2)$. We also record the time of flight of each ion in the pair $t_{\text{expt}}(i)$ by detecting the voltage spike on the MCP supply when an ion is multiplied. Hence, there are five times recorded for each ion arrival, four times from the wire anodes and the MCP conversion signal, and hence, ten times for each ion pair we detect.

The data processing involved in the PSCO experiment has been previously reported in detail. During an experimental run the ten times associated with each pair event detected are stored for off-line processing. To begin the off-line processing we construct a two-dimensional coincidence (“pairs”) spectrum, a histogram of the flight time of $t_{\text{expt}}(1)$ against $t_{\text{expt}}(2)$ for all this pairs detected. In this pairs the individual reaction channels appear as peaks allowing immediate identification of both product ions formed in the reaction. We can then select the groups of events from the pairs spectrum which correspond to each individual reaction channel detected. These subsets of the data can then be processed further to reveal the dynamics of individual reactive channels.

To derive the details of the reaction dynamics and kinematics for each selected channel we need to determine the $x$, $y$, and $z$ velocity components for both product ions in the laboratory (LAB) frame and then convert to the center-of-mass (c.m.) frame for ease of interpretation. To derive the $x$ and $y$ velocity components of an ion in the LAB frame, $\nu_x(i)$ and $\nu_y(i)$, we need to know the position of the ion’s arrival at the position-sensitive detector. These positions $x(i)$ and $y(i)$ are measured relative to the center of the detector and are determined from the difference between the times of arrival of the charge pulse at the ends of each delay line together with the calibrated relationship between position and time ($1.96 \text{ ns mm}^{-1}$) for the delay lines:

\[ x(i) = \frac{(t_{x0}(i) - t_{x0}(i))}{1.96}, \]  
\[ y(i) = \frac{(t_{y0}(i) - t_{y0}(i))}{1.96}. \]

To determine $\nu_z(i)$ and $\nu_y(i)$, we also need to know the position $(x_0, y_0)$ of the region where the dication pulses interact with the neutral gas. The coordinates $x_0$ and $y_0$ are readily determined from the $x, y$ positions of the unreacted dication beam at the detector. We also require the total flight time of the ion from the reaction region to the detector. This total flight time is $t_{\text{expt}}(i)$ plus the electronic delay $c$ between the pulsing of the repeller and the start of data collection, where $c$ can be determined by calibration of the mass spectrum. Hence we have

\[ \nu_x(i) = \frac{(x(i) - x_0)}{(t_{\text{expt}}(i) + c)}, \]  
\[ \nu_y(i) = \frac{(y(i) - y_0)}{(t_{\text{expt}}(i) + c)}. \]

The $z$ velocity component for each product ion $\nu_z(i)$ is determined from the deviation of $t_{\text{expt}}(i)$ from the flight time of an ion of the same mass but with zero initial kinetic energy $t_0$ using Eq. (16). Again, the appropriate value of $t_0$ can be determined by calibration of the mass spectrum. In Eq. (16), $e$ is the charge on an electron, $Z$ is the charge number of the ion, and $F$ is the electric-field strength in the source region determined via a calibration experiment:

\[ \nu_z(i) = -\frac{(t_{\text{expt}}(i) - t_0(i))eZF}{m(i)}. \]
sented in the c.m. frame. To convert the pairs of the LAB velocity vectors, \( v(i) \) to pairs of velocity vectors \( w(i) \) in the c.m. frame requires the velocity, in the LAB frame, of the c.m. of the collision system \( v_c \). In general, \( v_c \) can be determined from the velocity of the dication in the LAB frame \( v_{\text{di}} \) and the mass of the dication and neutral:

\[
v_c = m_{\text{di}} v_{\text{di}} / (m_{\text{di}} + m_{\text{mu}}).
\]

(17)

