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The stereochemistry of the $O(^{1}D) + N_{2}O \rightarrow NO + NO$ reaction *via* velocityaligned photofragment dynamics

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Velocity-aligned, superthermal O(¹D) atoms generated via the photodissociation of N₂O have been employed to investigate the stereodynamics of the title reaction. The power of this experimental technique, when coupled with Doppler-resolved, polarized laser-induced fluorescence probing of the reaction products, is demonstrated by reference to the specific reaction channel leading to NO(v'=0) + NO(v'=16,17), which is shown to proceed via direct stripping dynamics. Furthermore, the observed product-state selective linear and angular momenta disposals imply that the reaction is stereodynamically constrained to occur via collinear collision geometries.

I. INTRODUCTION

This paper describes an experimental investigation of the stereodynamics of the bimolecular reaction

 $O(^{1}D) + N_{2}O \rightarrow NO + NO, \quad \Delta H_{0}^{\Theta} = -341 \text{ kJ mol}^{-1}.$

The strategy employed, which may be termed "velocityaligned photofragment dynamics," is a new polarized laserpump-Doppler-resolved laser-probe technique which allows determination of both linear and angular momenta disposals in photon-initiated bimolecular reactions at the product-state selective level.¹⁻⁵ These studies, which build on the existing knowledge of photofragment scalar and vector properties, employ molecular photodissociation to generate a well characterized, anisotropic distribution of the reagent relative velocity vector, k. Under singlecollision conditions, it is this reagent translational anisotropy which provides a reference vector by which to measure the angular distributions and rotational alignments of the reaction products. One of the aims of this article is to emphasize that the information provided by these experiments is product rovibrational state selective. This selectivity is essential for the study of the title reaction since the reaction exothermicity is channeled near exclusively into the internal degrees of freedom of the NO products and is sufficient to populate ~ 1000 NO rovibrational states. In addition, the data are considerably easier to obtain than they are from conventional crossed-beam experiments, where the number densities can be orders of magnitude lower than in the bulk experiments to be described below. although the angular resolution of the latter is somewhat poorer than in beam studies, due to the inherent thermal motions of the photolysis precursor and target reagent molecules.

Following the Introduction, Experiment and Data Analysis sections, the paper describes the overall energy disposals in the $O(^{1}D) + N_{2}O \rightarrow NO + NO$ reaction at an average collision energy of (50-60) kJ mol⁻¹ and summarizes our previous findings for this process.^{4,5} The bulk of the Results and Discussion sections then focus on the detailed energy and moment disposals in the vibrational channel:

 $O(^{1}D) + N_{2}O \rightarrow NO(v'=0) + NO(v'=16,17).$

We demonstrate that this superthermal reaction proceeds via a stripping-type mechanism.

II. EXPERIMENT

The apparatus has been described in detail previously.⁵ Briefly, the laser system comprised an excimer photolysis laser ($\lambda \sim 193$ nm, < 40 mJ pulse⁻¹) and an electronically delayed, polarized excimer pumped dye laser ($\lambda \sim 400-500$ nm) with an etalon narrowed bandwidth of 0.04 cm⁻¹. The NO products born in vibrational levels $10 \le v' \le 18$ were probed on the $B(^{2}\Pi) \leftarrow X(^{2}\Pi) \beta$ band system⁶ and the laser-induced fluorescence was observed through a broadband (225-500 nm) filter. Photomultiplier signals were averaged on a boxcar integrator and transferred to a microcomputer for normalization to the probe laser power and signal averaging. Due to the poor transmittance of the polarizer at 193 nm, Doppler-resolved profiles were recorded primarily without polarization of the photolysis beam in geometries with propagation vectors $\mathbf{k}_{p} || \mathbf{k}_{q}$ and $\mathbf{k}_n \perp \mathbf{k}_a$. The polarizer, however, was employed to check that the excimer beam was genuinely unpolarized. Measurement of product rotational alignments for the highly rovibrationally excited NO fragments has not been attempted because the $Q\uparrow$ branch lines of the ${}^{2}\Pi - {}^{2}\Pi$ transition employed were too weak to be observed under single-collision conditions (see Sec. IV).

The typical delay time (τ) between photolysis and probe laser pulses was between 100 and 200 ns and the pressure p of flowing N₂O was maintained at 150–250 mTorr. The flow rate of the N₂O entering the cell was estimated to be approximately ten times greater than that required to evacuate the viewing region between successive laser pulses. Product rovibrational and velocity distributions appeared to be insensitive to variations within these $p \times \tau$ conditions, although complete rotational and translational relaxation was observed at higher pressures and delays of ~2 μ s. As stated previously,⁵ no NO signals could be detected at delay times of less than 50 ns and pressures of < 30 mTorr, and the rates of growth at longer delays

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were consistent with the known room-temperature rate constant for the $O(^{1}D) + N_{2}O$ reaction. (Thermal rate constant data for this reaction can be found in the review given in Ref. 7.) These observations demonstrate that all the NO signals arose from photoinitiated reaction rather than from direct N₂O photolysis, and that there was no residue of relaxed NO remaining in the probed region from previous laser shots.

