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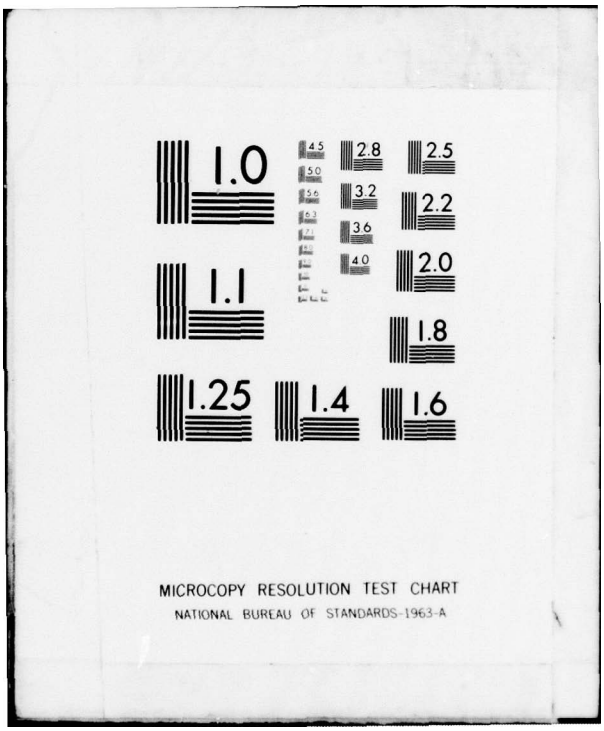
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(6) Reactions and Energy Transfer of Excited Molecules

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REACTIONS AND ENERGY TRANSFER OF EXCITED MOLECULES

Final Report

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Chemical reactions almost always proceed more rapidly when the reagents are heated, and the rate usually increases exponentially with temperature according to the Arrhenius Law, $R \propto A \exp(-E_a/RT)$. The constant E_a, the "activation energy", has become so much a part of modern kinetics that it is usually mystically regarded as the energy required to bring the reagents into some critical configuration.

Theoretical interpretation of E_a is incomplete even though Tolman showed many years ago for systems in quasi-equilibrium that E_a was the difference in the average energy of reacting molecules and the average energy of all molecules. In order to probe the nature of the "activation energy" and the "activation" process itself, we have initiated a program whereby we seek to study different ways to activate a reaction.

The time-honored method of measuring activation energies has been to measure the rate of reaction (the rate constant, actually) in a bulk phase medium (usually gas or liquid) as a function of temperature. Most reactions are sufficiently slow compared to energy transfer processes that the bulk medium can be considered to be in Boltzmann equilibrium with respect to its internal degrees of freedom. Heating the sample, consequently, increases the average energy stored in translational [T], rotational [R], vibrational [V], and electronic states [E]. By studying reactions in crossed molecular beams where there are no equilibrating collisions we are

able to break out of the confines of Boltzmann equilibrium and study separately the effects of T, R, V, or E in activating a reaction. These studies certainly offer us an opportunity to probe the activation process, but they also provide information about the practical behavior of systems which are not in equilibrium. These non-equilibrium states exist in flames, electric discharges, and in laser media, and, of course, can be produced by laser irradiation.

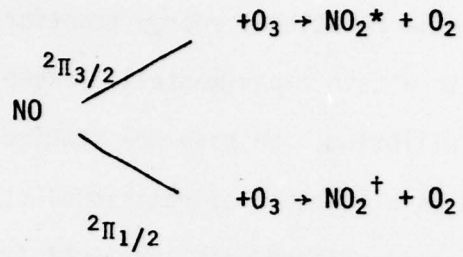
For our initial studies we have chosen the prototype chemical reaction $K + HCl \rightarrow KCl + H$. This reaction appeared to have a small (~2 Kcal/mole) activation energy, and laser excitation of the HCl vibration was possible with the resonant HCl chemical laser. (The reagents are cheap and easily produced and the products can be detected as well.) We had previously shown that one quantum of HCl vibration (8.3 Kcal/mole) increased the probability of reaction ~100 X over that of the ground vibrational state at the same speed. In a complementary experiment we investigated the effect of translational energy [T] on reaction for the ground vibrational state. We found that reaction probability increased a factor of only ten for a total energy comparable to the vibrational excitation experiments. There is thus a real <u>dynamical</u> difference between adding energy ("activating") in [T] or in [V].

When we attemped to increase [T] beyond 12 Kcal/mole it was necessary to heat the nozzle. These measurements showed reaction probability decreasing at higher [T], but they also showed some scatter which we suspected might be due to effects from different rotational states.

Rotational state effects on chemical reactions have largely been ignored, mainly because the rotational levels are so closely spaced that energies are essentially the same on a chemical scale. This close spacing

also makes for very facile rotational energy transfer and rotational disequilibrium is harder to attain experimentally (except for very high J) than vibrational disequilibrium. We have now studied the reaction $K + HCl(V=1) \rightarrow KCl + H$ as a function of rotational state of the HCl. The molecular beam of HCl is irradiated with the light from a CW-HCl chemical laser grating-selected to oscillate on a single P-branch transition. We find no discernable difference in reaction mechanism (kinematic effects make this a weak conclusion), but we find a large dependence of reaction probability on J: one quantum of rotation decreases the reaction probability about a factor of 2! (The energy difference between J = 1 and J = 2 is 40 cm^{-1} or 0.1 Kcal/mole.) This is a much larger effect than had been anticipated and is not at all understood. We are presently seeking to extend these measurements to higher J states and to study the effect of orienting the plane of rotation during the collision (by polarizing the laser light).