Here we assume the dication beam is directed exactly along the \( z \) axis, a reasonable assumption given the quality of our ion beams, and the velocity of the dication is much larger than that of the effusive neutral molecule, again a good assumption at the collision energies we employ. The velocity of the dication is well defined by the voltages used to allow the ions to pass through the hemispherical energy analyzer. The above procedure gives us an average value of \( v_c \) for a given experiment. For a two-body reaction, \( v_c \) can also be determined from the product velocities for each event detected:

\[
v_c = (m(1) v(1) + m(2) v(2)) / (m(1) + m(2)).
\]

(18)

These two methods provide values for \( v_c \) in excellent agreement. Once a value of \( v_c \) has been determined we can convert the product velocities in the LAB frame to the c.m. frame:

\[
w(i) = v(i) - v_c.
\]

(19)

If the reaction of interest involves the formation of a third, undetected, neutral species, its velocity can be determined via conservation of momentum in the c.m. frame:

\[
w(3) = - [m(1) w(1) + m(2) w(2)] / m(3).
\]

(20)

The above procedure results in the c.m. velocity vectors of the reaction products for each reactive event detected. To reveal the dynamics of the reaction we must then examine the correlations between these velocity vectors.

An initial probe of the reaction mechanism and dynamics is to examine the scattering of the product velocities, in the c.m. frame, with respect to \( v_c \). This angular scattering is represented using polar histograms, more commonly known as scattering diagrams. A scattering diagram is constructed using the magnitude of \( w(i) \) as the radial coordinate and the angle \( \varphi \) of \( w(i) \) with respect to \( v_c \) as the angular coordinate. The angle \( \varphi \) is determined from the dot product of \( w(i) \) and \( v_c \). Since \( 0^\circ \leq \varphi \leq 180^\circ \) the scattering data for one product can be plotted in the upper half of the scattering diagram, while the data for a second product can be plotted in the lower half, as shown in Fig. 4.

For a two-body reaction the angle between the velocities of the two ionic products will always be \( 180^\circ \) due to conservation of momentum.\(^{85}\) However, for three-body reactions the scattering of two of the products relative to the third product, the internal frame scattering, is a very powerful probe of the reaction mechanism.\(^{87}\) Internal frame scattering diagrams can be constructed to show the scattering of any two products relative to the third product. Internal frame scattering diagrams are again polar histograms using the magnitude of the velocity of a given ion, for example, \( w(1) \), as the radial coordinate and the angle \( \theta \) between \( w(1) \) and \( w(2) \), if ion 2 is to be the reference ion, as the angular coordinate. Again, \( \theta \) can be determined from the dot product of \( w(1) \) and \( w(2) \). As with the regular scattering diagram, as \( 0^\circ \leq \theta \leq 180^\circ \), the internal frame scattering data for ion 1 with respect to ion 2 can be plotted in the upper half of the diagram and the data for ion 3 with respect to ion 2 can be displayed in the lower half, as shown in Fig. 5. Of course, the velocity of any of the three products can be used as the reference velocity for an internal frame scattering diagram.

The PSCO experiment also provides energetic information on the reactive events that are detected. The translational exothermicity, \( \Delta E_T \), for each reactive event can be expressed in terms of the kinetic-energy release of the reaction in the c.m. frame \( T \) and the c.m. collision energy \( E_c \):

\[
\Delta E_T = E_{\text{products}} - E_{\text{reactants}} = T - E_c.
\]

(21)

where the energies of the products and reactants \( (E_{\text{products}}, E_{\text{reactants}}) \) may contain contributions from rotational, vibrational, and electronic excitation. If there is no internal excitation carried by either the products or the reactants, then \( \Delta E_T \) is equal to the thermodynamic exothermicity of the reaction. The kinetic-energy release \( T \) can be determined from the magnitudes of the c.m. velocity vectors and \( E_c \) can be determined from the dication velocity and the reduced mass of the reactants. Therefore, a histogram of the \( \Delta E_T \) values for each reactive event detected can be constructed. Such a translational exothermicity spectrum may be used to provide information on the states of the reactant dication present in the beam and the product states populated in dication-neutral reactions.\(^{72,93,94}\)

III. RESULTS AND DISCUSSION

The bimolecular reactions between \( \text{N}_2^+ \) and \( \text{O}_2 \) have been studied using the PSCO technique at a range of c.m. collision energies \( (4.27, 4.95, 7.08, 7.47, 9.22, \text{and} \ 11.73 \text{ eV}) \) with a repeller plate voltage of 300 V. In addition, to try and achieve better energy resolution in the translational exothermicity spectra, the experiments were also carried out at a c.m. collision energy of 7.08 eV with a lower repeller plate voltage of 100 V.

