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Citation: The Journal of Chemical Physics **72**, 6521 (1980); doi: 10.1063/1.439154
View online: http://dx.doi.org/10.1063/1.439154
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/72/12?ver=pdfcov
Published by the AIP Publishing

Reaction of magnetically state selected NO with O_3: Effect of *fs* states and rotational states on reactivity

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(Received 28 January 1980; accepted 27 February 1980)

The visible chemiluminescent channel of the $NO+O_3 \rightarrow NO_2+O_2$ reaction is studied to determine the effect of the NO *fs* states ($^2\Pi_{1/2}$ and $^2\Pi_{3/2}$) on reactivity. Chemiluminescence is observed from an ozone-filled scattering cell through which a NO beam passes. Molecules in both the upper and lower *fs* states are present in the beam, and the intensity of molecules in the upper state can be enhanced by magnetic focusing. Although the beam intensity is observed to increase upon focusing, the increase in chemiluminescence is much smaller showing that the upper state is not solely responsible for chemiluminescence. However, the magnetically selected molecules are rotationally cooler than the unselected molecules, and a reasonable interpretation of the small increase in chemiluminescence is that for the chemiluminescent channel both *fs* states are equally reactive, but that the reactive cross section increases rapidly with rotational state.

I. INTRODUCTION

Both the influence of electronic state of reagents on reaction path and rate and the formation of molecules in electronically excited states by chemical reaction are of great current interest[1,2] from intrinsic as well as practical points of view. Intrinsically, the consumption and disposal of all forms of energy in chemical reactions are sensitive probes of the reaction dynamics.[3] Practically, a knowledge of the reactivity of different reagent states might allow unprecedented control of reactions by irradiating with lasers, and knowledge of the conditions under which electronically excited species are formed would greatly assist in the development of visible chemical lasers.

Most chemical reactions involve ground electronic state reagents and products because electronic energies are usually large in comparison to thermal and chemical energies. An electronically excited state is typically a major perturbation on the system[4] and, for example, an electronically excited reagent could be responsible for a strongly endoergic reaction being converted into a strongly exoergic reaction. As a consequence, any subtle differences between reactivity of different states would be lost in the large differences between endoergic or exoergic reaction.

In order to assess the differences between electronic states without large concomitant energy effects we have studied the chemiluminescent channel of the reaction $NO+O_3 \rightarrow NO_2^* + O_2$ to see how the fine-structure (fs) states of NO affect the reactivity. Here the reaction is 16 800 cm^{-1} (48 kcal/mole) exoergic,[5] whereas the fs states ($^2\Pi_{1/2}$ and $^2\Pi_{3/2}$) are separated by only 121 cm^{-1}. Despite this small difference in energy, Redpath *et al.*[6] have suggested that NO_2^* is formed mainly from the upper fs state, $^2\Pi_{3/2}$, and that $NO_2^\dagger$ is mainly formed from the lower, $^2\Pi_{1/2}$, state, where NO_2^* denotes NO_2 in the $^2B_1$ or $^2B_2$ excited electronic state and $NO_2^\dagger$ denotes vibrationally excited NO_2 in the ground $^2A_1$ state.[7] On energetic grounds, of course, one might expect the two fs components to react similarly so the formation of the chemiluminescent product would not depend on fs state. Suggesting that the product channel can be almost exclusively determined by the fs state of NO implies that incredibly restrictive (and interesting) conditions must be satisfied to initiate reaction and has prompted this study.

II. EXPERIMENTAL

The apparatus consists of three differentially pumped chambers and is shown schematically in Fig. 1. Relevant dimensions are given in Table I. In brief, the NO beam is directed along the axis of an inhomogeneous magnetic field and then passes through a scattering cell

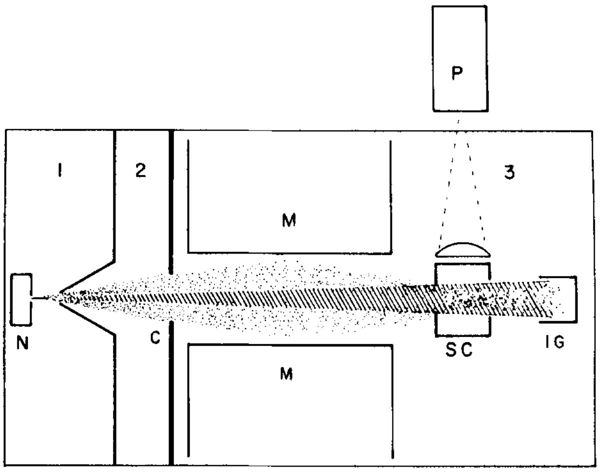

FIG. 1. Schematic diagram of apparatus. Seeded beam expands from nozzle (N) in chamber 1 and after collimation (C) in buffer chamber 2 passes through the inhomogeneous magnet (M) in chamber 3. In the absence of a magnetic field a small portion of the beam (shown cross-hatched) passes through the scattering cell (SC) and into an ionization gauge detector (IG). Chemiluminescence is observed with the photomultiplier (P). When the magnet is energized the beam originally passing through the SC is essentially undisturbed, but $\Omega = \frac{3}{2}$ molecules (shown dotted) are focused into the SC. Defocused molecules do not enter the SC and are not shown. (Deflections are greatly exaggerated.)