Considerable effort has been expended recently in the search for a visible electronic transition chemical laser. This requires an electronic state population inversion, and criteria are not well developed for determining which different electronic states will be formed. There is consequently great practical interest in the role played by electronic excitation of reagents. Electronic excitation of our prototype reaction K + HCl is possible but difficult (K^* could be prepared but a cw laser is not presently available to us). We have consequently focussed our attention on a different reaction, $NO + O_3 \rightarrow NO_2 + O_2$. This reaction had been reported to proceed via two different paths depending on the initial electronic state of NO:



where NO_2^* denotes electronically excited (and visibly chemiluminescent) NO_2 in the $^2B_2$ or $^2B_1$ electronic state and $NO_2^\dagger$ denotes vibrationally excited NO_2 in the $^2A_1$ ground state. These two routes were alleged to be determined by the NO fine structure state, $^2\Pi_{1/2}$ or $^2\Pi_{3/2}$. This was indeed tantalizing because the energy spacing is only 121 cm^{-1}, and if such a unique branching were to occur, we would have a clear-cut opportunity to unravel the dependence of reactivity upon energy and electronic state.

We have produced molecular beams of NO which have been enriched in the upper fs component, $^2\Pi_{3/2}$. This beam then reacts with ozone contained in a scattering cell and we observe the chemiluminescent product NO_2^*. We find that the beam intensity can be increased but that there is no corresponding increase in chemiluminescence. We are forced immediately to conclude that $^2\Pi_{3/2}$ is <u>not</u> more reactive than the lower $^2\Pi_{1/2}$ state. Our data can actually be interpreted to mean that the lower state is more reactive, but this is not compatible with previous observations that chemiluminescence increases as NO is heated. All of these observations can be reconciled if we assume that the electronic states are <u>equally</u> reactive and that the reactivity increases with rotational state. (Details of the experiments and interpretation can be found in the attached preprint.)

These two experiments show that rotational effects in chemical reaction are extremely important.

Publications

"Molecular Beam Reaction of K with HCl: Effect of Rotation of HCl", H. H. Dispert, M. W. Geis, and P. R. Brooks, J. Chem. Phys. 70, 5317 (1979).

"Reaction of Magnetically-State Selected NO with O_3: Effect of fs States and Rotational States on Reactivity", S. L. Anderson, P. R. Brooks, J. D. Fite, and O. V. Nguyen, J. Chem. Phys. (Submitted for Publication).

REACTION OF MAGNETICALLY - STATE SELECTED NO WITH O_3: EFFECT OF fs STATES AND ROTATIONAL STATES ON REACTIVITY

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Abstract

The visible chemiluminescent channel of the $NO + O_3 \rightarrow NO + O_3$ 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. Both fs states are present in the beam, but 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 less, and shows that the upper state is not solely responsible for chemiluminescence. The magnetically selected molecules are rotationally cooler than the unselected molecules and the small increase in chemiluminescence is interpreted to suggest that both fs states are equally reactive, but that the reactive cross section increases rapidly with rotational state.

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Introduction

Most chemical reactions proceed on the lowest potential surfaces of the system, principally because chemical energies are small in comparison to energies usually required to populate excited electronic states. Exceptions to this rule are extraordinarily important and include flame processes as well as photosynthesis. These processes are of great current interest[1] because a variety of experimental techniques have recently become available for the study or the stimulation of reaction on excited surfaces. Considerable interest revolves around lasers, of course, since it may be possible to produce reagents in specific states, or conversely, find chemical reactions which would be suitable sources for a visible chemical laser.

Despite interest in these processes, the ability to predict the dominant path of an electronically non-adiabatic reaction is quite limited.[2] Several reactions involving excited (spin-orbit) states of atoms have been studied,[3] but as long as the reaction is exoergic, there seems no clear-cut guide as to which states are most efficient in initiating reaction. In order to divorce energy considerations from the role played by electronic state symmetry, we have studied the effect of NO fine structure states on the very exoergic reaction $NO + O_3 \rightarrow NO_2^* + O_2$, where NO_2^* denotes NO_2 in the $^2B_1$ or $^2B_2$ excited electronic state. The separation between fs states, 121 cm^{-1}, is small compared to the exoergicity to form ground state products, 16,800 cm^{-1}(48 Kcal/mole), and one might expect on energetic grounds that the two fs components would display equal reactivity. However, on symmetry grounds, the $\Omega = 1/2$ state might be expected [4c] to yield mainly ground state NO_2, and by implication,

Ω = 3/2 NO might be primarily responsible for NO_2^* formed. This suggestion has indeed been advanced by several workers.[4,10]

In many respects the reaction of NO with O_3 is an enigma:

(i) The reaction appears to proceed[5] via two channels,

$$NO + O_3 \begin{cases} \rightarrow NO_2^* + O_2 \\ \rightarrow NO_2^\dagger + O_2 \end{cases}$$

where NO_2^*($^2B_1$ or $^2B_2$) chemiluminesces in a broad region from ~500 nm - ~2500 nm and $NO_2^\dagger$ denotes vibrationally excited NO_2 which emits in the infrared. Whether or not two separate channels actually exist is controversial due to the extensive mixing[6] of the $^2B_2$ NO_2 states with excited vibrational levels of the $^2A_1$ ground state. Nevertheless, Redpath, et al.,[4] have extensively studied the energy dependence of (1a) and (1b) in beam-gas experiments and have found different translational energy dependences. They also found that increasing the internal energy of NO (at constant translational energy) increased the chemiluminescence (CL) which they interpreted to suggest that the upper fs state, $^2\Pi_{3/2}$, was the main precursor to NO_2^*.

(ii) Electronically excited states of O_2($^1\Delta_g$ and $^1\Delta_g$) are energetically accessible and permitted by symmetry, but they account for less than 0.5% of reaction.[7]

(iii) Vibrational excitation of O_3 accelerates reaction,[8] but so does vibrational excitation of NO[9]. (Only the Ω = 3/2 state of NO can be vibrationally pumped by Zeeman tuning to a CO laser line. The experiments of ref. 9 thus suggest that Ω = 3/2 reacts, but no comparison between Ω = 3/2 and Ω = 1/2 can be made.)