Five dominant bimolecular reactions can clearly be seen in the coincidence (pairs) spectra we recorded following collisions of \( \text{N}_2^+ \) with \( \text{O}_2 \) at the above collision energies. A section of a typical coincidence spectrum is presented in Fig. 2. The reactions we observed are listed below and correspond to nondissociative electron transfer \([\text{Eq. (22)}]\), dissociative electron transfer \([\text{Eq. (23)}, \text{Eq. (24)}, \text{Fig. 2}]\), and two bond-forming channels \([\text{Eq. (25)}, \text{Eq. (26)}, \text{Fig. 2}]\):

\[
\text{N}_2^+ + \text{O}_2 \rightarrow \text{N}_2^+ + \text{O}_2^+.
\]

(22)

\[
\text{N}_2^+ + \text{O}_2 \rightarrow \text{N}_2^+ + \text{O}^+ + \text{O},
\]

(23)

\[
\text{N}_2^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{N}^+ + \text{N},
\]

(24)

\[
\text{N}_2^+ + \text{O}_2 \rightarrow \text{NO}^+ + \text{O}^+ + \text{N},
\]

(25)
The relative intensities of the different reactive channels

The relative intensities of the different reactive channels can be measured by comparing the numbers of

\[ \text{counts in each coincidence peak in the pairs spectrum.} \]

Before performing this analysis the contribution of the false coincidences must be subtracted from the reactions which form \( N^+ \) as one of the charged products. The false coincidences are easily identified, and removed from the dataset, as the “false” \( N^+ \) ions appear as a sharp peak in the velocity distribution of the \( m/z=14 \) product. After this false coincidence subtraction we see that the dissociative electron transfer and bond-forming channels, reactions (23), (24), (25), and (26), give coincidence intensities in an approximate ratio of 5:7:4:9:1:1.4, respectively. That is, the chemical channels are approximately five times less intense than the dissociative electron transfer reactions.

The electron transfer reactivity of small molecular dications, and \( N_2^+ \) in particular, has been extensively investigated and rationalized using a model based on the Landau-Zener theory. Hence in the remainder of this paper we focus on the bond-forming reactions, reactions (25) and (26).

Figure 3 shows the relative intensity of the chemical reaction forming \( \text{NO}^+ + \text{O}^+ + \text{N} \) [reaction (25)] with respect to the intensity of a dissociative electron transfer reaction [reaction (23)] as a function of collision energy. Figure 3 shows that even over the restricted energy range of collision energies we have studied, there is a significant variation in the relative intensities of these channels. Figure 3 emphasizes that it is vital for reliable ionospheric modeling that we have reliable measurements of the absolute cross sections of the different reactive channels, following dication-neutral collisions, as a function of collision energy.

B. Formation of \( \text{NO}^+ + \text{O}^+ + \text{N} \)

1. Reaction energetics

As described above and illustrated in the literature, the PSCO technique can be used to derive information on the translational exothermicity of the reactive events that are detected in the pairs spectrum. However, the translational exothermicity spectra generated for reactions (25) and (26) are broad and unresolved, even at a repeller plate voltage of 100 eV. Such unresolved spectra are indicative of a significant number of reactant and/or reactant vibronic states being involved in the reaction. The translational exothermicity spectra we derive from the pairs data for the formation of \( \text{NO}^+ + \text{O}^+ + \text{N} \) only indicate that the translational exothermicity is distributed between \( \sim 1 \) and 12 eV with a maximum at...
approximately 4 eV. However, despite this lack of resolution in the spectra, a few observations on the energetics of this reactive channel can be made.