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J. Chem. Phys. 72(12), 15 June 1980 0021-9606/80/126521-08$01.00

TABLE I. Apparatus dimensions (mm).

	Distance		Diameters	
l_0	Nozzle–skimmer	19	Nozzle	0.25
l_1	Nozzle–collimator	180	Skimmer	1.0
l_2	Nozzle–magnet exit	460	Collimator	2.5
l_3	Nozzle–SC entrance	524	Magnet gap	3.2
			SC entrance	3.2
			SC exit	5.1

containing ozone. Molecules in the upper electronic state, ${}^2\Pi_{3/2}$, are focused when the magnet is energized and the flux of molecules in the upper state which enter the scattering cell (SC) increases. Molecules in the lower, ${}^2\Pi_{1/2}$, state are essentially unaffected. Chemiluminescence from the SC is monitored with a photomultiplier, and reactivity of "normal" NO can be compared with "upper state enhanced" NO.

Because the translational energy threshold[6] for the reaction is 3.2 kcal/mole and the cross section increases drastically with energy,[6,8] the NO (Matheson, C.P.) is accelerated to an average collision energy[9] of 10.8 kcal/mole by seeding 4% NO in He at stagnation pressures 150–250 Torr. This expands from an oven at 300 °C (to increase the population in the upper state) and is skimmed in chamber 1. In chamber 2 the beam is modulated and further defined by a collimating orifice (C) which can be moved under vacuum to position the beam coaxially with the magnet in chamber 3. Typical pressures under operating conditions are 2×10^{-6} Torr and 6×10^{-7} Torr in chambers 1 and 3, respectively. The central portion of this beam passes through a stainless steel scattering cell containing ozone (prepared according to Clough and Thrush[10]) at room temperature and at a pressure sufficient to attenuate the NO beam ~50% (~5×10^{-4} Torr). The beam which passes through the SC is entirely intercepted by an ionization gauge and the intensity is monitored by synchronously detecting the ac component of the ion current. Spurious effects in the ionization gauge (IG) caused by stray axial magnetic fields (~5 G) are eliminated by shielding the IG with two concentric steel tubes.

The SC is a stainless steel cylinder closed on the bottom by a gold-coated spherical mirror and on the top by a glass lens which together direct light toward the RCA C31034 photomultiplier tube (PMT). Light could not be imaged because of the long radiative lifetime of NO_2^*. The PMT is cooled to ~50 °C and is operated in the pulse-counting mode. The signal was the chopper-open–chopper-closed difference. The PMT is located 23 cm from the axis and is observed not to be affected by stray fields from the magnet.

The inhomogeneous magnet is constructed[11] from six pole pieces 28 cm long symmetrically spaced about a circular gap 3 mm in diameter. Current and cooling water are carried by 3 mm copper tubing insulated with fiberglass sleeves wound around each pole piece so that adjacent pole tips have opposite polarity. This produces a magnetic field of 7 kG measured at the pole tips for a current of 67 A per pole. The field has a minimum on the axis and increases in magnitude as r^2, which insures that molecules with a positive first-order Zeeman effect are focused.

III. ZEEMAN EFFECT

For low rotational states, NO is well described by Hund's case (a) coupling.[12] The spin angular momentum is coupled to the field along the internuclear axis and has component along the axis, $\Sigma = \frac{1}{2}$. The electron orbital angular momentum is also coupled to the axis with component $\Lambda = 1$. The total angular momentum along the axis is $\Omega = |\Sigma + \Lambda|$ and is $\frac{1}{2}$ or $\frac{3}{2}$. The angular momentum of rotation of the molecule, O, adds vectorially to Ω to form **J**, the total angular momentum exclusive of nuclear spin.

A molecule in an inhomogeneous field experiences a force[13] $\mathbf{F} = -\nabla \mathbf{W}$, where $W = -\boldsymbol{\mu}\cdot\mathbf{H}$ is the energy of interaction between the molecule and the magnetic field. This is quite different for $\Omega = \frac{1}{2}$ and $\Omega = \frac{3}{2}$. In the $\Omega = \frac{1}{2}$ state, Λ and Σ are opposed, and since the g factor for the electron is 2, the spin magnetic moment essentially cancels the orbital magnetic moment and $W \simeq 0$. However, for the $\Omega = \frac{3}{2}$ state these moments add, giving a magnetic moment comparable to the Bohr magneton. If this moment is averaged over rotation,[12] $W = -3\mu MH/[J(J+1)]$. Molecules with $\Omega = \frac{1}{2}$ are therefore undisturbed by the field. Molecules with $\Omega = \frac{3}{2}$ can be deflected, and in the magnetic six-pole field are deflected toward the axis and focused if $M < 0$. They are defocused for $M > 0$.

Positive and negative M states are equally populated so the apparatus geometry is crucial to the separation of the two states. A beam defining aperature allows only the small central portion of the beam to enter the scattering cell. Only those molecules in this small central portion will be perceived as having been defocused, but molecules in a much larger solid angle (depending on field intensity and state) can focus, so the focused molecules can considerably outweigh those which defocus. When the magnet is off, both the $\Omega = \frac{1}{2}$ and $\Omega = \frac{3}{2}$ states will enter the SC. When the magnet is energized, the $\Omega = \frac{1}{2}$ flux is unaffected but the $\Omega = \frac{3}{2}$ flux is increased because more molecules are focused than are defocused.

