Anisotropy and Energy Disposal in the 193-nm N_2O Photodissociation Measured by VUV Laser-Induced Fluorescence of $O(^1D)$

L. L. Springsteen, S. Satyapal, Y. Matsumi,[†] L. M. Dobeck, and P. L. Houston*

Department of Chemistry, Cornell University, Ithaca, New York 14853-1301

Received: March 3, 1993

Laser-induced fluorescence near 115 nm has been used to measure the Doppler profile of the $O(^1D)$ product of 193-nm N_2O photolysis. The anisotropy of product recoil vectors is characterized by the parameter $\beta = 0.50 \pm 0.05$. The measured velocity distribution can be used to calculate a distribution of recoil energies that is in reasonable agreement with that reported recently by Felder, Haas, and Huber; an average of 27.3 kcal/mol is deposited into translation, leaving ≈37 kcal/mol for the internal excitation of the N_2 fragment.

1. Introduction

The photodissociation of N_2O in the region near 193 nm is known to produce $O(^1D)$ almost exclusively,[1-3] although $O(^1S)$ is energetically allowed and $O(^3P)$ is energetically favorable but spin forbidden. Nitrogen in its electronic ground state ($^1\Sigma_g^+$) is also produced:

$$N_2O + h\nu \rightarrow O(^1D) + N_2(^1\Sigma_g^+,v,j) \qquad (1)$$

N_2O is important in the chemistry of the stratosphere, where it is involved both in the production of $O(^1D)$ by direct photolysis and in its loss through reactions producing N_2 and O_2 or 2NO.[4,5] Consequently, both the natural and man-made sources of N_2O have received considerable recent attention.[6,7] In the troposphere however, photolysis of N_2O has been shown to be of negligible importance.[8]

The photodissociation dynamics of N_2O have come under more recent investigation because of the elegant experiments by Simons and co-workers in which the photolysis of N_2O with a polarized laser is used to create velocity-aligned, superthermal $O(^1D)$ atoms in order to study the stereochemistry of the $O(^1D) + N_2O \rightarrow NO + NO$ reaction.[9-11] By measuring the Doppler profile of NO(v'=16,17) produced coincidentally with NO(v'=0), these investigators were able to show that the reaction leading to this specific channel proceeds by direct stripping dynamics through collisions dominated by a collinear geometry. A necessary input for their interpretation is the anisotropy of $O(^1D)$ fragment recoil in the 193-nm photodissociation of N_2O. The anisotropy is determined by measuring the distribution of the angle θ between the photofragment velocity and the direction of polarization of the photolysis laser and then expressing the distribution in terms of the parameter β

$$I(\theta) = [1 + \beta P_2(\cos\theta)]/4\pi \qquad (2)$$

where $P_2(\cos\theta)$ is the second Legendre polynomial.

The anisotropy parameter, β, and average translational energy of $O(^1D)$ from the photodissociation of N_2O have been studied by Felder, Haas, and Huber[12] at 193 nm using the molecular beam/time-of-flight mass spectrometry (MS-TOF) technique and by Shafer *et al.*[13] at 205.47 nm using sub-Doppler resolution of the profile of the resonance-enhanced multiphoton ionization transition in a one-laser experiment. These two studies gave widely differing results for both β and the fraction of available energy deposited in product translation. Felder, Haas, and Huber found that $\beta = 0.48 \pm 0.02$ and that an average of 26.8 kcal/mol (41.5% of the available energy, E_{av}) was deposited into product recoil. In contrast, Shafer *et al.* found that $\beta \approx 2.0$ and that an average of 53.3 kcal/mol (84% of E_{av}) went into translational degrees of freedom. The former result was used for the interpretation of the velocity-aligned $O(^1D) + N_2O$ results.

The purpose of the work reported here was to measure β and the energy disposal for the 193-nm photolysis of N_2O using the newly developed method of tunable vacuum ultraviolet (VUV) laser-induced fluorescence (LIF) of $O(^1D)$ near 115 nm. By determining the Doppler profile measured using light propagating either parallel or perpendicular to the electric vector of the photolysis laser, we have determined that $\beta = 0.50 \pm 0.05$ and that an average of 27.3 kcal/mol (42.3% of E_{av}) is deposited into product recoil.