Experimental studies of the electron transfer reactivity of N$_2$$^+$ have concluded that ion beams of this dication are principally composed of ions in the X($^1\Sigma^+$) electronic state, which lies 43.00 eV above the ground state of N$_2$$^+$, and the c($^3\Sigma^+$) excited state, which lies 1.51 eV above the X($^1\Sigma^+$) ground state of N$_2$$^+$. Some confusion has been created by the fact that different authors have associated different labels with this $^3\Sigma^+$ excited state of N$_2$$^+$. Wetmore and Boyd$^{13}$ labeled this state the C($^3\Sigma^+$) state, Koslowski et al.$^{14}$ labeled it the c($^3\Sigma^+$) state, and in Fig. 2 of Lundqvist et al.$^{29}$ the state is labeled D($^3\Sigma^+$). Whatever its label, and we will label it c($^3\Sigma^+$), this excited state has a potential well at least 2 eV deep and an equilibrium bond length close to that of N$_2$$^+$. A reaction from N$_2$$^+$ + O$_2$ in their ground electronic states to form NO$^+$ + O$^+$ + N in their ground electronic states has an exothermicity of 11.7 eV. This thermodynamic limit is derived from literature values of the heats of formation of the relevant neutrals and monocations and the double ionization potential of N$_2$$^+$ derived from electron-electron coincidence measurements.$^{25,26,41,102}$ This exothermicity agrees well with the largest translational exothermicity (\sim 12 eV) we observe in the translational exothermicity spectrum. However, the majority of reactive events have translational exothermicities less than this limiting value. These lower translational exothermicities must be due to the population of excited electronic or vibrational states of the products. Considering first vibrational excitation of the NO$^+$ product, the dissociation energy of the ground electronic state of NO$^+$ is approximately 11 eV.$^{102}$ Thus, varying degrees of vibrational excitation of the NO$^+$ product in its ground electronic state can account for translational exothermicity signals from 11.7 to 0.7 eV, a range of exoergicities overlapping almost exactly the experimental spectrum. Considering the possibility of the formation of electronically excited states of the products, the range of translational exothermicities observed experimentally encompasses the formation of excited states of the atomic products arising from their ground $(2p^3)$ configurations together with the ground electronic state of NO$^+$. Similarly, the experimentally observed range of translational exothermicities could also be explained by the formation of NO$^+$ in a number of its electronic excited states, which lie within 12 eV of the NO$^+$ ground state.$^{102}$ Our experimental spectra cannot decide definitively between these different options of how the internal energy is distributed in and between the NO$^+$, O$^+$, and N products. However, as shown below, the collision complexes which we deduce below are involved in the formation of the NO$^+$ product that have N–O bond lengths markedly different from that of NO$^+$(r$_c$=1.06 Å) in its ground electronic state. Thus, one might expect a significant vibrational excitation of the NO$^+$ product. This observation, coupled with the good agreement between the range of translational exothermicities we observe and the dissociation energy of the X($^1\Sigma^+$) state of NO$^+$, perhaps hints that a significant number of reactive events involve the formation of the products in their ground electronic states with the NO$^+$ ion possessing a range of vibrational excitation.

In contrast to the rather inconclusive energetic analysis presented above, the angular scattering information we derive from the PSCO data provide a powerful probe of the mechanisms of the bond-forming reactions between N$_2$$^+$ and O$_2$.

2. Angular scattering

In this section we will discuss the scattering diagrams derived from the PSCO data recorded with a repeller plate voltage of 300 V, where the full angular distributions of the reaction products are recorded. The scattering diagrams derived from the PSCO data for the formation of NO$^+$ + O$^+$ + N (Fig. 4) show that all the products from this channel are predominantly sideways scattered, relative to the velocity of the center of mass, over a relatively large range of scattering angles. Such strong sideways scattering which is symmetrical about a plane at $\varphi$=90$^\circ$, unlike the forward scattering observed for simple electron transfer reactions,$^{53,94}$ is a very strong indication that the products have been formed from the breakup of some sort of collision complex: [N$_2$O$_2$]$.^+$ For a collision complex, with a lifetime that is several times longer than its own rotational period, exists in a molecular collision system, then the products of the decay of the complex will be symmetrically scattered with respect to a plane passing through the center of mass and perpendicular to the relative velocity of the collision system, at $\phi$=90$^\circ$. Such symmetric scattering may be, depending on the angular momentum constraints, forward and backward, sideways, or isotropic. In our experiment, both sideways and isotropic scattering will translate, when integrated over all the possible values of the azimuthal angle, to a symmetrical distribution in $\phi$ peaked at 90$^\circ$, as we observe in Fig. 4.