III. DOPPLER PROFILE ANALYSIS

The analysis and interpretation of Doppler-resolved profiles of the products generated via linearly polarized photon-initiated bimolecular reactions is involved⁸ and only the general principles will be outlined here. As with direct photodissociation, each Doppler profile is sensitive to nine (velocity dependent) bipolar moments, $\beta_0^k(k_1,k_2)$, in 1+1 laser-induced fluorescence (LIF) studies,^{9,10} which describe the correlated angular distribution of the vectors \mathbf{k} , \mathbf{v}' , and \mathbf{j}' (the reagent relative velocity and product laboratory-frame velocity and rotational angular momentum, respectively). As pointed out by Dixon,⁹ the profiles are usually dominated by only five of these moments and, in the limit of single product velocity, v', the Doppler lineshape function may be written as

$$I(v'_k) = \frac{C}{2v'} [g_0 + g_2 P_2(v'_k/v')], \qquad (1)$$

where

$$g_0 = b_0 \beta_0^0(00) + b_1 \beta_0^2(02),$$

$$g_2 = b_2 \beta_0^2(20) + b_3 \beta_0^0(22) + b_4 \beta_0^2(22),$$
(2)

and v'_k is the component of the velocity along the probe laser propagation vector. Equations (1) and (2) apply equally to direct photodissociation and to photon-initiated bimolecular reactions, except that the coefficients b_0-b_4 take slightly different values. In particular, the multipliers b_1 , b_2 , and b_4 for reactive studies must be multiplied by $\beta_{\rm eff}/2$ compared with those employed in photodissociation studies where β_{eff} represents the anisotropy of the reagent relative velocity, k [defined in Eq. (10), Sec. IV below].^{4,5} This factor ensures that the vector correlations are referenced to $\hat{\mathbf{k}}$ rather than $\hat{\mu}$, as they are in photodissociation studies. The multipliers employed in the present study, in which no polarizer was used in the photolysis beam, are presented in Table I.

Equations (1) and (2) apply to photon-initiated bimolecular reactions under a rather stringent limiting case, where the reagent relative velocity is of fixed magnitude, and the magnitude of the product relative velocity, k', greatly exceeds that of the center of mass, v_{cm} . Under these circumstances, the bipolar moments have the following interpretation in the high-j limit^{1,3-5} (with the Dixon notation in angular brackets⁹):

TABLE I. (a) Multipliers b_0-b_4 , for the bipolar moments [defined in Eqs. (2) and (5)] employing unpolarized photolysis radiation. β_{eff} [see Eq. (10)] is <0.48 for the N₂O+O(¹D) system studied, and "||" and "1" refer to pump-probe geometries with $\mathbf{k}_p || \mathbf{k}_a$ and $\mathbf{k}_p || \mathbf{k}_a$. (b) High-*j* limiting values of q_0 and q_2 (Ref. 10).

(a)							
Case	<i>b</i> ₀	<i>b</i> ₁	<i>b</i> ₂	<i>b</i> ₃	<i>b</i> ₄		
	q 0	$\frac{\beta_{\text{eff}}}{10} \cdot q_2$	$\frac{-\beta_{\rm eff}}{2} \cdot q_0$	$-q_{2}$	$\frac{-\beta_{\rm eff}}{7} \cdot q_2$		
Ţ	q_0	$\frac{\beta_{\text{eff}}}{10} \cdot q_2$	$rac{oldsymbol{eta}_{ ext{eff}}}{4}\cdot q_0$	- q ₂	$\frac{2\beta_{\rm eff}}{7} \cdot q_2$		
$\frac{2}{3}(\bot - \parallel)$	0	0	$\frac{\beta_{\text{eff}}}{2} \cdot q_0$	0	$\frac{2\beta_{\rm eff}}{21}\cdot q_2$		
$\frac{2}{3} \bot + \frac{1}{3} \Vert$	q 0	$\frac{\beta_{\text{eff}}}{10} \cdot q_2$	О Ъ)	$-q_{2}$	$rac{eta_{ ext{eff}}}{7} \cdot q_2$		
Transition	q_0	q_2					
P,R↑	$\frac{21}{20}$	$-\frac{33}{56}$					
Q†	<u>9</u> 10	4 <u>5</u> 56					

$$\beta_{0}[\equiv\beta_{0}^{0}(00)] = 1 \equiv \text{population},$$

$$\beta_{kj'}[\equiv\beta_{0}^{2}(02)] \equiv \langle P_{2}(\hat{\mathbf{k}}\cdot\hat{\mathbf{j}}')\rangle,$$

$$\beta_{kk'}[\equiv\beta_{0}^{2}(20)] \equiv \langle P_{2}\hat{\mathbf{k}}\cdot\hat{\mathbf{k}}')\rangle,$$

$$\beta_{k'j'}[\equiv\beta_{0}^{0}(22)] \equiv \langle P_{2}(\hat{\mathbf{k}}'\cdot\hat{\mathbf{j}}')\rangle,$$

(3)

and

 $\beta_{kk'i'} \equiv \beta_0^2(22) \equiv \text{triple vector correlation.}$

Equations (1)-(3) also apply if the product laboratoryframe velocity \mathbf{v}' is parallel to \mathbf{k} (and \mathbf{k}'), as would be the case for pure stripping dynamics.