The suggestion that the CL reaction cross section is highly dependent on fs state is surprising, even in light of the complexity of the reaction. We have, therefore, performed an experiment to directly measure the difference in reactivity of the NO fs states in producing NO_2^*. Our results do not support the view that reactivity is restricted to only one fs level.

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 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[4] for the reaction is 3.2 Kcal/mole and the cross section increases drastically with energy,[4,10] the NO (Matheson, C.P.) is accelerated to an average collision energy[11] of 6.5 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 (SC) containing ozone (prepared according to Clough and Thrush)[12] at room temperature and at a pressure sufficient to attenuate the NO beam ~50%, typically $\sim 5 \times 10^{-4}$ 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 gauss) 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[13] from six pole pieces 28 cm long symmetrically spaced about a circular gap 3 mm dia. Current and cooling water are carried by 3 mm copper tubing insulated with fiber-glass sleeves wound around each pole piece so that adjacent poletips have opposite polarity. This produces a magnetic field of 7 Kgauss measured at the pole tips for a current of 67A per pole. The field has a minimum on the axis and increases in magnitude as r^2, which insures that molecules with a first order Zeeman effect are focused.

Zeeman Effect

For low rotational states, NO is well described by Hund's case (a) coupling.[14] The spin angular momentum is coupled to the field along the internuclear axis, and has component along the axis, $\Sigma = 1/2$. 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 1/2 or 3/2. The angular momentum of rotation of the molecule, O, adds vectorially to Ω to form $\underset{\sim}{J}$, the total angular momentum exclusive of nuclear spin.

A molecule in an inhomogeneous field experiences a force[15] $F = -\nabla W$, where $W = \underset{\sim}{\mu}\cdot\underset{\sim}{H}$ is the energy of interaction between the molecule and the magnetic field, which is quite different for $\Omega = 1/2$ and $\Omega = 3/2$. In the $\Omega = 1/2$ 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 $W \simeq 0$. But for the $\Omega = 3/2$ state these moments add, giving a magnetic moment comparable to the Bohr magneton. If this moment is averaged over rotation,[14] $W = -3\mu MH/[J(J+1)]$. Molecules with $\Omega = 1/2$ are therefore undisturbed by the field, but molecules with $\Omega = 3/2$ can be deflected. Molecules in the magnetic six-pole field are deflected toward the axis and focused if $M < 0$. They are defocused for $M > 0$. A beam defining aperature allows only the small central protion of the beam to enter the scattering cell. Only those molecules in this small central portion can defocus, but molecules in a much larger annular ring (depending on field and state) can focus, so the focused molecules can considerably outweigh those which defocus. As a consequence, both the $\Omega = 1/2$ and $\Omega = 3/2$ states will enter the SC when the magnet is off. When the magnet is energized the $\Omega = 3/2$ flux is increased because more molecules are focused than are defocused, but the $\Omega = 1/2$ flux is unaffected.

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. Fortunately, due to rotational cooling in the nozzle expansion, this is only a minor effect. However, in order to quantitatively interpret the focusing experiments, magnetic moments have been calculated numerically

at 4 kG for intermediate coupling using Hill's equations[16] and the rotational parameters of Gallagher and Johnson.[17] Representative moments are shown in Table II, and illustrate the mixing of the two states.[18] As the molecular rotation increases, Σ is no longer well defined and the lower state, labeled "Ω" = 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" = 3/2, or F_2 levels) will increase when the magnet is energized and the flux in the lower state ("Ω" = 1/2, or F_2 levels) is essentially unchanged, but decreases very slightly.

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, respectively. Pure NO shows a greater enhancement in beam intensity because the molecules are slower and are more easily deflected since they spend more time in the field. 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,[19] 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.[11] In addition, the monatomic helium acts as a refrigerant[20] and quite effectively cools the internal degrees of freedom of NO. Using Anderson and Fenn's values for terminal Mach numbers[21] we calculate a terminal temperature $T_T \sim 7K$ for the NO in our experiments expanding from a 573K oven. Presumably $T_{rot} \gtrsim T_T$ and $T_e > T_{rot}$ where T_{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 the next section, 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[22] to be small (<10%), presumably due to the hydrodynamic defocusing of the light carrier[23] and the low ionization cross section for He.[24] The values in Fig. 2, therefore, represent lower limits to the fraction 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.(300-573K) No significant difference among these runs was evident. The most reliable data were accumulated at 250 torr and 573K, and yield a fractional increase in CL of $\Delta S/S^0 = .026 \pm .006$, (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 sensitivity 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.

Disscussion

The increase in chemiluminescence observed when the magnet is energized (2.6 ± .6)% (99% C.L.) 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. If molecules in the two fs states were equally reactive, the CL would increase 9.5%. On the other hand, if all CL were due to reaction of molecules in the upper fs state as proposed by Redpath, et al., the CL would increase by $9.5/f_{3/2}$% where $f_{3/2}$ is the fraction of upper fs state ("Ω" = 3/2) molecules in the beam transmitted when H = 0. If there is no electronic cooling $f_{3/2}(573K) = 0.6$ and a 16% increase in CL is expected. As discussed in the previous section, electronic relaxation occurs readily, $f_{3/2}$ is reduced considerably below 0.6, and the CL is expected to increase much more than 16% provided that only upper state molecules react. Since the observed CL increase is significantly less, we conclude that reaction is not restricted to NO molecules in the upper state. In fact, if we assume that only fs state is important in determining reaction to NO_2^*, our data indicate that NO $^2\Pi_{1/2}$ is at least five times more reactive than the $^2\Pi_{3/2}$ state. Details of the data reduction are in appendix B.

Previous workers[4,10] have studied the effect of internal energy on the CL channel reactivity and have concluded just the opposite: that $^2\Pi_{3/2}$ is much more reactive than $^2\Pi_{1/2}$. In their experiments, however,

the NO fs populations were varied by heating the nozzle. This also has the effect of raising the rotational temperature. Redpath, et al.,[4a] discussed the possibility that the NO rotational temperature was affecting the CL reaction, but rejected it as implausible.