2. Experimental Section

The apparatus has been reported in detail elsewhere[14] and will be described here only briefly. Neat N_2O was expanded through a pulsed molecular beam valve (Precision Instruments) with a 0.3-mm orifice. The 193-nm photolysis beam of approximately 100 mJ/pulse from an ArF laser (Lambda Physik LPX-100) was focused by an 18 in. focal length lens, passed through a polarizer consisting of stacked quartz plates with a calculated degree of polarization of 0.91, intersected with the molecular jet at 90°, and passed into a dye cell where the fluorescence was monitored by a photodiode. The photodiode signal was fed into a boxcar averager (Stanford Research Systems, SR250) and input as one of three channels to a laboratory computer (IBM, PS/2).

$O(^1D)$ laser-induced fluorescence (LIF) signals were recorded using the $2p^4 \rightarrow 3s^1$ transition at 115.215 nm. The vacuum ultraviolet (VUV) probe light was obtained by four-wave mixing in Hg vapor using an intermediate resonance with the 6s6d $^1D_2$ state of Hg. The output of a 308-nm XeCl excimer (Lambda Physik LPX205) was split (65%/35%) and used to pump two dye lasers (Lambda Physik 2002E). One dye laser operating at 560.6 nm (Coumarin 540A) was frequency doubled in KDP, while the second operated on the fundamental at 647.5 nm (DCM). The approximately 0.7 mJ/pulse of UV and 8 mJ/pulse of red were joined in a dichroic beam splitter (CVI, Y41025-45) and focused by a 250 mm focal length achromatic lens (Optics for Research, LAU-25-250) into a heat pipe containing 5 Torr of Ne and the equilibrium vapor pressure of Hg at 135-140 °C. The incident beams and the VUV exited the cell through a LiF window, propagated through the vacuum chamber in a direction mutually orthogonal to the molecular and photolysis beams, and passed through a monochromator (λMinuteman, 302-VM) to a solar-blind photomultiplier tube (PMT) (EMR 541G-08-17). The output of the PMT was fed through a boxcar averager and input as one channel of the laboratory computer for use as a power monitor. Laser-induced fluorescence was collected by a solar-

---

[†] Permanent address: Institute for Electrical Science and Graduate School for Environmental Earth Science, Hokkaido University, Sapporo 060, Japan.

0022-3654/93/2097-7239$04.00/0 © 1993 American Chemical Society

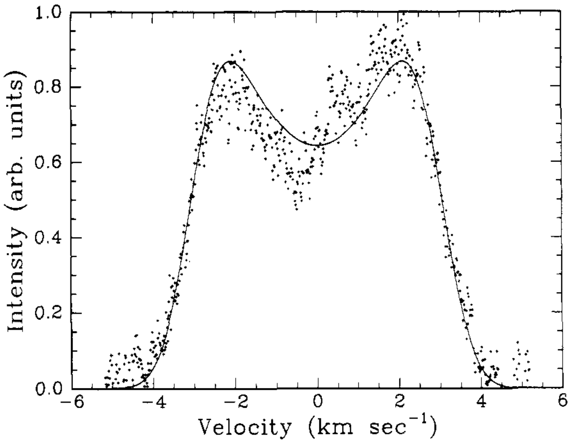

Figure 1. Doppler profile of O(^{1}D) produced in the 193-nm photodissociation of N_2O probed with 115-nm light propagating parallel to the electric vector of the photolysis light. The solid line is the profile expected for $\beta = 0.50$ and the translational energy distribution after convolution of the probe laser line width.

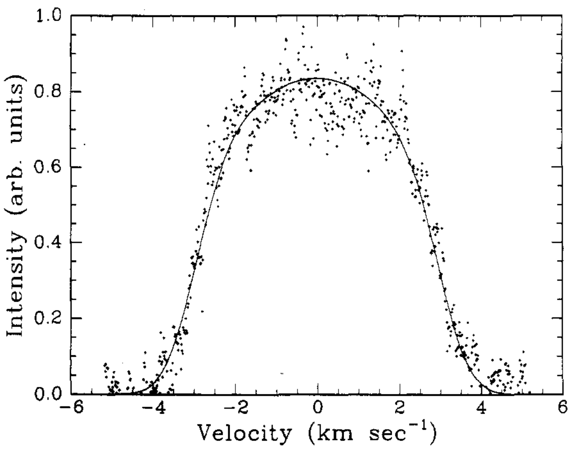

Figure 2. Doppler profile of O(^{1}D) produced in the 193-nm photodissociation of N_2O probed with 115-nm light propagating perpendicular to the electric vector of the photolysis light. The solid line is the profile expected for $\beta = 0.50$ and the translational energy distribution after convolution of the probe laser line width.

blind PMT (EMR 542G-08) in the plane of the lasers and at 45° to each of them. The fluorescence signal was sent through a boxcar averager to the third channel of the computer. The delay times between the photolysis and probe lasers were varied from roughly 200 to 400 ns to confirm that the translational energy distribution was not affected by collision or by the possible flight of products out of the probe region.