In general, there will be a spread of reagent relative velocities, induced by thermal motions of the photolysis precursor (AB) and target reagent (C) molecules. More importantly, the velocity of the center of mass will not be negligible compared with the *product* velocity \mathbf{k}' , and the latter vector must be replaced by the laboratory velocity v' in Eq. (3). This complication arises because v_{cm} is not isotropically distributed (as it is for photodissociation studies in the bulk), but instead approximately mirrors the angular distribution of relative velocity vectors k (see Sec. IV). This anisotropy leads to the bipolar moments becoming product laboratory velocity (v') dependent, even if the product *relative* velocity k' is of fixed magnitude.⁸

The approach adopted here is to recognize the possible product velocity dependence of the measured bipolar moments, induced by whatever cause, and rewrite Eqs. (1) and (2) as

$$I(v'_{k}) = C \int_{v'=|v_{k'}|}^{\infty} \frac{g_{0}(v')}{2v'} \left[1 + \frac{g_{2}(v')}{g_{0}(v')} P_{2}\left(\frac{v'_{k}}{v'}\right) \right] v'^{2} dv', \quad (4)$$

where

$$g_0(v') = b_0 \beta_0(v') + b_1 \beta_{kj'}(v')$$

and

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$$g_2(v') = b_2 \beta_{kv'}(v') + b_3 \beta_{v'j'}(v') + b_4 \beta_{kv'j'}(v')$$
(5)

Product laboratory velocity averaged bipolar moments may also be defined as, e.g.,

$$\langle \beta_{kv'} \rangle = \frac{\int_0^\infty \beta_{kv'}(v') v'^2 dv'}{\int_0^\infty \beta_0(v') v'^2 dv'}.$$
(6)

The product velocity-dependent bipolar moments, which provide the important indicators of the reaction stereodynamics,⁸ have been obtained by first taking weighted averages of Doppler profiles in different pump-probe geometries, and for different transitions as proposed by Docker.¹⁰ The relevant coefficients (or weighting factors) $b_0 - b_4$, used in the present study are given in Table I: note that the summed profiles are dominated by either the $\beta_{kv'}$ (column 3) or the β_0 and $\beta_{v'i'}$ (columns 1 and 4) bipolar moments. The resulting averaged profiles have then been inverted using the analytical Fourier-transform procedure proposed by Leone and co-workers^{11,12} to obtain the product velocity-dependent moments. This procedure involved initially fitting the summed profiles to a Hermite polynomial expansion¹² and we have found that both this fitting process and the overall inversion routine are rather more stable and efficient than alternative techniques available.¹³ The procedure has the added advantage that a functional form for the velocity-dependent moments does not have to be assumed.14

One minor complication in the present analysis is that the absence of observable Q^{\uparrow} branch transitions prevents the separate determination of the $\beta_0(v')$ and $\beta_{v'l'}(v')$ moments (see Table I). However, an approximate correction has been made to the Doppler profiles, which assumes that the average v'-j' correlation $\langle \beta_{v'j'} \rangle$ takes its maximum value of -0.5, i.e., $\mathbf{v'} \perp \mathbf{j'}$, and has the same product velocity dependence as the distribution $\beta_0(v')$. Modified values of the velocity distribution returned by the analysis were little affected by the inclusion of the v'-j' correlation correction, shifting the distribution by ~ 100 m/s to higher velocities and narrowing the width of the distribution at fullwidth at half maximum (FWHM) by ~ 200 m/s. While this correction to the data is an approximate one, it demonstrates that the estimated product lab velocity distributions $\beta_0(v')$ presented in Sec. IV closely approximate the true velocity distributions.

IV. RESULTS

A. Distribution of reagent velocities

The photodissociation dynamics of N₂O at 193 nm has been investigated recently by Huber and co-workers¹⁵ using molecular-beam, time-of-flight mass-spectrometry techniques. They present translational energy distributions of the N₂ and O(¹D) photofragments from which they deduce an average translational energy release equivalent to 42% of the available energy, $E_{avl} \sim 22500 \text{ cm}^{-1}$. From the absence of observable structure in their time-of-flight spectra it was inferred that the remaining energy, $0.58E_{avl}$, is probably channeled primarily into N₂ fragment rotation¹⁵ rather than N₂ vibration. Huber and co-workers¹⁵ were also able to measure the average translational anisotropy of the recoiling fragments, and quote a value of $\langle\beta\rangle = 0.48 \pm 0.02$.

