Photodissociation dynamics of N2O at 130 nm: The N2(A 3Σ_u^+, B 3Π_g) + O(3P_{J=2,1,0}) channels

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Oxygen Rydberg time-of-flight spectroscopy was used to study the vacuum ultraviolet photodissociation dynamics of N2O near 130 nm. The O(3P_J) products were tagged by excitation to high-n Rydberg levels and subsequently field ionized at a detector. In agreement with previous work, we find that O(3P_J) formation following excitation to the repulsive N2O D(1Σ_u^+) state produces the first two electronically excited states of the N2 counterfragment, N2(A 3Σ_u^+ and N2(B 3Π_g). The O(3P_J) translational energy distribution reveals that the overall branching ratio between N2(A 3Σ_u^+) and N2(B 3Π_g) formation is approximately 1:1.0 for J=1 and 2, with slightly less N2(B 3Π_g) produced in coincidence with O(3P_J). The angular distributions were found to be independent of J and highly anisotropic, with β=1.5±0.2. © 2005 American Institute of Physics.

I. INTRODUCTION

Nitrous oxide (N2O) is introduced into the atmosphere primarily through microbial action in soils. Once it is transported into the stratosphere, it absorbs strongly in the IR and is a much more potent greenhouse gas than CO2 on a per molecule basis. It has been estimated that increasing the atmospheric N2O concentration from 300 to 600 ppb (parts per 10^9) would cause the surface temperature of the Earth to increase by 0.3 K.1 Nitrous oxide also plays a role in the balance of atmospheric ozone. Consequently, although N2O is only a trace component of the atmosphere, doubling its concentration would result in a 12.5% depletion of O3; the effect is even more pronounced in the presence of chlorofluorocarbons (CFC’s).2 The sources and sinks of atmospheric N2O are therefore of interest to atmospheric scientists. One N2O sink is photolysis in the vacuum ultraviolet (vuv). Excitation near 130 nm falls close to the peak of the strongly allowed transition from the ground X(1Σ_g^-) state to the repulsive D(1Σ_u^+) state.3 The N2O absorption cross section near 130 nm has been reported to be 7×10^{-17} cm^2 molec^{-1}.4,5 A number of N2+O photodissociation channels are energetically possible:

\[ \text{N}_2\text{O} \rightarrow \text{N}_2(X^{1}\Sigma_g^+) + O(3P). \quad (1) \]

\[ \text{N}_2(X^{1}\Sigma_g^+) + O(1D), \quad (2) \]

\[ \text{N}_2(X^{1}\Sigma_g^+) + O(1S), \quad (3) \]

\[ \text{N}_2(A^{3}\Sigma_u^+) + O(3P), \quad (4) \]

\[ \text{N}_2(B^{3}\Pi_g) + O(3P). \quad (5) \]

It has been demonstrated that channel (3) is dominant, with a quantum yield of 0.90±0.05.6,7 The remaining product yield is divided between channels (2), (4), and (5). Although channel (2) has been studied extensively around 193 nm,8-12 it is relatively minor at 130 nm.

Reactions (4) and (5) are often probed indirectly through their contribution to NO γ band fluorescence from the reaction N2^+NO→N2+NO13,14 In the present study, we focused on reactions (4) and (5), which produce ground-state O(3P) atoms along with N2 in electronically excited triplet states. Black et al. have estimated that N2(A^{3}\Sigma_u^+) formation, channel (4), may comprise 10% of the total product yield.6 However, no estimate is available for channel (5), which is difficult to probe directly because N2(B^{3}\Pi_g) is quenched to N2(A^{3}\Sigma_u^+) by N2O at a nearly gas kinetic rate,15 and has a lifetime of only a few microseconds in the absence of quenching gas.16

Although there is no question that reactions (4) and (5) play a role in the vuv photodissociation of N2O, little information is available concerning their dynamics. In 1971 Gilpin and Welge recorded time-of-flight spectra for products from N2O photodissociation over three vuv wavelength regions.17 While they were able to identify several metastable reaction products including O(1S), O(1D), N(1D), N(1P), and N2(A^{3}\Sigma_u^+), the energy resolution of the technique employed in their study was insufficient to provide insight into the products’ angular distribution or into the level of vibrational excitation of the molecular fragments. We sought to obtain higher-resolution time-of-flight (TOF) spectra of O(3P) over a range of laboratory angles in order to understand the N2O photodissociation process in greater detail.