For higher rotational states, the spin is no longer coupled to the axis, Ω is no longer a good quantum number, and the angular momentum coupling is intermediate between Hund's cases (a) and (b). As a consequence, the Zeeman effect for the two states is a bit more complicated, although the essential aspects are quite well covered using the simple case (a) description given above. Fortunately, due to rotational cooling in the nozzle expansion, this decoupling is only a minor effect and is described in Appendix A.

IV. RESULTS

A. Magnetic focusing

An increase in beam intensity is observed when the magnet is energized. This is shown in Fig. 2, where the fraction focused, $\Delta I/I^0 \equiv (I^H - I^0)/I^0$ with I^H and I^0 denoting beam intensities with magnet on and magnet off,

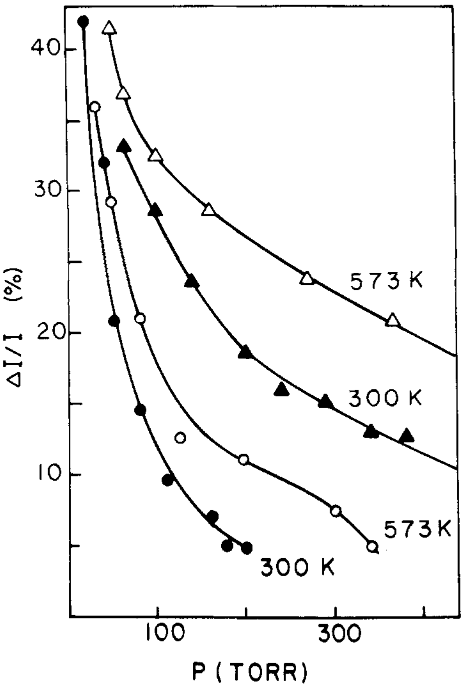

FIG. 2. Fractional change in NO beam intensity on energizing the focusing magnet as a function of stagnation pressure and nozzle temperature. Triangles denote measurements for pure NO beams; circles denote measurements for 4% NO seeded in helium. For pure NO, measurements were made at higher stagnation pressures than shown in figure.

respectively. Pure NO shows a greater enhancement in beam intensity because the molecules are slower, spend more time in the field, and are, therefore, more easily deflected. Heating the oven increases the fraction focused mainly because the focusing state, $^2\Pi_{3/2}$, is more populated at higher temperatures. Collisional relaxation of the $^2\Pi_{3/2}$ state to the $^2\Pi_{1/2}$ state is very facile, requiring some 15–70 collisions,[14] and this electronic cooling is responsible for the decrease in the fraction focused as the stagnation pressure is increased. Molecular rotations also relax, of course, but the lower rotational states are easier to focus, and rotational cooling alone is calculated to slightly increase the focused fraction.

The helium-seeded NO beam is harder to focus because the NO beam is accelerated by the helium to a speed roughly equal to that of the helium.[9] In addition, the monatomic helium acts as a refrigerant[15] and quite effectively cools the internal degrees of freedom of NO. Using Anderson and Fenn's values for terminal Mach numbers,[16] we calculate a terminal temperature $T_T \sim 7$ K for the NO in our experiments expanding from a 573 K oven. Presumably $T_{\rm rot} \gtrsim T_T$ and $T_e > T_{\rm rot}$, where $T_{\rm rot}$ and T_e are the final rotational and electronic temperatures. These temperatures and the extent to which the final rotational state distribution may be characterized by one temperature are not known but, as mentioned in Sec. V, they play only a minor role in interpretation of the experiments.

No focused signal is observed for either pure helium or pure argon beams. This means that ΔI can be entirely attributed to focused NO. The ionization gauge cannot distinguish between He and NO, however, so I^0 includes a contribution from the helium beam. This contribution is observed[17] to be small (< 10%), presumably due to the hydrodynamic defocusing of the light carrier[18] and the low ionization cross section for He.[19] The values in Fig. 2, therefore, represent *lower limits* to the fraction of NO focused.

B. Chemiluminescence

Chemiluminescence (CL) is easily observed and typical results are shown in Fig. 3. Total count rates are ~100–300 $\sec^{-1}$, the dark rate is ~10 $\sec^{-1}$, and a small (~20 $\sec^{-1}$) residual signal is observed with the NO beam flag closed. As is evident in Fig. 3, energizing the magnet has little effect on the CL. Similar results were obtained at several different stagnation pressures in the range 150–250 Torr and at several different nozzle temperatures (300–573 K). No significant difference among these runs was evident. The most reliable data were accumulated at 250 Torr and 573 K, and averaging many runs similar to Fig. 3 yields a fractional increase in CL of $\Delta S/S^0 = 0.026 \pm 0.006$ (99% confidence limit), where $\Delta S/S^0 \equiv (S^H - S^0)/S^0$ with S^H and S^0 denoting signal with magnet on and magnet off, respectively.