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 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 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 <u>equal</u> reactivity and attribute all of our observations to variation of reactivity with rotational state. This alternative was discounted by Redpath, et al.[4] largely because the rotational effects on reaction known at the time were too small. But we have recently observed large rotational effects in the (crossed-beam) reaction K + HCl → KCl + H where the HCl was laser excited to different rotational levels of the V=1 state.[25] For the first few J levels the cross section decreases roughly a factor of two per rotational state. Similar effects have been observed in the CL depletion studies of Polanyi and co-workers.[26] Rotation could, then, play 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,

$$\sigma \propto E^{n}_{rot} \qquad (1)$$

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.,[4] 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 450K and 170K.

From Fig. 5 it appears that a reactive cross section increasing with J roughly reproduces the results we have obtained, 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_{rot}^{n}, where n ~1.5 -2.5.

The origin of such an effect is not clear. The CL cross section increases with translational energy as $E_{trans}^{3.75}$, so apparently rotational energy is not quite as efficient in initiating reaction as is translational energy. A similar effect has been observed[27] for the endoergic reaction K + CsF → 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 in decreasing the reactive decay of the complex for the exoergic reaction K + RbF → KF + Rb. The reaction between NO and O_3 would be classed as endoergic at room temperature, but the analogy cannot be extended because the crossed beam studies of Valentini, et al.,[28] have shown that a long-lived complex is not formed. Molecules in higher rotational states bring

more rotational angular momentum into the collision, but this is small compared to the orbital angular momentum (~12h for E ≃ 7 Kcal/mole and $\sigma \sim .2\mathring{A}^2$).

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. If the $\Omega = 1/2$ state is to be five times more reactive in the CL reaction, there must be an avoided crossing with the $\Omega = 3/2$ state at some point along the reaction coordinate. But 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 five 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 non-chemiluminescent channel.

Acknowledgements

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APPENDIX A

Focusing of Molecules in an Inhomogeneous Magnetic Field

A molecule in state J, M, Ω will enter the scattering cell (SC) 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,

$$F_r = -\frac{\partial W}{\partial r} = -\frac{\partial W}{\partial H}\frac{\partial H}{\partial r} = -\mu\frac{\partial H}{m\partial r} \qquad A1$$

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

$$r = \dot{r}_1/\omega \sin \omega t + r_1 \cos \omega t \qquad A2$$

where r_1, $\dot{r}_1$ 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 defocuse and the hyperbolic functions sinh, cosh must replace sin, cos.)

After traversing the field free distance $\ell_{23} = \ell_3 - \ell_2$ in time $t = \ell_{23}/v$ the displacement of the molecule at the entrance of the SC is given by

$$r_3 = r_2 + \dot{r}_2 t = (\frac{\dot{r}_1}{\omega} - r_1\theta)\sin\theta + (r_1 + \frac{\dot{r}_1\theta}{\omega})\cos\theta \qquad A3$$

where $\theta = \omega\ell_{23}/v$. If r_1 and $\dot{r}_1$ are expressed in terms of the incident angle α, we have $r_1 = \ell_1 \tan\alpha$ and $r_1 = v \sin\alpha$ (and $\tan\alpha \approx \sin\alpha \approx \alpha$) and find that in order for $r_3 \leq r_{sc}$, the incident angle α must be less than α_0 where

$$\alpha_0 = |r_{sc}[(v/\omega - \ell_1\theta)\sin\theta + (\ell_1 + \ell_{23})\cos\theta]^{-1}| \qquad A4$$

Molecules incident with $\alpha \leq \alpha_0$ enter the SC when the magnet is on, but

only molecules with $\alpha \leq \beta = r_{sc}/(\ell_1 + \ell_{12} + \ell_{23})$ enter when the magnet is off, where $\ell_{12} = \ell_2 - \ell_1$. The beam flux entering the SC is then given by

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

or

$$\Delta I/I_{off} = (I_{on} - I_{off})/I_{off} = (\alpha_0^2 - \beta^2)/\beta^2 \qquad \text{A5}$$

If the molecule is in a defocusing state (μ is positive) eqn A4 becomes

$$\alpha_0 = r_{sc}[(v/\omega + \ell_1\theta)\sinh\theta + (\ell_1 + \ell_{23})\cosh\theta]^{-1} \qquad \text{A6}$$

Eqns A5 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 A4 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

$$\alpha_1 = r_0[(v/\omega)\sin\delta + \ell_1\cos\delta]^{-1} \qquad \text{A7}$$

where $\delta = \tan^{-1}(v/\ell_1\omega)$.

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

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

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 Eq 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 adequately given by[21]

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

where $s = v_s/(2kT_{trans}/m)^{1/2}$, a distribution centered on the nominal rms

speed of the seed gas, and $V_s = (3KTs/Ms)^{\frac{1}{2}}$ and characterized by a (low) translational temperature T_s.

APPENDIX B

Estimation of Fraction of Molecules with $\Omega = 3/2$

In order to more 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 A 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" = 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

$$\Delta I/I_0 = (I^H_{3/2} + I^H_{1/2})/(I^0_{3/2} + I^0_{1/2}) = (F_{3/2}R + F_{1/2})/(R + 1)$$

where $R = f_{3/2}/f_{1/2} = I^0_{3/2}/I^0_{1/2}$ and $F_\Omega = I^H_\Omega/I^0_\Omega$. 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[21] for our nozzle expansion conditions is ~7K corresponding to Mach number M = 17. Actual velocity measurements in a similar apparatus yielded M = 10. for HCl[29] which suggests that a more conservative Mach number is appropriate. But even with M = 10, the terminal temperature is 17K, suggesting that while T_R is not known, it is likely to be ~20K. 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

$$\Delta S/S_0 = (\sigma_{3/2} I^H{}_{3/2} + \sigma_{1/2} I^H{}_{1/2})/\sigma_{3/2} I^0{}_{3/2} + \sigma_{1/2} I^0{}_{1/2})$$

$$= (QF_{3/2}R + F_1)/(QR + 1)$$

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 ~five times more reactive than the upper state.