The hydrogen Rydberg time-of-flight (HRTOF) method was originally developed by Schnieder et al.18 In HRTOF, the H or D atom products from a reaction or photodissociation process are photoexcited to high-n Rydberg levels immediately following their formation in the interaction region,
and allowed to fly as neutrals to a detector where they are field ionized and counted. Some advantages of the method over other methods are the elimination of space-charge effects, high tagging efficiency, high velocity resolution, and high sensitivity. 19 We have recently upgraded oxygen Rydberg time-of-flight (ORTOF) in our laboratory as a means of extending the advantages of Rydberg tagging to processes generating ground-state, $^3P_J$, oxygen atoms. Previously, we characterized this method through studies of the photodissociation of NO$_2$. We established that the lifetimes of oxygen atoms in intermediate Rydberg states ($n=19–40$) are sufficiently long to survive flights on the order of a few hundred microseconds without deliberate perturbation using external electric fields, which have been shown to extend Rydberg lifetimes by orders of magnitude. 20, 21

II. EXPERIMENT

The experiments were carried out using a fixed source, rotatable detector crossed molecular-beams apparatus. 19, 22 The apparatus was recently upgraded by installing an oil-free turbomolecular pump and a dry pump to evacuate the main chamber. The base pressure of the scattering chamber was 1 x 10$^{-6}$ Torr with the beam running. A molecular beam of N$_2$O was created by expanding 5-psi (gauge) near N$_2$O (airgas 99.0%) from a piezoelectrically actuated pulsed valve (30 Hz). The N$_2$O beam was generated in a separately pumped chamber and collimated by a skimmer (Precision Instruments Inc.) before crossing the lasers in the main chamber about 8 cm away from the nozzle orifice.

The vuv radiation used for photolysis and product tagging was generated by resonance-enhanced four-wave mixing ($\omega_{\text{vuv}}=2\omega_{\text{R}}-\omega_{\text{IR}}$) in a krypton gas cell. 23 The wavelength of the frequency-doubled dye laser ($\omega_R$) was fixed to the two-photon resonance transition to the 5$P[1/2]$ level of Kr near 212 nm, and that of the other dye laser ($\omega_{\text{IR}}$), operating near 580 nm, was varied to generate tunable vuv light near 130 nm. The exact wavelength of the photolysis light ranged from 130.27 nm for O$_3$ to 130.60 nm for O$_3$. The laser powers used in these experiments were as follows: $P(\omega_R)=0.5$ mJ; $P(\omega_{\text{IR}})=10$ mJ; and $P(\text{Rydberg})=4$ mJ. The $\omega_R$ and $\omega_{\text{IR}}$ laser beams were combined using a dielectric mirror and focused by an achromatic doublet ($f=30\text{ cm}$) into the gas cell. The generated vuv light then passed through a MgF$_2$ lens ($f=20\text{ cm}$) into the main chamber where it crossed the molecular beam 4.5 cm away from the detector entrance aperture. The vuv radiation was linearly polarized, and its wavelength was tuned to the $3S_1-3P_1$ transition of oxygen. Excitation of O($^3S_1$) atoms to $n=19$ was accomplished using the doubled output of a third dye laser operating near 305 nm (Rydberg Laser). All three dye lasers (Lambda Physik Scanmate 2) were pumped by a single Continuum Powerlite 9030 Nd:YAG (yttrium aluminum garnet) laser; their optical paths were carefully adjusted for spatial and temporal overlaps.

The “tagged” O atoms flew 34 cm through a field-free region, and were field ionized (2300 V/cm) and counted using a microchannel plate (Galileo). The ion signal was amplified by an EG&G VT120 preamplifier; TOF spectra were recorded by a Stanford Research Systems SR 430 multichannel scaler. A small dc voltage (+30 V) was applied to a thin-wire mesh (Precision Electroforming; 90% transmission) placed just in front of the multichannel plate (MCP) in the detector. This served to repel any ions that may have been produced in the main chamber from unintended processes such as multiphoton ionization.