The goal of these experiments has been to compare the reactivities of the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states of NO for those channels of the reaction

$$NO + O_3 \rightarrow NO_2 + O_2$$

which produce NO_2^* emitting in the visible. A determination of *relative* reactivities is sufficient for this purpose and obviates the need for determination of light collection efficiency, for determining the sensitivity of the PMT as a function of wavelength, or for measuring absolute beam intensities. All that is needed are relative measurements of CL and beam intensity with magnet on and magnet off. The apparatus geometry, PMT sensi-

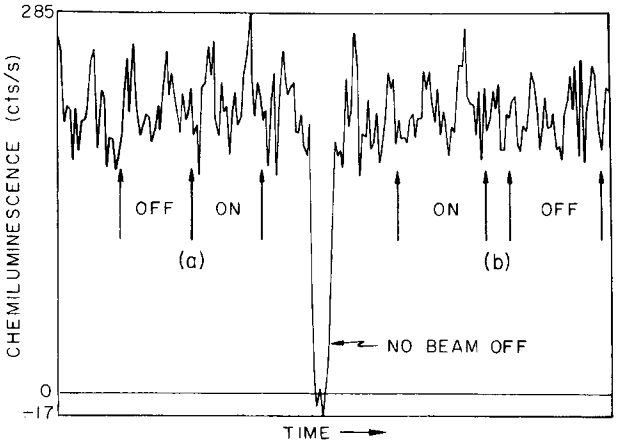

FIG. 3. Chemiluminescent signal with magnet on and off. Total counts for magnet on and for magnet off, respectively, are 6411 ± 98 and 6257 ± 98 for the (a) sequences; 7561 ± 107 and 7427 ± 107 for the (b) sequence. Even though the signal of interest is the time integral of the count rate, an increase in CL as large as the increase in beam intensity (Fig. 2) would have been easily discernible in the raw data.

tivity, and beam intensity (at magnet entrance) are all the same and cancel out. We must emphasize, however, that we are comparing only those channels which form products that chemiluminesce in the visible.

V. DISCUSSION

The increase in chemiluminescence observed when the magnet is energized $(2.6 \pm 0.6)\%$ is clearly less than the increase in beam intensity, 9.5%. As discussed below, the increase in beam intensity is due solely to molecules in the upper fs state. We therefore conclude that CL reaction is not restricted to the upper, ${}^2\Pi_{3/2}$, level as previously suggested.

In order to quantitatively compare reactivities of the two fs states it is necessary to know $f_{3/2}$, the fraction of molecules in the beam in the $\Omega = \frac{3}{2}$ state when $H = 0$. In the absence of electronic cooling during the nozzle expansion $f_{3/2}$ is given by Boltzmann statistics to be 0.42 (573 K). If all of the CL were due to reaction of upper state molecules as suggested by Redpath *et al.*,[6] the CL would increase $9.5/f_{3/2} = 22\%$. As discussed previously, electronic relaxation is very facile and the effective (and unknown) electronic temperature is expected to be much less than 573 K, so $f_{3/2}$ is expected to be less than 0.42 The CL is thus expected to increase by *more* than 22% provided that only upper state molecules react. (If both states reacted equally, a 9.5% increase would be expected.) Since the observed increase is considerably less, we must conclude that assumption is invalid and that reaction is not restricted to NO molecules in the upper fs state. In fact, if we assume that fs state is the only factor determining reactivity to NO_2^*, our data indicate that NO ${}^2\Pi_{1/2}$ (the *lower* state) is about five times more reactive than the ${}^2\Pi_{3/2}$ state. Details of the data reduction are in Appendix C.

A. Effect of rotation

Previous workers[6,8] have studied the effect of internal energy on the CL channel reactivity and have determined internal energy to be more efficient than translation. In their experiments, however, the NO fs populations were varied by heating the nozzle (while adjusting conditions to maintain a constant translational energy). This also has the effect of raising the rotational temperature. Redpath *et al.*,[6b,c] discussed the possibility that the NO rotational temperature was affecting the CL reaction, but rejected it as implausible, and concluded that the ${}^2\Pi_{3/2}$ state is more reactive than ${}^2\Pi_{1/2}$.

TABLE II. Representative magnetic moments in Bohr magnetons (calculated at 4 kG).

	"$\Omega = \frac{3}{2}$"			"$\Omega = \frac{1}{2}$"		
J	$M = -J$	$M = +J$	M (case a)	$M = +J$	$M = -J$	M (case a)
$\frac{1}{2}$	···	···	···	0	0	0
$\frac{3}{2}$	−1.164	1.167	1.2	−0.035	0.034	0
$\frac{5}{2}$	−0.786	0.797	0.86	−0.068	0.062	0
$\frac{7}{2}$	−0.560	0.583	0.67	−0.103	0.087	0
$\frac{9}{2}$	−0.399	0.443	0.55	−0.139	0.110	0
$\frac{11}{2}$	−0.273	0.345	0.46	−0.177	0.129	0
$\frac{13}{2}$	−0.164	0.274	0.40	−0.217	0.126	0
$\frac{15}{2}$	−0.066	0.223	0.35	−0.287	0.130	0