Doppler scans of the O(^{1}D) line were made after installing etalons in both of the dye lasers. The line width in the VUV was approximately 0.3 cm^{-1}.

3. Results

The Doppler profiles obtained for the cases of the probe direction parallel and perpendicular to the electric field vector of the photolysis laser are shown as the points in Figures 1 and 2 and are typical of what would be expected for a slightly positive value of the anisotropy parameter.[21] As a starting point for the fitting procedure, the effective anisotropy parameter β_{eff} was extracted from the Doppler profiles using the method of Bersohn and coworkers[15]

$$\beta_{\text{eff}} = \frac{5(\langle v_\parallel^2\rangle - \langle v_\perp^2\rangle)}{\langle v_\parallel^2\rangle + 2\langle v_\perp^2\rangle} \qquad (3)$$

where $\langle v_\parallel^2\rangle$ and $\langle v_\perp^2\rangle$ are the second moments of the two profiles. The average squared velocity can be determined from the profiles in velocity space, $\langle v^2\rangle = \langle v_\parallel^2\rangle + 2\langle v_\perp^2\rangle$, and can then be used to calculate the average translational energy release of the photodissociation. Our results give $\beta = 0.45$ and $\langle E_{\text{trans}}\rangle = 34.6$ kcal/mol. However, these values for β and $\langle E_{\text{trans}}\rangle$ do not take into account the effect of the laser line width.

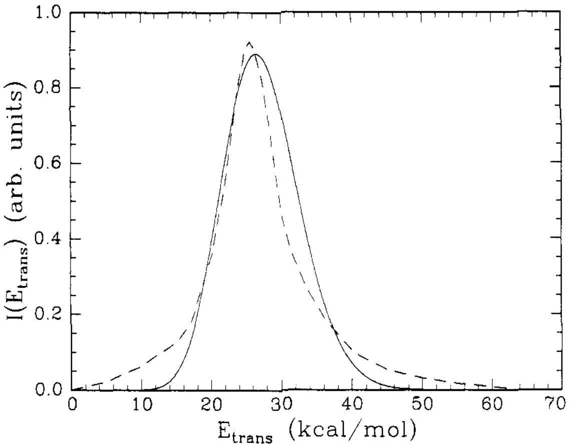

Figure 3. (Solid line) Translational energy distribution used to model the Doppler profiles of Figures 1 and 2. (Dashed line) Translational energy distribution measured by Felder *et al.*[12]

TABLE I: Anisotropy Parameters and Average Translational Energy for 193-nm N_2O Photodissociation

β	E_{trans} (kcal/mol)	ref
0.48 ± 0.02	26.8	12
2.0	53.3	13
	28.4	16
0.50 ± 0.05	27.3	this work

Starting from the parameters given above, we simulated Doppler profiles using a chosen anisotropy parameter and a Gaussian distribution of energy with two adjustable parameters, the average energy of the distribution and the width of the distribution. The overall width of the Doppler profiles is quite sensitive to the average energy disposed into translation, while the detailed shape of the profiles, particularly the slope of the sides in the case when the probe laser propagation direction is parallel to the electric vector of the photolysis light, depends sensitively on the width of the energy distribution. These simulated profiles were then convoluted with the laser line width of 0.3 cm^{-1} and compared to the data. Figures 1 and 2 show the best fits as solid lines. The anisotropy parameter which best fits the experimental Doppler profile is 0.50 ± 0.05, while the best energy distribution is shown as the solid line in Figure 3, which also presents the energy distribution determined by Felder *et al.*[12] as a dashed line. The average energy for the distribution fitting our data is 27.3 kcal/mol. Error limits for the anisotropy parameter were obtained by fixing the energy distribution and varying β until the fit became unacceptable.