As will be discussed below, we have performed ab initio calculations which reveal that at least two geometries of [N$_2$O$_2$]$^+$ possess potential-energy minima; these minima possesses $C_{2v}$ and $C_{i}$ symmetry. We estimate$^{93}$ that the rotational period for both these complexes in our experiments is of the order of 20 fs, indicating that the [N$_2$O$_2$]$^+$ collision
complex must survive for approximately 100 fs before dissociating.

How does the formation of NO\(^+\)+O\(^+\)+N proceed after the formation of the collision complex? The internal frame scattering diagram presented in Fig. 5 shows that there is a marked anticorrelation between the velocities of the charged products NO\(^+\) and O\(^+\), that is, the O\(^+\) ion is scattered strongly in the opposite direction to the NO\(^+\) product. Conversely, Fig. 5 also shows that the velocity of the N atoms is not strongly correlated with either of the velocities of the charged products.

Considering the possible mechanisms for the decay of the [N\(_2\)O\(_2\)]\(^2+\) collision complex, the complex can initially charge separate into two monocations, one of which subsequently dissociates (27), or the complex may initially lose a neutral species and with the resulting dication later dissociating (28):
\[
\text{[N}_2\text{O}_2\text{]}\text{^2+} \rightarrow \text{NO}^+ + \text{NO}^+ \quad \text{then} \quad \text{NO}^+ \rightarrow O^+ + N, \quad (27)
\]
\[
\text{[N}_2\text{O}_2\text{]}\text{^2+} \rightarrow \text{NO}_2^+ + N \quad \text{then} \quad \text{NO}_2^+ \rightarrow \text{NO}^+ + O^+. \quad (28)
\]

If the mechanism which involves initial charge separation is operating [reaction (27)], then we would expect the velocity of the N atom to be strongly correlated with that of the O\(^+\) ion and anticorrelated with that of the NO\(^+\) ion. This relationship will arise as the significant Coulomb repulsion, several electron volts, in the primary charge-separation step would give the nascent pair of NO\(^+\) ions significant velocities in opposite directions. In this mechanism [reaction (27)] one of these primary NO\(^+\) ions would then subsequently dissociate, with an energy release one would expect to be significantly less than the initial Coulomb repulsion between the pair of NO\(^+\) ions. Thus, the result of this mechanism should be that the N atom and the O\(^+\) ion will be moving in the same direction and that the neutral species will have a comparable velocity to the O\(^+\) ion. Exactly this form of scattering is observed in the dissociative electron transfer reactions of molecular dications, where electron transfer analogously generates a pair of monocations which then separate before one of these monocations subsequently dissociates.\(^72\) However, the scattering we observe from the PSCO experiments (Fig. 5) clearly shows that the velocity of the N atom is markedly lower than, and is not strongly correlated with, the velocities of either of the charged products. Thus, the scattering we observe is not consistent with the initial charge separation of the collision complex [reaction (27)].

The alternative mechanism for the decay of the collision complex involves the initial loss of the neutral species (28). In this pathway one would expect the initial loss of the N atom from the [N\(_2\)O\(_2\)]\(^2+\) complex to occur with a relatively small energy release, giving the N atom a small velocity in the c.m. frame. If the [N\(_2\)O\(_2\)]\(^2+\) complex lives for a time comparable with its rotational period before the N atom is lost, one would expect the N atom to be symmetrically scattered in the c.m. frame; indeed we observe approximately isotropic scattering of the N atom. If the resulting NO\(_2^+\) dication then lives for a time at least comparable with its rotational period before it dissociates, the velocity of the N atom will not be correlated with either of the ionic products, again as we observe. The velocities of the ionic products, since they are formed following the decay of two long-lived species (the [N\(_2\)O\(_2\)]\(^2+\) complex and the NO\(_2^+\) ion), will be symmetrically scattered in the c.m. frame, as we observe. In addition, the charged products should have mutually anti-correlated velocities, as they are both formed from the decay of the NO\(_2^+\) ion; this mutual anticorrelation is clearly exhibited in Fig. 5. Thus, the scattering we observe is clearly consistent with reaction (28).