Before we can properly interpret Q, we must digress slightly to point out that the $\Omega = 3/2$ 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 ($T_T \lesssim 100K$), the final speed distribution is changed very slightly. The reactive cross section is strongly dependent on speed ($\sigma \propto v^{7.5}$),[10] 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.

TABLE I

Apparatus Dimensions (mm)

Distances		Diameters	
Nozzle - Skimmer	19	Nozzle	0.25
Nozzle - Collimator	180	Skimmer	1.0
Nozzle - Magnet Exit	460	Collimator	2.5
Nozzle - SC Entrance	524	Magnet Gap	3.2
		SC Entrance	3.2
		SC Exit	5.1

TABLE II

Representative Magnetic Moments in Bohr Magnetons

(Calculated at 4kgauss)

	"Ω = 3/2"			"Ω = 1/2"		
J	M = -J	M = +J	M (case a)	M = +J	M = -J	M (case a)
1/2	--	--	--	0	0	0
3/2	-1.164	1.167	1.2	-.035	.034	0
5/2	- .786	.797	.86	-.068	.062	0
7/2	- .560	.583	.67	-.103	.087	0
9/2	- .399	.443	.55	-.139	.110	0
11/2	- .273	.345	.46	-.177	.129	0
13/2	- .164	.274	.40	-.217	.126	0
15/2	- .066	.223	.35	-.287	.130	0

TABLE III

Calculated Magnetic Field Transmission Characteristics

T_R	$F_{3/2}$	$F_{1/2}$	R	$f_{3/2}$	T_e	Q
20	.301	-.002	.470	.320	120	.216
30	.220	-.004	.564	.361	138	.216
50	.225	-.008	.794	.443	188	.217
60	.210	-.011	.923	.480	225	.218
70	.198	-.014	1.055	.513	272	.219
80	.189	-.017	1.18	.542	332	.221
100	.179	-.028	1.409	.585	497	.228
200	.192	-.055	1.54	.606	666	.215

TABLE IV

Effect of Beamspeed Distribution on Reactivity

T_b	T_{rot}	$F_{3/2}$	E
20	10	.351	.345
	20	.312	.306
	30	.280	.274
	50	.234	.228
	100	.187	.182
40	10	.351	.340
	20	.311	.301
	30	.279	.268
	50	.233	.223
	100	.186	.177
50	10	.353	.340
	20	.313	.301
	30	.281	.268
	50	.234	.222
	100	.187	.175
100	10	.350	.330
	20	.310	.287
	30	.277	.254
	50	.231	.208
	100	.185	.163

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Figure Captions

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 $\Omega = 3/2$ molecules are focused into the SC. Defocused molecules do not enter the SC and are not shown. (Deflections are greatly exaggerated.)

Fig. 2 - Fractional change in NO beam intensity on energizing the focusing magnet as a function of stagnation pressure and nozzle temperature. For pure NO measurements were made at higher stagnation pressures than shown on figure.

Fig. 3 - Chemiluminescent signal with magnet on and off.

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.

Fig. 5 - a) Increase in CL calculated by assuming $\sigma \propto E_{rot}^{n}$ and convoluting over rotational distributions shown in Fig. 4. Curvature at high rotational temperatures is due to some high-J molecules. (See Table II). The experimental range of $\Delta S/S^0$ lies within the horizontal dashed lines.

b) Ratio of cross section for NO from "hot" nozzle to "cold" for the conditions of ref. 4 calculated by convoluting eqn (1) over thermal distributions of NO at ~450K and ~170K. Dashed curved lines reflect the large uncertainty in rotational temperatures, and observed cross section ratios of ref. 4 are contained within the horizontal dashed lines.