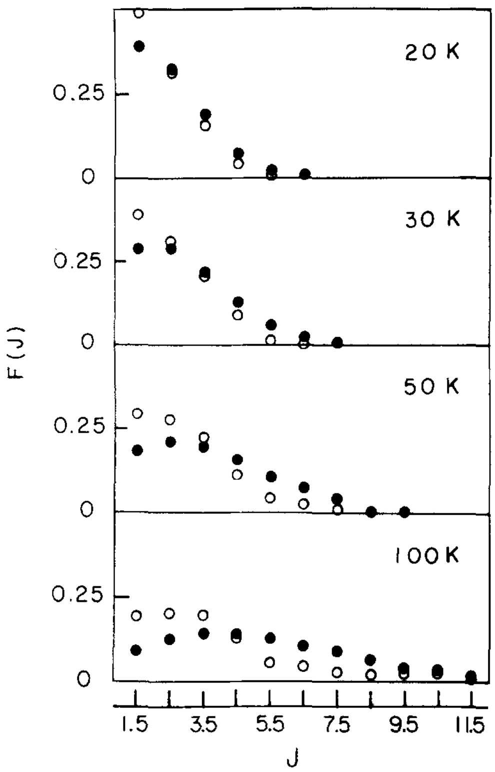

FIG. 4. Calculated rotational state distributions for upper fs state. Filled points correspond to Boltzmann distributions characterized by the temperature indicated in each panel. Open points correspond to distribution of molecules transmitted by the magnet at 4 kG.

In our experiment, on the other hand, raising the fs state temperature (by magnetic focusing) effectively decreases the rotational temperature. The effective magnetic moment and the resulting focusing depend on rotational state as discussed in the Appendixes and shown in Table II. Focused molecules are weighted towards low rotational states, and rotational state distributions as modified by the magnetic focusing are shown in Fig. 4 for several assumed initial rotational temperatures. (The initial rotational temperature is unknown and is regarded as a parameter.)

The changes in rotational state distributions shown in Fig. 4 could be regarded as minor. On the other hand, we could assume that both Ω states have *equal* reactivity and attribute all of our observations to variation of reactivity with rotational state. This alternative was discounted by Redpath *et al.*,[6] largely because the rotational effects on reaction known at the time were too small. However, we have recently observed large rotational effects in the (crossed-beam) reaction $K + HCl \rightarrow KCl + H$, where the HCl was laser excited to different rotational levels of the $V = 1$ state.[20] For the first few J levels the cross section decreases roughly a factor of 2 per rotational state. Similar effects have been observed in the CL depletion studies of Polanyi and co-

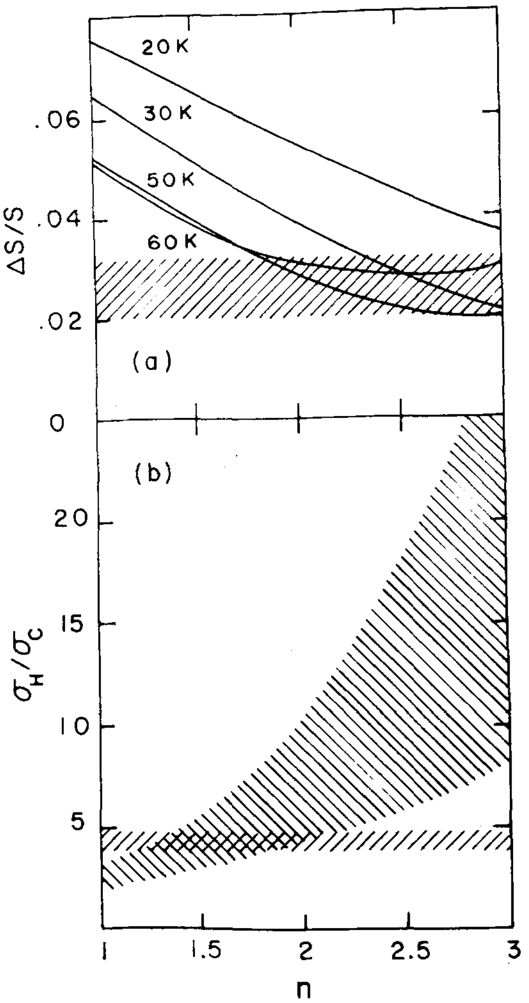

FIG. 5. (a) Increase in chemiluminescence, $\Delta S/S_0$, predicted by the rotationally dependent model cross section, $\sigma \propto E^n_{\mathrm{rot}}$. Model is averaged over rotational states transmitted by the magnet (Fig. 4) for various beam rotational temperatures and for various values of the exponent n. Predicted values lying within cross-hatched region are in agreement with these experiments. (b) Model predictions for the ratio of cross sections measured with "hot" (~450 K) and "cold" (" 170 K) nozzles. Cross-hatched area represents the range of predicted values consistent with the large uncertainty in rotational temperature of Ref. 6. Doubly cross-hatched area is in agreement with the experimental values of Ref. 6. The experiments of Ref. 6 and those reported here are simultaneously in agreement for $n \sim 2$.

workers.[21] We suggest that rotation plays a role of comparable importance in the NO + O_3 reaction.