Further evidence in favor of the above reaction mechanism, involving initial neutral loss from the collision complex, is provided by consideration of the magnitudes of the velocities of the products. The modal velocity of the N fragment is 0.6 cm \(\mu\)s\(^{-1}\). Thus, by conservation of momentum,
the velocity of the NO$_2^+$ ion formed in the initial neutral-loss step should be 0.18 cm $\mu$s$^{-1}$. If the ‘neutral-loss’ mechanism (28) is operating, we would expect the NO$_2^+$ to be moving away from the center of mass at 0.18 cm $\mu$s$^{-1}$ in the opposite direction to the N atom. Satisfyingly, as shown in Fig. 6 the centers of the distributions of the charged species are indeed displaced from the velocity of the c.m. by close to 0.18 cm $\mu$s$^{-1}$. When viewed in this displaced frame, as illustrated in Fig. 6, the velocities of the ionic products are consistent with the two-body dissociation of a NO$_2^+$ ion; that is, the magnitudes of the momenta of the NO$^+$ and the O$^+$ ions are equal (between 12 and 13 amu cm $\mu$s$^{-1}$). Indeed, the velocities of the O$^+$ and NO$^+$ indicate an average kinetic-energy release upon dissociation of 7.8 eV, in excellent agreement with the energy release of 8 eV which has been reported for the dissociation of long-lived NO$_2^+$ ions.\textsuperscript{104,105}

In light of the above, we conclude that the PSCO data clearly indicate that this reactive channel proceeds, as indicated in Eq. (28), via initial neutral loss from a collision complex followed by charge separation of the resulting NO$_2^+$ dication.

### 3. Minima on the potential-energy surface

As described above, the PSCO spectra clearly show that the formation of NO$^+$+O$^+$+N proceeds via a collision complex [N$_2$O$_2$]$_2^+$. In order to support this observation we have investigated the stationary points on the [N$_2$O$_2$]$_2^+$ potential-energy surface (PES) using GAUSSIAN98.\textsuperscript{106} Reviewing the literature we find that quantum-chemical investigations\textsuperscript{107,108} predict N$_4$, an isoelectronic species to [N$_2$O$_2$]$_2^+$, to have a tetrahedral ground singlet state, a prediction now supported by matrix-isolation spectra.\textsuperscript{109} In addition, mass spectrometric experiments have recently\textsuperscript{110} detected the [N$_3$O]$_+$ ion, again isoelectronic to [N$_2$O$_2$]$_2^+$. The [N$_3$O]$_+$ ion has a lifetime of at least 500 ns. Quantum-chemical calculations on [N$_3$O]$_+$ reveal a so-called tetrahedral (C$_{4v}$) minimum on the singlet surface and a linear (C$_{2v}$, N–N–N–O) minimum on the triplet surface.\textsuperscript{110} The above calculations hint that [N$_2$O$_2$]$_2^+$ PES may well possess one or more bound minima. Considering the singlet surface, MP2 geometry optimizations, using a cc-pVTZ basis set, readily converge to a “tetrahedral” [N$_2$O$_2$]$_2^+$ (C$_{4v}$) geometry, analogous to that predicted for N$_4$ and N$_3$O$^+$. CCSD(T)/cc-pVTZ calculations at this calculated equilibrium geometry indicate that this singlet state lies 4.8 eV below the reactant asymptote of N$_2^+$($^1\Sigma^+_g$)+O$_2$($^3\Sigma^+_g$).