The product angular distribution for the reaction was measured in two different ways. With the vuv polarization fixed along the molecular-beam axis, the MCP detector was rotated in the plane of the N$_2$O beam, and the TOF spectra were recorded over a range of laboratory angles. We also obtained the angular distribution by rotating the photolysis polarization angle with respect to the molecular beam, and monitoring the ORTOF signal at a fixed detector angle. This was done by inserting a double Fresnel rhomb into the path of the 580-nm tunable dye laser and rotating it from 0° to 200°. Since the polarization of $\omega_{\text{IR}}$ determines the polarization of the vuv, 24, 25 by rotating the 580-nm polarization (measured to be >99% polarized), we rotated the probe polarization as well. In order to ensure that rotating the $\omega_{\text{IR}}$ laser did not affect the laser alignment, O($^3P_2$) was generated by 212-nm photodissociation of SO$_2$ and probed by ORTOF. The signal level in that experiment was found to be independent of rhomb angle. Consequently, the strong variation in the ORTOF signal observed in the N$_2$O experiments as the rhomb was rotated must result from photofragment anisotropy.

III. RESULTS AND DISCUSSION

Figure 1 shows the TOF spectra (open circles) at four different laboratory angles for O($^3P_2$). The fast and slow peaks observed in the TOF spectra clearly correspond to the formation of N$_2$(A $^2S_2^+$) and N$_2$(B $^2II_2$), respectively. The solid line in each graph is the fit generated using a forward convolution program. The program took as input a translational energy distribution, $P(E)$, the photofragment anisotropy parameter, $\beta$, and experimental parameters including the beam spatial width, beam velocity spread, detector distance from the interaction region, and width of detector apertures. The program then convoluted over these parameters and observed the resulting distribution.

FIG. 1. Time-of-flight spectra at indicated laboratory angles relative to the plane containing the molecular beam and the vuv laser.
to generate simulated TOF spectra. The $P(E)$ and $\beta$ parameters were iteratively adjusted until the simulated spectra agreed with the experimental ones.

The translational energy resolution of the apparatus using ORTOF was checked in a separate series of experiments involving the 130.2-nm photodissociation of $O_2$. At this wavelength, both the $O(3P) + O(3D)$ and $2O(3P)$ channels are formed. The two narrow peaks in the TOF spectra were fitted using the forward convolution program using the known apparatus function, measured beam velocity distribution and the known thermodynamic values for the two photodissociation channels. The only adjustable parameters were the width of the kinetic-energy distributions, $P(E)$, for each channel, which were found to have full width at half maxima of approximately 0.2 kcal/mol.

A. Translational energy distribution

The available translational energy ($E_t$) is given by

$$E_t = E_{hv} - D_0(N_2-O) - E_{INT}(N_2) - E_{INT}(O).$$

As $\omega_f$ is varied in order to probe different $O(3P)$ states, both $E_{hv}$ and $E_{INT}(O)$ are changed. Consequently, the $P(E)$ used to fit $O(3P)$ is shifted from that used to fit $O(3P)$ by twice the difference in the $\omega_f$. This is illustrated in Fig. 2, in which all three $P(E)$’s are plotted together. Integrating the two product manifolds that comprise each $P(E)$, we obtain a branching ratio for $N_2(A^3\Sigma_u^+):N_2(B^3\Pi_g)$ formation of 1.0:1.0 for $O(3P)$, 1.0:1.0 for $O(3P)$, and 1.0:0.7 for $O(3P_0)$, indicating that some correlation between the internal energy of the two fragments exists. Specifically, $O(3P)$ products with the highest degree of internal energy ($J=0$) are more likely to be correlated with $N_2(A^3\Sigma_u^+)$. As illustrated in Fig. 2, the structure in the $P(E)$ at energies below 13 kcal/mol is clearly due to the formation of $N_2(B^3\Pi_g)$ in $v=0$ and 1. From the $P(E)$, the ratio between $v=0$ and $v=1$ formation is approximately 2:1. The total available energy is only slightly above the threshold for the formation of $N_2(B^3\Pi_g)$ in $v=2$. No evidence was seen for this channel.