These data allow calculation of the distribution of the relative reagent velocity vectors, **k** (and that of the centerof-mass velocity) by convolution of the O(¹D) velocity distribution, f(u), with the thermal velocities of the photolysis precursor (*AB*) and target reagent (*C*). The resulting distribution may be written as

$$F(\mathbf{k}) = \frac{f_0(k)}{4\pi} \left[1 + \beta \frac{f_2(k)}{f_0(k)} P_2(\cos \theta_k) \right], \tag{7}$$

where

$$\int_0^\infty f_0(k)k^2dk=1$$

and

$$\cos \theta_k = \hat{\mathbf{k}} \cdot \hat{\boldsymbol{\epsilon}}_k$$

The reagents' speed distribution $f_0(k)$ is given by the following integral over the O(¹D) speed distribution observed experimentally [f(u)] [This equation (8) agrees with the energy distribution quoted in Ref. 16. Equations (7) and (9), which include the effects of thermal motions of *both AB* and *C*, appear here for the first time (see, however, Ref. 11 and 3)]:

$$f_0(k) = C \int_0^\infty \frac{f(u)}{(uk)^{1/2}} \cdot e^{-\gamma(u^2 + k^2)} \cdot I_{1/2}(2\gamma ku) 4\pi u^2 du,$$
(8)

where

$$C = \gamma/2\pi,$$

$$\gamma = \frac{M_{AB}M_C}{(M_{AB} + M_C)} \cdot \frac{1}{2kT},$$

and $I_n + (1/2)(x)$ are the modified spherical Bessel functions. The reagents' speed dependence of the translational anisotropy may be expressed compactly as

$$f_2(k) = C \int_0^\infty \frac{f(u)}{(uk)^{1/2}} e^{-\gamma(u^2 + k^2)} \cdot I_{5/2}(2\gamma ku) 4\pi u^2 du.$$
(9)

The speed distribution for the $O({}^{1}D) + N_{2}O$ reaction, $f_{0}(k)$, is plotted in Fig. 1. The distribution is somewhat broader than that of the $O({}^{1}D)$ atoms, f(u), and peaks at slightly higher speeds. In general, because $f_{2}(k) < f_{0}(k)$, the effective translational anisotropy of the reagents,

$$\beta_{\text{eff}} = \beta \frac{f_2(k)}{f_0(k)},\tag{10}$$

is less than β and depends on the relative speed k. Values of β_{eff} , using the velocity averaged value of $\langle \beta \rangle = 0.48$,¹⁵ are also plotted as a function of k in Fig. 1; because the O(¹D) atoms are moving with nearly ten times the average thermal velocity, the effect of thermal reagent motions on the translational anisotropy of the relative velocity vectors is seen to be a minor one in the present study.

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FIG. 1. The distribution of relative reagent speeds (bottom curve) k, and the effective translational anisotropy of the reagent relative velocity (top curve), β_{eff} [see Eqs. (7)–(10)], for the O(¹D) + N₂O reaction.

Although the anisotropy of the $O({}^{1}D)$ atoms from $N_{2}O$ photodissociation is seen to be small compared with the maximum possible $[\beta = +2$ in Eq. (10)] it will be shown below to be sufficient to allow determination of the important features of the stereochemistry of the $O({}^{1}D) + N_{2}O$ reaction.

B. Average energy disposals

Table II shows the average energy disposals for NO fragments born in v'=0 to v' < 18; it also includes estimates of the average internal energies of the unobserved NO fragment pairs, calculated on the basis of energy conservation and the known reaction exothermicity [~28 500 cm⁻¹ (Ref. 7)]. Fragments born in v'=16-18 have energies which exceed the reaction exothermicity and can only be accessed by virtue of the high reagent collision energies. Their partner fragments are necessarily born with little internal excitation; energy disposals and vector correla-

tions in the rotationally and translationally cold NO(v'=0) products have been reported previously.^{4,5} Products born in levels v'=1-15 have partners populating a much broader range of rovibrational levels and the product pair correlations for these species (Table II) are more speculative. Detailed isotopic labeling experiments would help to confirm these suggested pair correlations.^{17,18}

In our previous preliminary report,^{4,5} the pattern of energy disposals and reaction product vector properties were rationalized by assuming the occurrence of two (limiting) types of collision dynamics: one a direct "stripping" reaction yielding NO(v'=0) + NO(v'=16-18) and an indirect process in which the collision complex survives for a sufficient time to allow for extensive rovibrational energy redistribution, thus leading to the formation of rotationally excited NO products in v' = 1-15. In the absence of detailed NO vibrational populations (the populations in the vibrational levels 15, 16, and 17 have been estimated and decrease monotonically in the ratio 5:2:1), it is not possible to assess the relative importance of these two processes. However, our NO(v'=0) signals were considerably more intense than those observed for $v' \ge 1$ and we assume that the channel leading to NO(v'=0) + NO(v'=16-18) is at least as important as those generating intermediate NO vibrational levels.

The remainder of this paper concentrates exclusively on the channel which generates NO(v'=0)+NO(v'=16,17) fragments and, in particular, on the product state populations and vector properties of NO(v'=16 and 17). We demonstrate that the latter products are indeed generated *via* a stripping-type reaction mechanism.

C. Detailed energy and momenta disposals in NO(v' = 16,17)

An assigned portion of the NO LIF spectrum is presented in Fig. 2, and the resulting rotational distributions for NO v'=16 and 17 are given in Fig. 3. These were obtained exclusively from $P\uparrow$ (or $R\uparrow$) branch data and have not been corrected for the effects of rotational alignment, which will be small in the present case due to the low value of the term β_{eff} which appears in the multiplier b_1

TABLE II. Average energy disposals for the $O(^{1}D) + N_{2}O$ photoinitiated bimolecular reaction.