<table>
<thead>
<tr>
<th>Asymptote</th>
<th>Relative energy (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2^+$(X$^1\Sigma^+_g$)+O$_2$(X$^3\Sigma^+_g$)</td>
<td>0</td>
<td>25, 26, and 41</td>
</tr>
<tr>
<td>[N$_2$O$_2$]$_2^+$</td>
<td>4.8</td>
<td>This work</td>
</tr>
<tr>
<td>[N$_2$O$_2$]$_2^+$</td>
<td>8.2</td>
<td>This work</td>
</tr>
<tr>
<td>NO$_2^+$(X$^1\Sigma^+_g$)+N$(^1\Sigma^+_g$)</td>
<td>2.7</td>
<td>102, 104, and 105</td>
</tr>
<tr>
<td>N$_2$O$^+$(X$^3\Sigma^+_g$)+N$(^1\Sigma^+_g$)</td>
<td>3.9</td>
<td>102 and 115</td>
</tr>
<tr>
<td>NO$(^1\Sigma^+_g$)+NO$(^3\Sigma^+_g$)</td>
<td>22.6</td>
<td>102</td>
</tr>
<tr>
<td>NO$(^1\Sigma^+_g$)+N$(^1\Sigma^+_g$)+O$(^1\Sigma^+_g$)</td>
<td>10.8</td>
<td>102</td>
</tr>
<tr>
<td>NO$(^1\Sigma^+_g$)+O$(^1\Sigma^+_g$)+N$(^1\Sigma^+_g$)</td>
<td>11.7</td>
<td>102</td>
</tr>
</tbody>
</table>

Geometric parameters for this singlet minimum are listed in Table I. MP2/cc-pVTZ calculations on the triplet surface do not converge to a stable [N$_2$O$_2$]$_2^+$ geometry. Such behavior has also been noted on the analogous triplet surface of [N$_3$O]$_+$.\textsuperscript{110} However, again as in the case of [N$_3$O]$_+$, MP3/cc-pVTZ calculations converge to a “linear” (C$_{4v}$) minimum (Table II) with connectivity N–N–O–O. A [N$_2$O$_2$]$_2^+$ triplet minimum of essentially the same geometry is also located by a B3LYP/cc-pVTZ density-functional optimization. CCSD(T)/cc-pVTZ calculations locate this linear triplet minimum 8.2 eV below the N$_2^+$($^1\Sigma^+_g$)+O$_2$($^3\Sigma^+_g$) reactant asymptote. As in other dication-neutral reactions, these computational studies support the experimental conclusion that doubly-charged collision complexes are energetically accessible stationary points on the reactive potential-energy surfaces.\textsuperscript{73,80,82,86–88} Of course, our calculations are not by any means a complete investigation of the whole of the [N$_2$O$_2$]$_2^+$ potential-energy surface. However, they do show that the singlet and triplet [N$_2$O$_2$]$_2^+$ potential-energy surfaces each support at least one stable and accessible collision complex, supporting the deductions from the PSCO data.

The energies of the [N$_2$O$_2$]$_2^+$ complexes revealed by the calculations are listed in Table III together with the energies of the reactants and the various product asymptotes. As can be seen from Table III, all the intermediates on the reaction pathway deduced from the PSCO data [reaction (28)] can be reached exothermically from the reactant asymptote. As described above, our reactant ion beam of N$_2$O$_2$ was almost certainly N$_2$O$^+$ almost certainly contains dications in the X($^1\Sigma^+_g$) ground state and also dications in the c($^3\Sigma^+_g$) state. Hence, in principle, both the singlet and triplet complexes are accessible in spin-allowed processes from our ensemble of reactant molecules. Intuitively, given their respective connectivity, it is easier to envisage the singlet tetrahedral [N$_2$O$_2$]$_2^+$ complex dissociating directly to NO$_2^+$+N than the linear triplet complex with its N–N–O–O atomic arrangement. Indeed, we have searched computationally for a stable N–O–O$^+$+N structure for the dication intermediate, which intuitively could be more readily formed from the linear collision complex, but cannot locate a bound state.
with this connectivity. If the reaction conserves spin and proceeds via the singlet tetrahedral complex, this would imply the $c(\Sigma_u^{\pm})$ state of $N_2O^+$ as the reactant, although spin-flipping processes in dicationic dissociations are known.$^{111}$