4. Discussion

Table I summarizes the results of this work and compares them with two previous studies and with a recent communication. It is clear that our results are in close agreement with those of Felder *et al.* The two values for the anisotropy parameter are equal to within experimental error, and our value for the average energy disposed into translation is close to that of Felder *et al.* Our translational energy distribution, shown in Figure 3, has a slightly higher average energy and is somewhat broader than that measured by Felder *et al.*, but the agreement is still very good. As a test to see whether the distribution of Felder *et al.* is really outside the error limits of our Doppler measurement, we transformed their energy distribution to a Doppler profile, convoluted it with the probe laser line, and compared the result to our experimental result for the parallel configuration. The distribution of Felder *et al.* fit our data to within the experimental error.

We have recently learned of a study by Hanisco and Kummel (accompanying article) in which the internal energy of the N_2 molecule has been measured. Our results for the translational energy are in good agreement with those of this new study.[16]

Our results are not in good agreement with those of Shafer *et al.*[13] Values of $\beta = 2.0$ and $\langle E_{\text{trans}} \rangle = 53.3$ kcal/mol are outside our error limits. It is possible that the values change dramatically between 193 and 205 nm. However, we also note that it is much more difficult to determine these parameters from a one-laser experiment where one cannot vary the polarization direction of the photolysis light with respect to the propagation direction of the probe.

Absorption in the region near 193 nm[17] is part of a weak continuum peaking near 182 nm. Selwin and Johnston[18] have investigated the temperature dependence of the absorption and found both a structured component corresponding to a magnetic dipole allowed $\tilde{A}^1\Sigma^- \leftarrow \tilde{X}^1\Sigma^+$ transition and a continuum component corresponding to the forbidden $\tilde{B}^1\Delta \leftarrow \tilde{X}^1\Sigma^+$ transition. Their work along with the theoretical work of Hopper[19] on the electronic structure of N_2O provides insight into the absorption. In C_s symmetry the structured transition $1^1A''(\tilde{A}^1\Sigma^-) \leftarrow 1^1A'(\tilde{X}^1\Sigma^+)$ becomes allowed with the transition moment perpendicular to the plane of the molecule.[20] The $^1\Delta$ state splits into two components in C_s symmetry and both the $2^1A'(\tilde{B}^1\Delta) \leftarrow 1^1A'(\tilde{X}^1\Sigma^+)$ transition, with the transition moment in the plane of the molecule, and the $2^1A''(\tilde{B}^1\Delta) \leftarrow 1^1A'(\tilde{X}^1\Sigma^+)$ transition are allowed. However, as can be seen in Figure 6 of ref 13, the $2^1A''$ state is of much higher energy and need not be considered for our excitation energy of 6.4 eV. Selwin and Johnston found that the structured transition was due to molecules with one quanta of the ν_2 bending vibration while the continuum absorption was due primarily to molecules in the ground vibrational state. For molecular beam experiments, in which the bending mode of the parent molecule is not appreciably populated, the transition is most likely $2^1A'(\tilde{B}^1\Delta) \leftarrow 1^1A'(\tilde{X}^1\Sigma^+)$.

It is clear from both the present results and those of Felder *et al.* that a substantial fraction (about 58%) of the $\approx$22 500-cm^{-1} available energy must go into the N_2 internal degrees of freedom. Felder *et al.* argue from the resolution of their instrument and the lack of vibrational structure in their measured distribution that much of the energy must go into rotation. The signal-to-noise ratio in our experiment does not permit any conclusion concerning the division between vibrational and rotational excitation. However, previous studies of OCS photodissociation on the transition implicated in the 193-nm photolysis of N_2O have shown that a substantial fraction of the available energy is deposited into CO rotation.[22,23] Thus, it would not be surprising if the N_2 fragment of N_2O photodissociation were also rotationally excited. Indeed, the accompanying paper by Hanisco and Kummel shows that nearly all of the internal N_2 energy is in the form of rotation.[16] This observation is also consistent with the reduction in the measured anisotropy parameter β from its limiting value of 2.0. Dissociation from a bent upper level would not only reduce the value of β but also produce rotationally excited N_2, as observed by Hanisco and Kummel.