$NO(v_1')$	$E_{\rm vib}$ (cm ⁻¹)	$\langle E_{\rm rot} \rangle$ $(\rm cm^{-1})^a$	$\langle E_T^{\rm lab} \rangle$ (cm ⁻¹)	$E_{\rm tot}^{\rm NO(\nu_1')}$	$E_{\rm tot}^{\rm NO(\nu_2')}$	$NO(v_2')$
0	0	200 ± 20	110 ± 20	310	~ 30 000	16–18
1	1 876	4000 ± 400	690 ± 70	6570	27 930	14-15
3	5 544	> 4000	1350 ± 250	10 890	23 610	11-12
10	17 500	1020(N'=27)	1280 ± 200	19 800	14 710	4-5
14	23 714	1050 ± 150	1500 ± 200	26 260	8 240	1–2
15	25 197	1870(N'=35)	1500 ± 200	28 570	5 930	0–1
16	26 650	1050 ± 150	b	~30 000	~ 300	0
17	28 075	430 ± 50	ь	~30 000	~ 300	0
18°	29 470					0

*State-specific values (figures in parentheses indicated individual rovibronic lines).

^bSee Table III for state specific energy disposals.

 $^{\circ}v = 18$ observed but energy disposal data not measured.



FIG. 2. A portion of the NO($B^2\Pi - X^2\Pi$) LIF spectrum in the region of the (a) 3 – 17 and (b) 2 – 16 vibronic bands obtained from the 193 nm photoinitiated O(¹D) + N₂O bimolecular reaction ($\tau \sim 200$ ns, $p \sim 250$ mTorr).



FIG. 3. The rotational populations, P(N'), for NO(v'=16) (\blacksquare) and NO(v'=17) (\bigcirc) fragments generated from the superthermal O(^{1}D) + N₂O reaction. The v'=16 and 17 data have been scaled to their relative vibrational populations, $P(v'=16)/P(v'=17) \sim 2$.

given in Table I. The observed rotational distributions are somewhat colder than observed for the vibrational levels in the range 1-15 (see Table II),⁵ and yield average rotational excitations of 1050 ± 150 cm⁻¹ and 430 ± 50 cm⁻¹ for v' = 16 and 17. The two spin-orbit states of NO appeared to be near equally populated. Under Doppler resolution it is possible to resolve the A-doublet splitting in transitions with N' > 10, although we have been unable to observe any preferential population in either A-doublet state under the $p \times \tau$ conditions employed. This contrasts with the NO(v'=0) fragments which showed a high-*j* limiting value of the relative Λ -doublet population $\Pi(A'):\Pi(A'')$, tending to 2.⁵ The latter data were obtained under lower $p \times \tau$ conditions than employed in the present study and it is possible that partial relaxation is responsible for the equal populations observed here. Indeed, it is reasonable to assume that equilibration of the Λ -doublet levels (which are separated by only a few wave numbers for $N' \leq 30$) will be rather more efficient than rovibrational relaxation.19

Figure 4 displays representative Doppler profiles for the NO v'=16 and 17 fragments. These data are averages of at least seven separate laser scans. As described in Sec. III, we have adopted the Fourier-transform inversion technique proposed by Leone and co-workers¹² and illustrate the data analysis by reference to the $v'=16 P_{11}(N'=32)$ transition, which was the most extensively studied. In Fig.



FIG. 4. Representative Doppler broadened profiles for (a) NO(v' = 16, N' = 32) in pump-probe geometry $\mathbf{k}_{p} || \mathbf{k}_{a}$, (b) as for (a) but with $\mathbf{k}_{p} \perp \mathbf{k}_{a}$, and (c) NO(v' = 17, N' = 23) with $\mathbf{k}_{p} || \mathbf{k}_{a}$.

5 the product velocity distribution, $\beta_0(v')v'^2$, and the velocity dependence of the translational anisotropy, $\beta_{kv'}(v')/\beta_0(v')$ (note that this ratio must lie between the limits -1/2 to +1), are plotted as functions of v'. $\beta_{kv'}(v')$ was determined with less precision than $\beta_0(v')$, due to the small value of the reagent O(¹D) translational anisotropy (β) and the rather poor signal-to-noise ratio of the Dop-



FIG. 5. The experimentally determined NO(v'=16,N'=32) product lab velocity distribution, $\beta_0(v') \cdot v'^2$, and (see insert) the velocity dependence of the translational anisotropy, $\beta_{kv'}(v')/\beta_0(v')$, arising from the photoinitiated O(¹D) + N₂O reaction.



FIG. 6. Schematic Newton diagram for the $O({}^{1}D) + N_2O$ system, illustrating how an angular spread of k' about k will induce a spread in both the NO(v'=0) and NO(v'=16,17) product lab velocities, v'.

pler profiles obtained in geometries with $\mathbf{k}_p \perp \mathbf{k}_{a'}$ the velocity dependence of the translational anisotropy (shown in Fig. 5) is necessarily rather approximate. However, the relative integrated amplitudes of $\beta_{kv'}(v')$ and $\beta_0(v')$, which can be determined with much greater precision, yield an estimate of the velocity averaged moment $\langle \beta_{kv'} \rangle = 1.05 \pm 0.15$ [see Eq. (6)]. This value is very close to the *limiting* value of $\langle P_2(\hat{\mathbf{k}} \cdot \hat{\mathbf{v}}') \rangle$ [$\equiv \langle P_2(\hat{\mathbf{k}} \cdot \hat{\mathbf{k}}') \rangle$, Eq. (3)] = +1 for \mathbf{v}' ($\equiv \mathbf{k}'$)|| \mathbf{k} expected for the forward scattered NO(v'=16) fragments generated *via* a stripping mechanism.