We have used an arbitrary model where the reactive cross section *increases* with J,

$$\sigma \propto E^n_{\mathrm{rot}} , \qquad (1)$$

and have averaged this over the rotational states calculated to be present with magnet on and magnet off to predict the increase in CL, $\Delta S/S^0$. Values of $\Delta S/S^0$ are calculated for various values of n and rotational temperatures and are shown in Fig. 5. This model has also been averaged over the rotational states for the conditions of Redpath *et al.*,[6] and the ratio of cross sections for hot and cold nozzle, σ_H/σ_C, is shown in Fig. 5. The rotational temperatures are taken to be the streaming temperatures of Ref. 4 and are 450 and 170 K.

From Fig. 5 it appears that a reactive cross section increasing with J roughly reproduces the results we have obtained (over a variety of possible beam temperatures) as well as those obtained under the different conditions of Redpath *et al.* In neither of these experiments is the distribution of rotational states well known, however, so the particular form of the rotationally dependent cross section should not be emphasized. These results merely show that the cross section increases with J and varies roughly as E^n_{rot}, where $n \sim 1.5-2.5$. Note that comparison between beam experiments and gas phase experiments will be difficult because rotation and translation are equilibrated in the gas.

The origin of such an effect is not clear. The CL cross section increases[8] with translation energy as $E^{3.75}_{\mathrm{trans}}$ so σ varies roughly as $E^2_{\mathrm{rot}} E^{3.75}_{\mathrm{trans}}$. Comparison of rotational and translation energy can be made in two ways. The increase in cross section for a unit change in rotational energy compared to the analogous quantity for translational energy yields

$$[\partial\sigma/\partial E_{\mathrm{rot}}]/[\partial\sigma/\partial E_{\mathrm{trans}}] \simeq 0.5\, E_{\mathrm{trans}}/E_{\mathrm{rot}} \simeq 50$$

and can be compared with Van den Ende and Stolte's value of 4.6 at somewhat higher energy.[8] This suggests that rotational energy is more efficient in initiating reaction than is translational energy, but fails to account for the large disparity in magnitude of the average energy in the two modes. It is more illustrative to compare instead the increase in cross section for a given *fractional* increase in energy,

$$[\partial\sigma/\partial f_{\mathrm{rot}}]/[\partial\sigma/\partial f_{\mathrm{trans}}]$$
$$=[E_{\mathrm{rot}}\, \partial\sigma/\partial E_{\mathrm{rot}}]/[E_{\mathrm{trans}}\, \partial\sigma/\partial E_{\mathrm{trans}}] \simeq 0.5 \ .$$

Apparently rotational energy is not quite as efficient in initiating reaction as is translational energy. A similar effect has been observed[22] for the endoergic reaction $K + CsF \rightarrow KF + Cs$: translation and rotation both increase the reactive decay of the complex, but translational energy is more efficient. On the other hand, translation and rotation are roughly equally effective[22] in decreasing the reactive decay of the complex for the exoergic reaction $K + RbF \rightarrow KF + Rb$. The reaction between NO and O_3 is exoergic and might therefore be expected to behave similarly to the K, RbF reaction where both translation and rotation are roughly equally effective. The analogy cannot be extended, however, because the crossed-beam studies of Valentini *et al.*[23] have shown that a long-lived complex is not formed.

VI. CONCLUSION

We have presented two alternative explanations of our data: either the lower Ω state is about five times more reactive than the upper or both Ω states are roughly equally reactive and the cross section increases with molecular rotation. (For simplicity, we assume no coupling.) We favor the second alternative for two reasons. (1) This provides a means of explaining both our experiments and those of Redpath *et al.* (2) The lower Ω state must correlate to the ground electronic state of the products.[6c] If the $\Omega = \frac{1}{2}$ state is to be five times more reactive in the CL reaction, there must be an avoided crossing with the $\Omega = \frac{3}{2}$ state at some point along the reaction coordinate. However, the two states are strongly mixed by the collision. The two states would consequently be expected to behave similarly, which is not consistent with a factor of 5 difference in reactivity. Even without such a crossing, the collision is expected to heavily perturb the two states, and it is unlikely that a significant difference in reactivity could persist.

We emphasize that no information has been obtained about the nonchemiluminescent channel.

ACKNOWLEDGMENTS

We acknowledge with thanks financial support from the Robert A. Welch Foundation, the National Science Foundation, and the Air Force Office of Scientific Research.

APPENDIX A: ZEEMAN EFFECT IN INTERMEDIATE COUPLING

In order to quantitatively interpret the focusing experiments, magnetic moments have been calculated numerically at 4 kG for intermediate coupling using Hill's equations[24] and the rotational parameters of Gallagher and Johnson.[25] Representative moments are shown in Table II, and they illustrate the mixing of the two states.[26] As the molecular rotation increases, Σ is no longer well defined and the lower state, labeled "Ω" $= \frac{1}{2}$ in case (a) coupling, acquires a significant magnetic moment. The two states can still be magnetically separated, however, because the magnetic moments are still different and also depend on M for a given state. Molecules focus if the moment is positive and defocus if the moment is negative. For a given J in the upper fs state, the magnitude of the focusing moment is larger than that for the defocusing moment, and more molecules will be focused than will be defocused. The opposite is true for the lower state, and the net result is a slight defocusing of that state. The flux of molecules in the beam in the upper state ("Ω" $= \frac{3}{2}$, or F_2 levels) will increase when the magnet is energized, and the flux in the lower state ("Ω" $= \frac{1}{2}$, or F_1 levels) is essentially unchanged, but decreases very slightly.