We were not able to resolve individual vibrational levels of the $N_2(A^3\Sigma_u^+)$ counterfragment. Since some rotational excitation may be imparted to $N_2$ if $N_2O$ bends during disso-

FIG. 2. $O$ atom center-of-mass translational energy distributions for $O(3P_{J>2,1,0})$. The maximum energies for the formation of $N_2(A^3\Sigma_u^+,B^3\Pi_g)$ in different vibrational levels are indicated for $O(3P)$.

B. Angular distributions

Figure 3 shows the experimental laboratory angular distribution measured by rotating the detector, together with the simulated angular distribution for $O(3P)$. The anisotropy parameter, $\beta$, is defined with respect to the laboratory angular distribution, $N(\theta)$, where $\theta$ is the angle between the polarization of the photolysis laser and the direction of product recoil:

$$N(\theta) = 1 + \beta P_2(\cos \theta),$$

where

$$P_2(\cos \theta) = (3 \cos^2 \theta - 1)/2.$$  

The range of $\beta$ is $-1 \leq \beta \leq 2$. In order to obtain the solid lines shown in Figs. 1 and 3, $\beta = 1.5$ was input into the forward convolution program. We found that a $\beta$ value of 1.5±0.3 for all three spin-orbit levels of oxygen provided the best simulation of laboratory angular distribution data.

FIG. 3. The experimental laboratory angular distribution, $N(\theta)$, along with the simulation using $P(E)$ and $\beta$ was shown.

FIG. 4. Experimental signal levels for $O(3P)$ (circles) and $O(3P_0)$ (open squares) as a function of vuv polarization angle. $\theta = 0^\circ$ corresponds to vuv polarization along the molecular-beam axis. The fits were generated from Eq. (7) for a range of $\beta$ parameters. $\beta = 1.5$ (solid line) gives the best fit to the experimental data for both spin-orbit levels.

FIG. 4. Experimental signal levels for $O(3P_j)$ (circles) and $O(3P_0)$ (open squares) as a function of vuv polarization angle. $\theta = 0^\circ$ corresponds to vuv polarization along the molecular-beam axis. The fits were generated from Eq. (7) for a range of $\beta$ parameters. $\beta = 1.5$ (solid line) gives the best fit to the experimental data for both spin-orbit levels.
A more sensitive measurement of the photofragment angular distribution involved a separate series of experiments, in which TOF spectra were recorded at a constant laboratory detector angle with the vuv polarization rotated to various angles. Since the N2\(A^3\Sigma_u^+\) and N2\(B^1\Pi_g\) contributions are well separated from one another, we first determined the integrated laser polarization angular distributions for each product channel separately. We found that they were the same for both channels to within the uncertainty of the measurement, so we integrated the whole TOF range to determine an overall angular distribution for the O\(^3P_{\ell}\) product channel. Figure 4 shows the signal level for O\(^3P_{2}\) and O\(^3P_{0}\) as a function of vuv polarization angle, with the detector held at 20° with respect to the molecular-beam axis. These points were fitted to the expression in Eq. (7), where a phase offset was added to \(\theta\) to convert the fits from the center-of-mass (CM) frame to the laboratory frame. We then varied \(\beta\) until the fit matched the experimental angular distribution. The figure shows the N (\(\theta\)) distributions for \(\beta=1.7, 1.5, 1.3\). The data for both O\(^3P_{2}\) and O\(^3P_{0}\) are best fitted with \(\beta=1.5\), confirming the value generated by the forward convolution program in the rotating detector experiments. These fits are quite sensitive to \(\beta\), allowing us to narrow our confidence interval to ±0.2. We observed no correlation between \(\beta\) and oxygen spin-orbit level, \(J\). In the accompanying paper, Lambert et al. report small differences in the angular distributions as a function of N2 and O\(^3P_{2,1,0}\) internal energy. The product angular distributions for N2O photodissociation producing O\(^3P_{\ell}\) was found to be independent of power for each of the three laser beams, indicating that saturation effects were not operative under our experimental conditions. Because photolysis and Rydberg tagging are accomplished using the same vuv pulse at 130 nm, it was not possible in our experiment to vary the relative polarization of the pump and probe lasers. Therefore, a small degree of alignment of O\(^3P_{\ell}\) or O\(^3P_{2}\) would probably be undetectable in our experiment.