The forms of the velocity distribution and the velocity dependence of the anisotropy shown in Fig. 5 are deserving of further consideration. Of particular note is the wide range of velocities seen in the $\beta_0(v')$ distribution. Although this broad spread of laboratory frame product velocities can have a variety of causes, distinguishing between them is made possible for this particular reactive system because both the NO(v' = 16,17) fragment and its partner NO born in v'=0 have now been observed.⁵ To reiterate our previous findings,⁵ the NO(v'=0) fragments are born both rotationally and translationally cold (see Table II). The absence of significant rotational excitation in NO(v'=0) means that the broad velocity distribution observed for NO(v'=16,17) cannot be induced by a range of internal excitation in its partner fragment. The form of $\beta_0(v')$ may, alternatively, reflect a spread in the angular distribution of k' about k (Ref. 8) (see Fig. 6). However, in the center-of-mass frame both NO(v'=16,17) and NO(v'=0) fragments must have the same angular and speed distributions, and thus a broad angular spread of k' about k would induce a broad spread of laboratory velocities in both the NO(v'=16,17) and NO(v'=0) products. This is at variance with our previous measurements which showed that the Doppler widths of the v'=0 fragments were very close to those expected for a "spectator" NO(v'=0) fragment, which would have a laboratory velocity distribution very close to that of the N₂O target

reagent (i.e., isotropic and Gaussian in form with a FWHM ~0.083 cm⁻¹). In fact, from the NO(v'=0) data, we may estimate that the maximum possible angular spread of k' about k must lie in the range 0° -30°. Such a small range of angles would generate a negligible spread in the NO(v' = 16.17) velocity distributions, $\beta_0(v')$, and only a slight dependence of the product translational anisotropy on $v'(\langle P_2(\hat{\mathbf{k}}\cdot\hat{\mathbf{y}}')\rangle \sim 0.88-1.0)$. One is forced to conclude that the wide distribution of NO(v' = 16,17) velocities primarily reflects the range of collision velocities (k) employed in the experiment (see Fig. 1) modified, of course, by the excitation function for the reaction (see Sec. V). Any velocity dependence of the product translational anisotropy would then be due to the dependence of the product angular distributions on the collision energy. Clearly, further experiments with a different $O(^{1}D)$ atom source would be valuable in establishing the k dependence of the reaction anisotropy. [It is possible that the $O(^{1}D)$ reagent translational anisotropy (β) is itself velocity dependent. This was not explicitly determined by Huber and coworkers (Ref. 15) but their time-of-flight spectra measured at different laboratory angles did not appear to show any marked variation of the translational anisotropy with velocity.]

 $\beta_0(v')$ distributions (with areas scaled to the relevant product state population) for a variety of selected rotational states of NO v' = 16 and v' = 17 are plotted in Fig. 7. These distributions may be used to obtain estimates of the average velocities of the NO products. The data are collected in Table III along with detailed energy disposal data for these specific rovibrational states. The last two entries in Table III show the average $O(^{1}D)$ translational energy, $\langle E_T^{O(^{1}D)} \rangle$ and the product NO(v' = 16,17) velocity $\langle v'_{NO} \rangle^{\text{stripping}}$, calculated on the assumption that the NO(v=0) + NO(v' = 16,17) channel is generated via a stripping mechanism, i.e., with the partner fragments to NO(v'=16,17) born in v'=0 (as dictated by energy conservation) and with the low translational and rotational excitations previously observed for these levels⁵ (see Table II). This enables an estimate of the total available energy to be made for each specific rovibrational state, from which it is possible to calculate $\langle E_T^{O(^{1}D)} \rangle$, given that ΔH_0^{Θ} for the reaction is ~28 500 cm^{-1.7} The predicted NO(v' = 16,17) velocity was then obtained by assuming conservation of the initial O(¹D) momentum. Bearing in mind the experimental uncertainties, as well as those in ΔH_0^{Θ} , the similarity between experimental $\langle v'_{NO} \rangle$ values and those obtained assuming stripping dynamics lends considerable support for the proposed reaction mechanism and also reinforces the interpretation given above for the $\beta_0(v')$ velocity distributions.