APPENDIX B: FOCUSING OF MOLECULES IN AN INHOMOGENEOUS MAGNETIC FIELD

A molecule in state J, M, Ω will enter the scattering cell if the displacement from the axis, r_3, at down stream distance l_3 is less than the radius of the scattering cell opening, r_{SC}. In the inhomogeneous field, each molecule experiences a radial force,

$$F_r = -\frac{\partial W}{\partial r} = -\frac{\partial W}{\partial H}\frac{\partial H}{\partial r} = -\mu\frac{\partial H}{m\partial r}\,, \tag{B1}$$

where W is the energy of the molecule and H the field intensity. The field is constructed so $\partial H/\partial r = 2H_0 r/r_0^2$,[13] where r_0 is the radius of the field and H_0 is the field intensity at the pole tips.

Solution of Newton's equation inside the field for negative μ gives

$$r = \dot{r}_1/\omega \sin\omega t + r_1 \cos\omega t\,, \tag{B2}$$

where r_1, $\mathring{r}_1$ are the radial position and radial speed at the field entrance, $\omega^2 = 2|\mu| H/(mr_0^2)$, and t is measured from the field entrance. (If μ is positive, molecules defocus and the hyperbolic functions sinh, cosh must replace sin, cos.)

After traversing the field free distance $l_{23} = l_3 - l_2$ in time $t = l_{23}/v$, the displacement of the molecule at the entrance of the SC is given by

$$r_3 = r_2 + \mathring{r}_2 t = \left(\frac{\dot{r}_1}{\omega} - r_1\theta\right)\sin\theta + \left(r_1 + \frac{\mathring{r}_1\theta}{\omega}\right)\cos\theta\,, \tag{B3}$$

where $\theta = \omega l_{23}/v$. If r_1 and $\dot{r}_1$ are expressed in terms of the incident angle α, we have $r_1 = l_1 \tan\alpha$ and $r_1 = v \sin\alpha$ (and $\tan\alpha \simeq \sin\alpha \simeq \alpha$), and we find that, in order for $r_3 \le r_{SC}$, the incident angle α must be less than α_0 where

$$\alpha_0 = \left| r_{SC}[(v/\omega - l_1\theta)\sin\theta + (l_1 + l_{23})\cos\theta]^{-1}\right|\,. \tag{B4}$$

Molecules incident with $\alpha \le \alpha_0$ enter the SC when the magnet is on, but only molecules with $\alpha \le \beta = r_{SC}/(l_1 + l_{12} + l_{23})$ enter when the magnet is off, where $l_{12} = l_2 - l_1$. The beam flux entering the SC is then given by

$$I_{on}/I_{off} = \alpha_0^2/\beta^2$$

or

$$\Delta I/I_{off} = (I_{on} - I_{off})/I_{off} = (\alpha_0^2 - \beta^2)/\beta^2\,. \tag{B5}$$

If the molecule is in a defocusing state (μ is positive), Eq. (B4) becomes

$$\alpha_0 = r_{SC}[(v/\omega + l_1\theta)\sinh\theta + (l_1 + l_{23})\cosh\theta]^{-1}\,. \tag{B6}$$

Equations (B5) remain unchanged but, since $\alpha_0 < \beta$ for defocusing states, $\Delta I/I$ is a negative number and reflects a decrease in intensity.

For large θ Eq. (B4) predicts α_0 to be so large that molecules hit the pole tips. In this case, the maximum incident angle allowing molecules to enter the SC is that for which the maximum excursion from the axis is equal to the radius of the field and is given by

$$\alpha_1 = r_0[(v/\omega)\sin\delta + l_1\cos\delta]^{-1} \tag{B7}$$

where $\delta = \tan^{-1}(v/l_1\omega)$.

To compare with experiment, it is necessary to average over all states present. This yields

$$\frac{I_{on}}{I_{off}} = \beta^{-2}\int_v f(v)\sum_J \sum_{M=-J}^{+J} \alpha_i^2(J, M, \Omega, v)\, g(J, M)\, dv\,, \tag{B8}$$

where α_i is the lesser of α_0, α_1, or α_2 (where α_2 is the half-angle of collimation of the beam entering the magnet, ~0.3°) and is calculated from Eqs. (5), (6), or (7) as appropriate. The fraction of molecules in state J, M, is $g(J, M)$ and is assumed thermal at T_{rot}. The speed distribution $f(v)$ is assumed to be[16]

$$f(v) = C(v/v_s)^2 \exp[(v - v_s)s/v_s]^2\,,$$

where $s = v_s/(2kT_{\mathrm{trans}}/m)^{1/2}$, a distribution centered on the nominal rms speed of the seed gas, $v_s = (3kT_s/M_s)^{1/2}$ of mass M_s and stagnation temperature T_s. Magnetic moments are calculated as described in Appendix A.