5. Conclusions

The 193-nm photodissociation of N_2O has been investigated by measuring the Doppler profile of the $O(^1D)$ product at 115 nm. The dissociation produces an anisotropic distribution of fragment recoil velocities characterized by an anisotropy parameter of 0.50 ± 0.05. Roughly 27.3 kcal/mol or 42.3% of the total available energy appears in translation, while the remaining energy is deposited into N_2 internal degrees of freedom. Our measurements are in excellent agreement with those of Felder *et al.* at 193 nm but disagree with measurements made by Shafer *et al.* at 205 nm.

Acknowledgment. We are grateful to Professor John Hepburn and Dr. Andreas Manck for advice on the generation of 115-nm light. The 115-nm generation and LIF detection system was assembled and tested by S. Satyapal, R. L. Miller, and P. Neill and has been used to detect $O(^1D)$ from ozone photodissociation in work to be described in a manuscript in preparation. This work was supported by the Air Force Office of Scientific Research under Grant F49620-92-0080. Y.M. thanks the Monbusho International Scientific Research Program.

References and Notes

(1) Preston, K. F.; Barr, R. F. *J. Chem. Phys.* **1971**, *54*, 3347.

(2) Jackson, W. M.; Okabe, H. *Adv. Photochem.* **1986**, *13*, 1.

(3) Zhu, Y. F.; Gordon, R. J. *J. Chem. Phys.* **1990**, *92*, 2897.

(4) Marić, D.; Hans, W.; Schurath, U. *J. Atmos. Chem.* **1989**, *8*, 19.

(5) Bates, D. R.; Hayes, P. B. *Plant. Space Sci.* **1967**, *15*, 189.

(6) Lui, S. C.; Cicerone, R. J.; Donahue, T. M.; Chameides, W. L. *Tellus* **1977**, *29*, 251.

(7) Schmidt, J.; Seiler, W.; Conrad, R. *J. Atmos. Chem.* **1988**, *6*, 95 and references therein.

(8) Stedman, D. H.; Cicerone, R. J.; Chameides, W. L.; Harvey, R. B. *J. Geophys. Res.* **1976**, *81*, 2003.

(9) Green, F.; Hancock, G.; Orr-Ewing, A. J.; Brouard, M.; Duxon, S. P.; Enriquez, P. A.; Sayos, R.; Simons, J. P. *Chem. Phys. Lett.* **1991**, *182*, 568.

(10) Brouard, M.; Duxon, S. P.; Enriquez, P. A.; Sayos, R.; Simons, J. P. *J. Phys. Chem.* **1991**, *95*, 8169.

(11) Brouard, M.; Duxon, S. P.; Enriquez, P. A.; Simons, J. P. *J. Chem. Phys.* **1992**, *97*, 7414.

(12) Felder, P.; Haas, B.-M.; Huber, J. R. *Chem. Phys. Lett.* **1991**, *186*, 177.

(13) Shafer, N.; Tonokura, K.; Matsumi, Y.; Tasaki, S.; Kawasaki, M. *J. Chem. Phys.* **1991**, *95*, 6218.

(14) Strauss, C. E. M.; McBane, G. C.; Houston, P. L.; Burak, I.; Hepburn, J. W. *J. Chem. Phys.* **1989**, *90*, 5364.

(15) Kim, H. L.; Satyapal, S.; Brewer, P.; Bersohn, R. *J. Chem. Phys.* **1989**, *91*, 1047.

(16) Hanisco, T. F.; Kummel, A. C. *J. Phys. Chem.*, following paper in this issue.

(17) Zeilkoff, M.; Wantanabe, K.; Inn, E. C. Y. *J. Chem. Phys.* **1953**, *21*, 1643.

(18) Selwin, G. S.; Johnston, H. S. *J. Chem. Phys.* **1981**, *74*, 3791.

(19) Hopper, D. G. *J. Chem. Phys.* **1984**, *80*, 4290.

(20) Herzberg, G. *Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules*; Van Nostrand Reinhold: New York, 1966; p 132.

(21) Houston, P. L. *J. Phys. Chem.* **1987**, *91*, 5388 and references therein.

(22) Sivakumar, N.; Burak, I.; Cheung, W.-Y.; Houston, P. L.; Hepburn, J. W. *J. Phys. Chem.* **1985**, *89*, 3609.

(23) Sivakumar, N.; Hall, G. E.; Houston, P. L.; Burak, I.; Hepburn, J. W. *J. Chem. Phys.* **1988**, *88*, 3692.