<table>
<thead>
<tr>
<th>(%O^3P_{\ell})</th>
<th>(3P_{2})</th>
<th>(3P_{1})</th>
<th>(3P_{0})</th>
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<tr>
<td>(N_2(A^3\Sigma_u^+):N_2(B^1\Pi_g))</td>
<td>50±5</td>
<td>35±5</td>
<td>15±5</td>
</tr>
<tr>
<td>(1:1)</td>
<td>(±0.1)</td>
<td>(±0.1)</td>
<td>(±0.1)</td>
</tr>
<tr>
<td>(\beta)</td>
<td>1.5±0.2</td>
<td>1.5±0.2</td>
<td>1.5±0.2</td>
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The potential-energy surfaces for N2O excited states in the range of 0–13 eV have been calculated.27,28 The continuum from 120 to 140 nm is known to correspond to excitation to the repulsive \(D^1\Sigma^+\) state, with 130.2 being very close to the peak of the absorption band. The \(D^1\Sigma^+\) state correlates adiabatically with N2\(X^1\Sigma_g^+\) + O\(^1S\). However, as noted by Hopper, this adiabatic dissociation involves a two-electron transition, \(2\pi^4 + 9\sigma^2 = 28\). The N2\(A^3\Sigma_u^+\) + O\(^3P\) and N2\(B^1\Pi_g\) + O\(^3P\) product states correlate to several different excited N2O levels in both a linear C\(\Sigma_u\) and bent C\(\Sigma_u\) geometry.28 In a C\(\Sigma_u\) configuration, N2\(A^3\Sigma_u^+\) may be produced either by direct dissociation from a repulsive \(1\Pi\) state, or from a \(1\Sigma^+\) state. On the other hand, N2\(B^1\Pi_g\) + O\(^3P\) correlates in C\(\Sigma_u\) geometry to N2O states of \(3\Delta\) or \(3\Sigma\) symmetry. Since interystem crossing of N2O\(O^3D(3\Sigma^+)\) to triplet excited levels should not play an important role in this fast dissociation process, the mechanism likely involves interactions between N2O bent (\(C\)) states. As excited N2O bends, the initially prepared \(D(3\Sigma^+)\) state transforms into states of \(A^6\) symmetry. As noted long ago by Chutjian and Sega1,27 a higher-lying-linear state of \(1\Pi\) symmetry, which correlates to N2\(A^3\Sigma_u^+\) + O\(^1P\), splits upon bending into the states of both \(A^6\) and \(A^8\) symmetries. Indeed, the quenching of N2\(A^3\Sigma_u^+\) + O\(^3P\) is known to be rather efficient, and produces N2\(X^1\Sigma_g^+\) + O\(^1S\), likely via bent states of N2O having \(A^6\) symmetry.29 Since dissociation from the initially prepared repulsive linear \(D(3\Sigma^+)\) state is expected to be fast, our observation that \(\beta\) is slightly reduced from the limiting value of 2.0 is likely due to some bending as N2O dissociates.

This work was part of a cooperative effort between our group and the Houston group here at Cornell, to fully characterize the dynamics of N2O dissociation at 130 nm. They have recently completed an extensive study of this system using photofragment ion imaging,30 and their conclusions for the N2\(A^3\Sigma_u^+\), B\(1\Pi_g\) + O\(^3P_{2,1,0}\) channels are in qualitative agreement with ours. They have also obtained angular and product energy distributions for channels (2) and (3) as well as for certain NO+N product channels.

C. Dissociation mechanism

In Table I, we summarize our measurements for each spin-orbit state of oxygen, including the overall \(J\) level branching ratio, the N2\(A^3\Sigma_u^+\): N2\(B^1\Pi_g\) branching ratio, and \(\beta\). In determining the spin-orbit branching ratio, we assumed that the absorption cross section of N2O between 130.26 and 130.60 nm is constant and that all \(J\)'s have the same oscillator strength for the \(3S_1\rightarrow3P_J\) transition. Within the error bars, our measured spin-orbit branching ratio of 5:3.5:1.5 is consistent with the 5:3:1 branching ratio expected for a statistical process.

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