V. DISCUSSION

The data presented in Sec. IV, along with those previously reported,⁵ provide convincing evidence that the reaction channel

$$O^{1}D + N_{2}O \rightarrow NO(v'=0) + NO(v'=16,17)$$



FIG. 7. (a) Experimental state-resolved product lab velocity distributions, $\beta_0(v')v'^2$, for NO born in (i) v'=16, N'=32; (ii) v'=16, N'=37; (iii) v'=17, N'=23; (iv) v'=17, N'=26; and (v) v'=17, N'=29. The areas of the distributions have been scaled by the appropriate rovibrational population (Fig. 3). (b) Calculated product lab velocity distribution, $f_0(v') \cdot v'^2$, in the stripping limit assuming a reaction cross section independent of k.

does proceed via a stripping-type mechanism. However, the results also allow greater insight into the reaction stereodynamics. For example, one striking feature of the results shown in Table III is the correlation between increasing fragment rotation (within each vibrational state) and increasing average product velocity. This trend is confirmed by the more detailed Doppler analysis shown in Fig. 7, in which the experimental velocity distributions $\beta_0(v')v'^2$ are displayed. Clearly, the experimental distributions shift to higher velocities with increasing product rotational excitation. Furthermore, since in the stripping limit v' and k are related by the equation $v' \approx (16/30)$ k, one must conclude that there is a similar correlation between the reagent relative velocity k and the product NO(v' = 16,17) rotational state.

The simplest explanation for the observed k-j' correlation is that it reflects a correlation between the reagent orbital angular momentum $(L \sim \mu kb)$ and j'. Because the rotational angular momenta of the N₂O target reagent and the NO($\nu'=0$) products are relatively small, angular mo-

TABLE III. State-specific energy disposals for the $O(^{1}D) + N_{2}O$ photoinitiated bimolecular reaction (energies in cm⁻¹, velocities in ms⁻¹).

, <u>, , , , , , , , , , , , , , , , , , </u>	<i>v</i> ′=16		<i>v</i> ′=17		
	N'=32	N'=37	N'=23	N'=26	N'=29
(V'NO)	1170 ± 100	1250 ± 170	1030 ± 100	1550 ± 180	1930± 230
$\langle E_{\rm trans}^{\rm NO(t'=16,17)} \rangle$	1730 ± 300	1970 ± 400	1330 ± 250	3000 ± 650	4670 ± 1100
E _{rot}	1680	2200	800	1130	1370
$\langle E_{\rm tot}^{t^2=16,17} \rangle$	$30\ 060 \pm 300$	$30\ 820\pm400$	30210 ± 250	$32\ 210\pm650$	$34\ 120 \pm 1100$
$\langle E_{\rm trans}^{(\rm O^{1}D)}\rangle^{a}$	1870 ± 300	2630 ± 400	2010 ± 250	4020 ± 650	5930 ± 1100
(V'NO) stripping	890±130	1060 ± 150	920±110	1310±200	1590± 280

*Errors in ΔH_0^{\ominus} are not included.

mentum conservation for this reaction may be written as

$$\mathbf{L} \sim \mathbf{L}' + \mathbf{j}'. \tag{11}$$

It is not possible to assume that $L' \sim 0$ for the O(¹D) + N₂O reaction, because it is not kinematically constrained.²⁰ The term

$$\cos^{2}\beta = \frac{M_{A}M_{C}}{(M_{A} + M_{B})(M_{B} + M_{C})} = 0.36$$
(12)

[where the masses in Eq. (12) are those appropriate for an A+BC reaction] as opposed to the value of zero necessary for the correlation L=j'. However, for a stripping reaction, for which k||k' then also L||L'. Thus provided that the exit orbital angular momentum is a constant fraction of the initial orbital angular momentum, a correlation between L and j' will be observed. Indeed, Levine and co-workers²¹ have recently pointed out that such a correlation, i.e.,

$$\mathbf{j}' = \alpha \mathbf{L}$$
 and $\mathbf{L}' = (1 - \alpha) \mathbf{L}$, (13)

where $\alpha \approx \text{const}$, will be valid for reactions which are highly collinearly constrained, even though they may be far from the ideal kinematic limit. They write the kinematic constraint in the more general form^{21,22}

$$\mathbf{j}' = \cos^2 \beta \mathbf{j} + \sin^2 \beta \mathbf{L} + \cos^2 \beta \mathbf{x}, \qquad (14)$$

where

$$\mathbf{x} = M_B(\mathbf{R}\Lambda\dot{\mathbf{r}} + \mathbf{r}\Lambda\dot{\mathbf{R}})$$

and represents the kinematic contribution arising from the shift in the center of mass in passing from reactants to products. For collinearly dominated reactions x will tend to lie parallel to L and provided that $\cos^2 \beta \mathbf{j} < \sin^2 \beta \mathbf{L}$, Eq. (13) automatically follows.

In summary, it is proposed that the observation that faster moving NO(v'=16,17) fragments are born in higher rotational states reflects the *vector* correlation $\mathbf{j}'=\alpha \mathbf{L}$ expected for collinearly dominated reactions. Clearly it would be of interest to probe the rotational alignment of the NO(v'=16,17) fragments to confirm the above mechanism. Unfortunately, this would require the use of the NO γ -band system which is rather weak for these very high vibrational levels; the transitions also lie in a very congested portion of the NO spectrum. However, rotational alignments for the NO(v'=0) fragments have been determined⁵ and yield values very close to the maximum ($\langle P_2(\hat{\mathbf{k}}\cdot\hat{\mathbf{j}}')\rangle = -0.5$) for $\mathbf{j}'\perp\mathbf{k}$. At first sight this result is surprising since the NO(v'=0) "spectator" product molecules might be expected to have an isotropic rotational distribution, mirroring that of the N₂O target reagents. Consideration of the collinear stereodynamical constraint described above, however, reveals that parent N₂O molecules with $\mathbf{j}\parallel\mathbf{k}$ are more likely to undergo (less-reactive) "side-on" collisions than N₂O molecules aligned with $\mathbf{j}\perp\mathbf{k}$, i.e., a steric constraint imposes m_j selectivity. A preferred collinear reactive geometry selects N₂O reagent molecules with $\mathbf{j}\perp\mathbf{k}$ ($m_j\sim 0$) and hence the product "spectator" NO(v'=0) molecules also have $\mathbf{j}'\perp\mathbf{k}$.