In conclusion, the PSCO spectra clearly indicate that the formation of NO$^+$+O$^+$+N from collisions of $N_2^+$ with $O_2$ proceeds via the formation of a collision complex which then dissociates, via neutral loss, to leave an NO$_2^+$ dication. This dication then decays to NO$^+$+O$^+$. Quantum-chemical investigations support this idea of local minima, corresponding to collision complexes, existing on the [N$_2$O$_2$]$^{2+}$ potential-energy surface.

C. Formation of NO$^+$+N$^+$+O

To extract the dynamical data for this channel, we first remove the false coincidences from the ion pairs corresponding to the NO$^+$+N$^+$ events in our coincidence spectra as described above. Once these false coincidences have been removed, the scattering diagrams we extract from the NO$^+$ +N$^+$ events (for example, Fig. 7) look exceptionally similar to those presented for the formation of NO$^+$+O$^+$+N (Fig. 6). The scattering diagrams show again that the products NO$^+$, N$^+$, and O are isotropically scattered in the c.m. frame. Again, as described above, this symmetrical scattering is a strong indication that the products have been formed from the breakup of a collision complex [N$_2$O$_2$]$^{2+}$ which has had time to rotate before dissociation. Again, analogous to reaction (28), the data show that there is a strong anticorrelation between the velocities of the charged products, NO$^+$ and N$^+$, while the velocity of the neutral fragment, O in this case, is not correlated with either of the charged products.

Hence, analogous to the reaction forming NO$^+$, N$^+$, and O, the data strongly indicate that the mechanism for the formation of NO$^+$+N$^+$+O is

$$N_2^+ + O_2 \rightarrow [N_2O_2]^{2+} \rightarrow [N_2O]^{2+} + O \rightarrow NO^+ + N^+ + O.$$  

Again, the N$_2$O$^{2+}$ dication is well known to possess long-lived metastable states, which could readily survive for several hundred picoseconds before dissociating to NO$^+$+N$^+$. It is also well established$^{112,113}$ that the ground state of N$_2$O$^{2+}$ dissociates to N$^+_2$+O$^+$ as well as to NO$^+$ +N$^*$. However, N$^+_2$+O$^+$ ion pairs from this channel, if present, are swamped in our PSCO spectra by coincidences between the same ions formed by dissociative electron transfer (23).

IV. CONCLUSION

We have studied the potentially ionospherically significant reaction between N$_2^+$ with O$_2$ using position-sensitive coincidence spectroscopy. We observe both nondissociative and dissociative electron transfer reactions as well as two channels involving the formation of NO$^+$. The NO$^+$ product is formed together with either N$^+$ and O in one bond-forming channel or O$^+$ and N in the other bond-forming channel. Scattering diagrams have been derived from the results of the experiment and show that all the products are approximately isotropically scattered in the center-of-mass frame. In the internal frame it is clear that the velocities of the charged products are strongly anticorrelated, while the velocities of the neutral products are not correlated with the velocities of the charged products. The interpretation of this scattering data clearly indicates that both bond-forming reactions proceed via a collision complex [N$_2$O$_2$]$^{2+}$. This collision complex then decays by loss of a neutral atom to from a daughter dication (NO$_2^+$ or N$_2$O$^+$), which then decays by charge separation to yield the observed products.

ACKNOWLEDGMENTS

The authors acknowledge the financial support of the EPSRC, the EU (RTN1-2000-00025), and the Leverhulme Trust. One of the authors (C.R.) also acknowledges the support of the EPSRC via a DTA studentship. The authors are also grateful for helpful discussions on theoretical methodology with Nik Kaltsoyannis and Natalie Lambert. The authors also gratefully acknowledge Roland Thissen and Odile Duttuit both for making their results on the reactivity of N$_2^+$ available prior to publication and for valuable discussions.