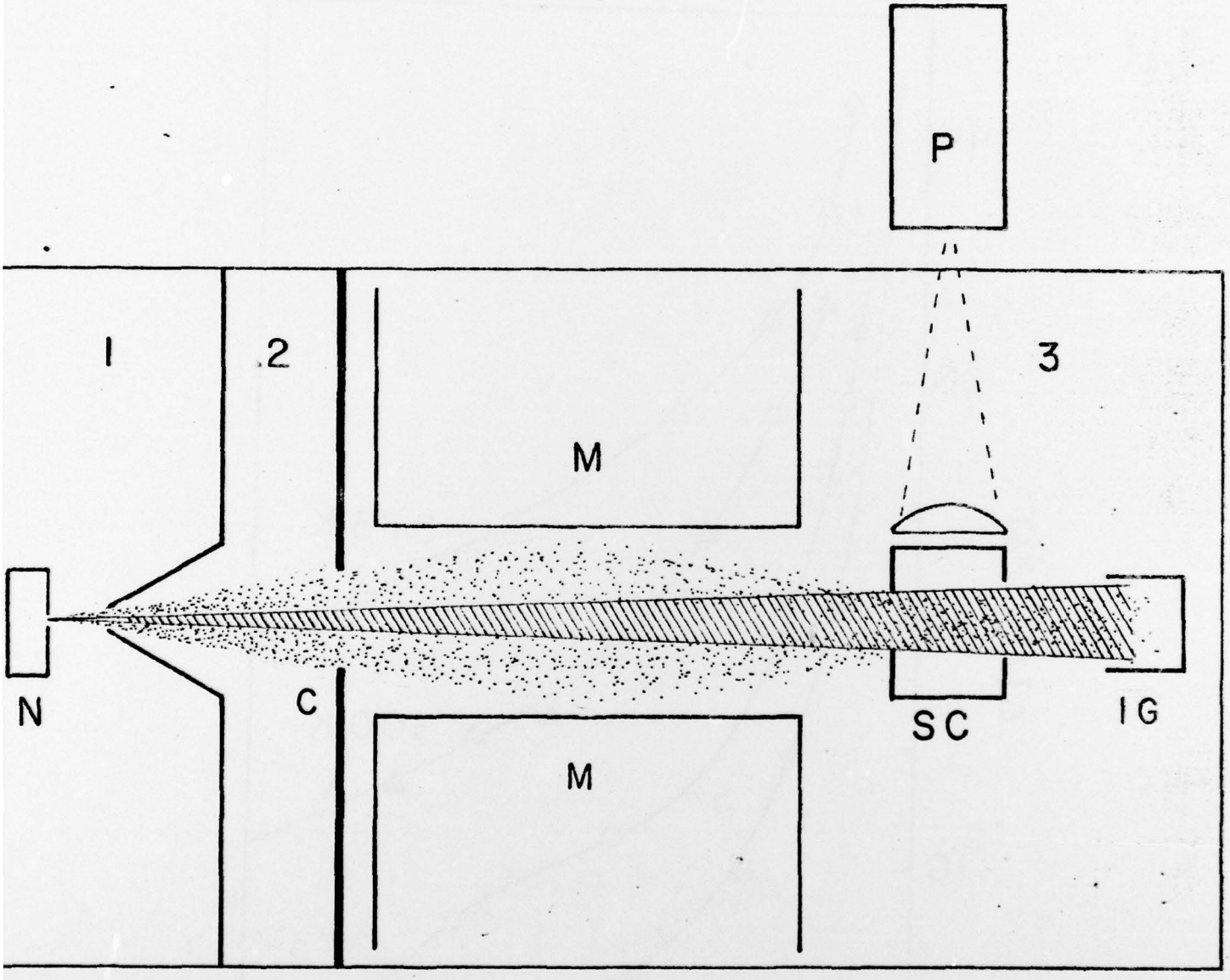

Fig 1
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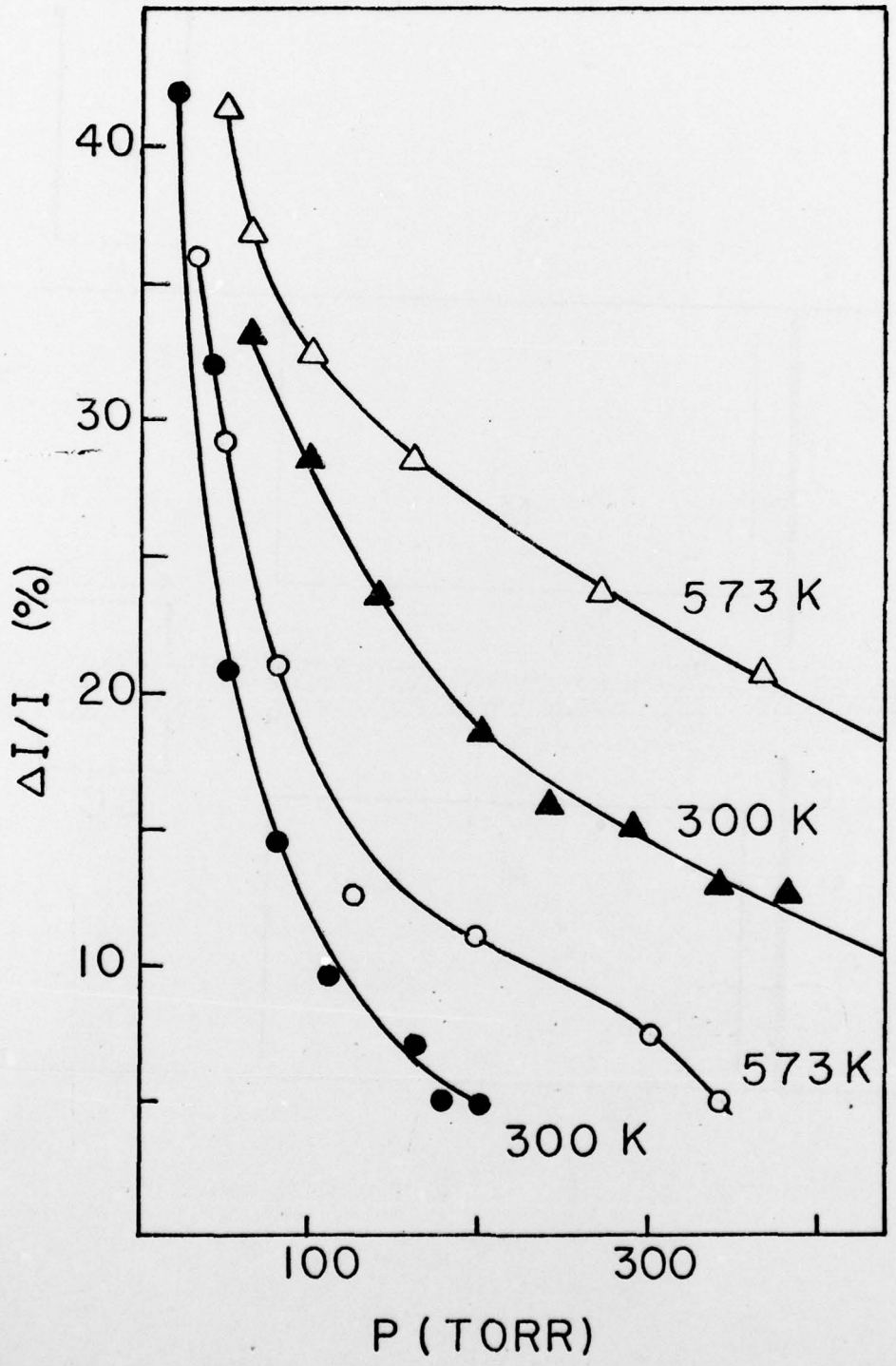
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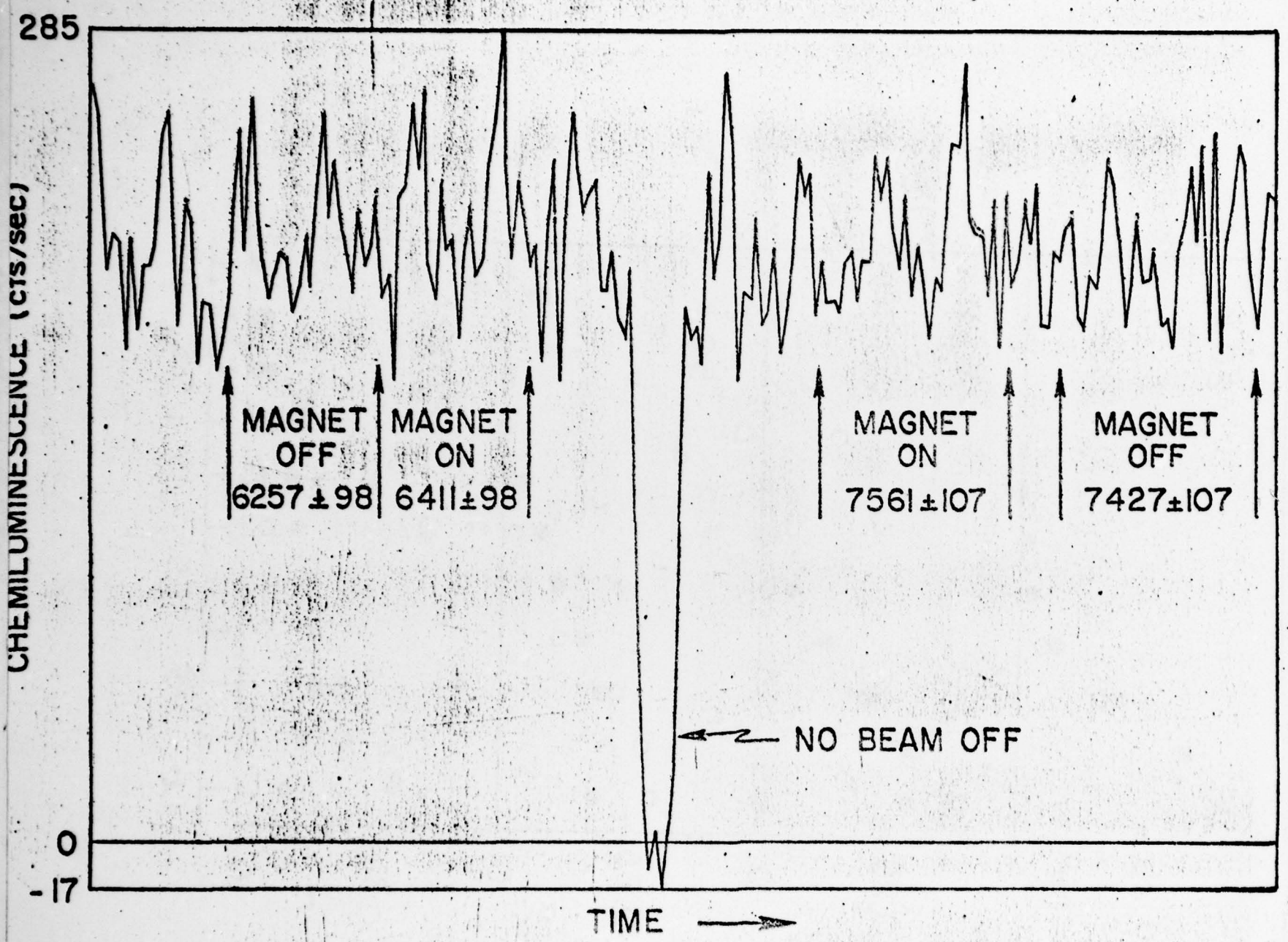
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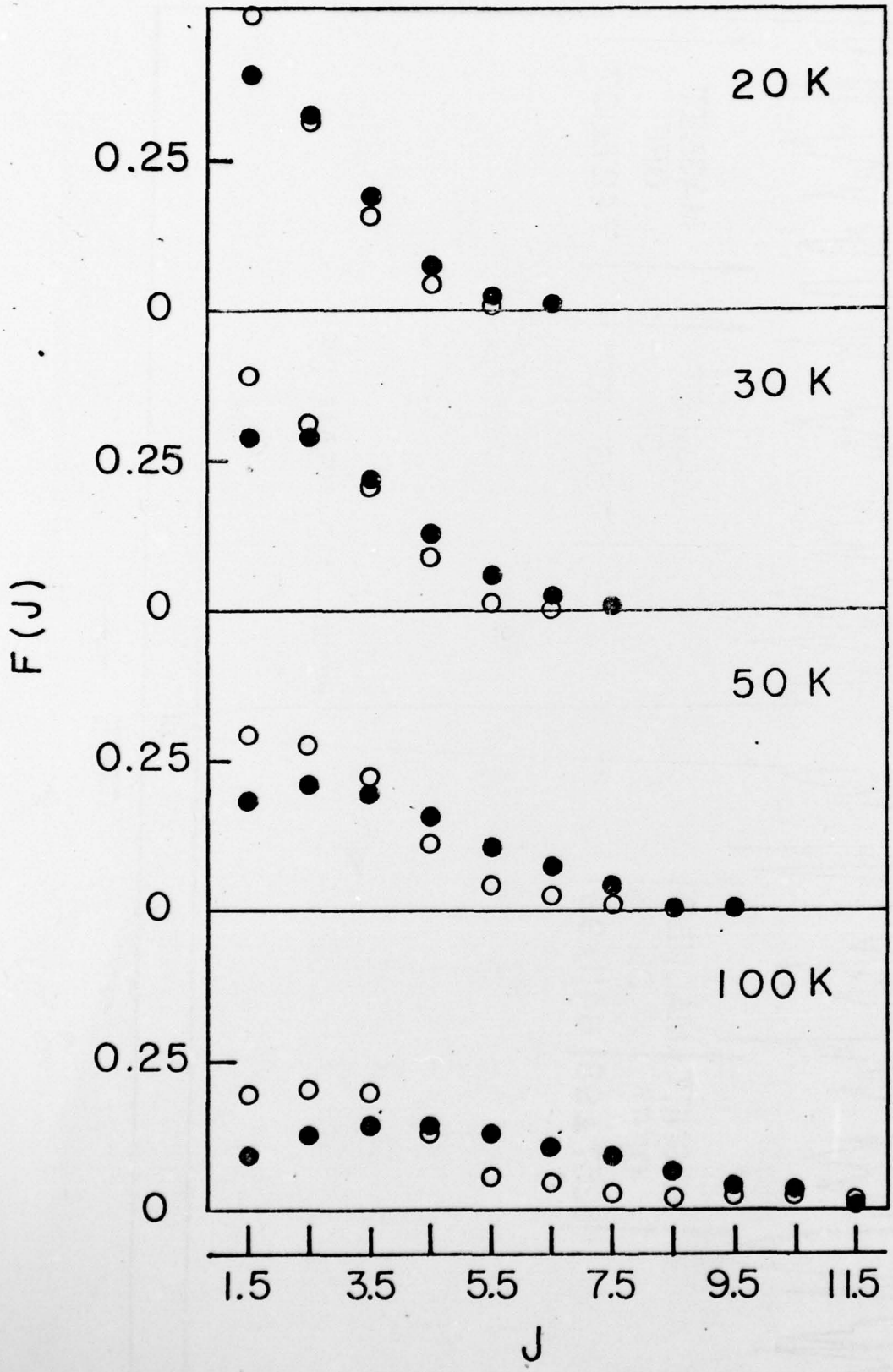