Further support for the notion of a collinearly constrained reaction is provided by recent simple selfconsistent-field molecular-orbital calculations by Honma and co-workers,¹⁸ who determine the energy of the $O(^{1}D)-N_{2}O$ system as a function of $O(^{1}D)-N_{2}O$ separation and angle of approach. Their calculations predict a significant minimum at the collinear $O(^{1}D)-N_{2}O$ geometry in the 3 Å separation region. Indeed Honma, Fujimura, and Kajimoto¹⁸ propose that $O(^{1}D)$ attack in this configuration leads to generation of NO products, while attack by $O(^{1}D)$ at the $N_{2}O$ oxygen atom, where a second potential minimum is evident, leads to $N_{2}+O_{2}$ formation.

Returning to the data given in Table III and Fig. 7, a second observation is that fragments born in v'=17 tend to be moving faster than those in v'=16, for similar values of j'. This partly just reflects the fact that population of v'=17 fragments is only energetically possible for collisions in the high velocity tail of the reagent relative velocity distribution (Fig. 1) but it also implies that for v'=17 fragments, less reagent orbital angular momentum is channeled into product rotation than for v'=16 products [see Eq. (13)]. This may arise because the reaction generating v'=17 fragments is less collinearly dominated than that generating v'=16.

A final important feature of the data presented in Sec. IV is that while the rotational distributions for NO(v'=16) and NO(v'=17) peak at N'~25 and 18, respectively, fragments born in these states will have mean



FIG. 8. The experimental relative reaction cross sections $[\sigma_{v'j'}(k)]$ as functions of v'[=(16/30)k] obtained from the product lab velocity distributions for v'=16, N'=32 (O) and N'=37 (\oplus) shown in Fig. 7(a).

velocities considerably lower than anticipated from the reagent relative velocity distribution. In fact, even in the tail of the v'=16 rotational distribution (e.g., N'=37) the mean velocity of the NO products is only 1250 m/s, considerably below 1550 m/s ($\equiv 16/30 \times k$). The data may be rationalized qualitatively by assuming that the overall reaction cross section

$$\sigma(k) = \sum_{v'} \sum_{j'} \sigma_{v'j'}(k)$$
(15)

(where v' represents the product vibrational state) decreases with increasing collision velocity k as would be anticipated for a reaction where there is a centrifugal barrier.

Relative state-specific cross sections, proportional to the $\sigma_{v'j'}(k)$ appearing in Eq. (15), can be obtained from the data given in Fig. 7(a) by dividing the observed $\beta_0(v')$ distributions by the distribution $f_0(v')$ [see Fig. 7(b)] which was calculated in the stripping limit $[\mathbf{v}' = (16/30)\mathbf{k}]$ assuming the reaction cross sections were independent of k. Example relative cross sections for NO(v'=16) N'=32and 37 are shown in Fig. 8. Note that these shift to higher velocities k at the higher values of N'. The general form of the relative cross sections, in particular the drop in $\sigma_{n'i'}(k)$ at low collision energies, is consistent with there being a rather narrow range of impact parameters for reactions generating specific rovibrational states of the products. Assuming the validity of Eq. (13), more precise information on the (scaled²¹) impact parameter distribution could be obtained if the data in Fig. 7 were available for the complete range of populated rotational states.²⁰ This would merely involve taking slices through the relative crosssection data at fixed values of k. At present, however, we simply note the general decrease in b as j' increases.

VI. CONCLUSIONS

The technique of velocity-aligned photofragment dynamics has been applied to a study of the superthermal reaction

$$O(^{1}D) + N_{2}O \rightarrow NO(v'=0) + NO(v'=16,17).$$

Energy and momenta disposals in both reaction products reveal that the reaction proceeds *via* a stripping-type mechanism in which the "old" NO(v'=0) fragment is left rotationally and translationally cold while the newly formed NO(v'=16,17) products are forward scattered with $\langle P_2(\hat{\mathbf{k}}\cdot\hat{\mathbf{k}}')\rangle$ close to unity. In addition, the observation that higher rotational excitation in the NO(v'=16,17) products is associated with higher fragment velocities is ascribed to the angular momentum correlation $\mathbf{j}'=\alpha \mathbf{L}$ and to the stereodynamical constraint of a preferred collinear reactive geometry. Finally, this paper also demonstrates how these results may be used to provide information about the relative product state specific reaction cross sections and the scaled opacity functions.

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