Rotational distributions for transmitted molecules are obtained by normalizing the probability of transmission for a given J, $P(J)$,

$$P(J) = \beta^{-2} \int_V f(V) \sum_{M=-J}^{+J} \alpha_i^2(J, M, \Omega, V)\, g(J, M)\, dv \; , \qquad \text{(B9)}$$

by $P_{\mathrm{rot}} = \sum p(J)$ given by Eq. (B8).

APPENDIX C: ESTIMATION OF FRACTION OF MOLECULES WITH $\Omega = \frac{3}{2}$

In order to quantitatively assess the relative reactivity of the two fs states, we must somehow estimate $f_{3/2}$, and we proceed as follows: the fraction of molecules focused for a given state, F_Ω, is calculated (see Appendix B for details) for each Ω, M, J, and v, and then averaged over *assumed* distributions of J and v characterized by rotational, T_{rot}, and translational, T_T, temperatures. Values of F for a variety of conditions are given in Table III. Note that $F_{1/2}$ is always small and negative (i.e., the lower state defocuses). The increase in beam intensity is due solely to molecules in the "Ω" $= \frac{3}{2}$ state. Once $F_{1/2}$ and $F_{3/2}$ have been calculated, $f_{3/2}$ may be calculated in terms of T_{rot} and T_T because

$$\Delta I/I_0 = (I_{3/2}^H + I_{1/2}^H)/(I_{3/2}^0 + I_{1/2}^0)$$
$$= (F_{3/2}R + F_{1/2})/(R+1) \; ,$$

where $R = f_{3/2}/f_{1/2} = I_{3/2}^0/I_{1/2}^0$ and $F_\Omega = I_\Omega^H/I_\Omega^0$. As might be expected, $f_{3/2}$ depends on the assumed value of T_R but depends only weakly on T_T. As expected, the electronic degrees of freedom are also cooled, but T_e lags T_{rot}.

The correct choice for T_R is not clear. The terminal temperature[16] for our nozzle expansion conditions is ~7 K corresponding to Mach number $M = 17$. Actual velocity measurements in a similar apparatus yielded $M = 10$ for HCl,[27] which suggests that a more conservative Mach number is appropriate. However, even with $M = 10$, the terminal temperature is 17 K, suggesting that while T_R is not known, it is likely to be ~20 K. As it turns out, T_R has only a mild influence on the reactivity ratio $Q = \sigma_{3/2}/\sigma_{1/2}$. The fractional increase in CL, $\Delta S/S_0$ is given by

$$\frac{\Delta S}{S_0} = \frac{(\sigma_{3/2} I_{3/2}^H + \sigma_{1/2} I_{1/2}^H)}{(\sigma_{3/2} I_{3/2}^0 + \sigma_{1/2} I_{1/2}^0)} = \frac{(QF_{3/2}R + F_1)}{(QR+1)} \; .$$

TABLE III. Calculated magnetic field transmission characteristics.

T_R	$F_{3/2}$	$F_{1/2}$	R	$f_{3/2}$	T_e	Q
20	0.301	−0.002	0.470	0.320	120	0.216
30	0.270	−0.004	0.564	0.361	138	0.216
50	0.225	−0.008	0.794	0.443	188	0.217
60	0.210	−0.011	0.923	0.480	225	0.218
70	0.198	−0.014	1.055	0.513	272	0.219
80	0.189	−0.017	1.18	0.542	332	0.221
100	0.179	−0.028	1.409	0.585	497	0.228
200	0.192	−0.055	1.54	0.606	666	0.215

TABLE IV. Effect of beam speed distribution on reactivity.

T_b	T_{rot}	$F_{3/2}$	E
20	10	0.351	0.345
	20	0.312	0.306
	30	0.280	0.274
	50	0.234	0.228
	100	0.187	0.182
40	10	0.351	0.340
	20	0.311	0.301
	30	0.279	0.268
	50	0.233	0.223
	100	0.186	0.177
50	10	0.353	0.340
	20	0.313	0.301
	30	0.281	0.268
	50	0.234	0.222
	100	0.187	0.175
100	10	0.350	0.330
	20	0.310	0.287
	30	0.277	0.254
	50	0.231	0.208
	100	0.185	0.163

Q is given in Table III for several choices of T_R. Fortunately, Q is quite insensitive to our assumptions about T_R and from $Q \simeq 0.2$ we find the *lower* state is approximately five times *more* reactive than the upper state.

Before we can properly interpret Q, we must point out that the $\Omega = \frac{3}{2}$ molecules focused by the field have a slightly different distribution of speeds and rotational states than do the molecules transmitted with the magnet off. The magnet preferentially focuses slow molecules and those in low rotational states.

As long as the initial speed distribution is narrow ($T_T \lesssim 100$ K), the final speed distribution is changed very slightly. The reactive cross section is strongly dependent on speed ($\sigma \propto v^{7.5}$),[6,8] and we have averaged this cross section over the final speed distribution to calculate E, the enhancement expected in CL (assuming CL depends only on speed) when the magnet is energized. Values of E are listed in Table IV for various combinations of beam parameters for the upper state. For almost all cases of interest, E is sufficiently close to the predicted increase in beam intensity that it is not necessary to consider the modified speed distribution further.

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