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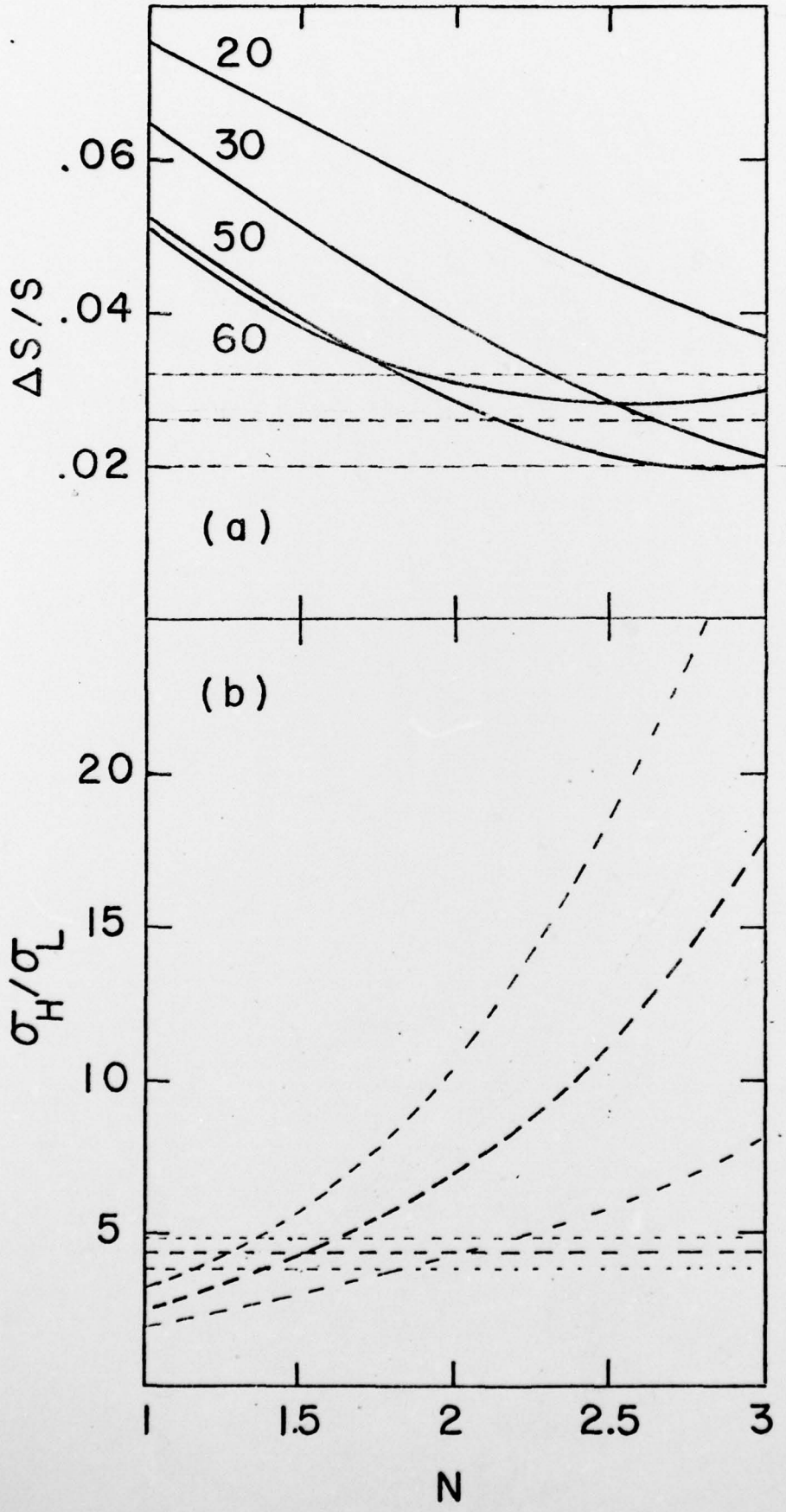
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The effect of reagent rotation is investigated for the reaction K + HCl = KCl + H and found to be more important than a similar amount of translational energy. Rotation decreases reactivity. Electronic excitation of NO in the reaction $NO + O_3 = NO_2^* + O_2$ was shown to roughly be equivalent to ground state reactivity. Reaction is apparently enhanced by rotation of the NO molecule. The origin of these effects is not yet understood.

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