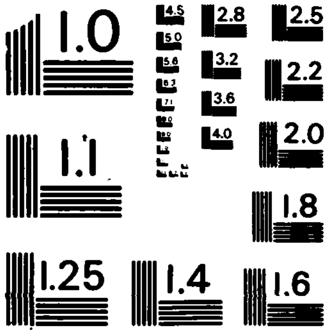
AD-A171 061 SPECTROSCOPIC STUDIES OF THE PRODUCTS OF THE REACTIONS 1/1
OF ELECTRONICALLY..(U) PITTSBURGH UNIV PA DEPT OF
CHEMISTRY M F GOLDE 16 JUN 86 AFOSR-TR-86-0504
UNCLASSIFIED AFOSR-83-0188 F/G 7/5 NL



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE

AD-A171 061

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
Unclassified

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

3. DISTRIBUTION / AVAILABILITY OF REPORT
Approved for public release;
Distribution unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
FQ8671-85-00800

5. MONITORING ORGANIZATION REPORT NUMBER(S)
AFOSR.TR. 86-0504

6a. NAME OF PERFORMING ORGANIZATION
University of Pittsburgh

6b. OFFICE SYMBOL (If applicable)

7a. NAME OF MONITORING ORGANIZATION
AFOSR/NC

6c. ADDRESS (City, State, and ZIP Code)
Department of Chemistry,
Pittsburgh, PA 15260

7b. ADDRESS (City, State, and ZIP Code)
Bldg. 410
Bolling AFB, DC 20332-6448

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
AFOSR

8b. OFFICE SYMBOL (If applicable)
NC

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
AFOSR 83-0188

8c. ADDRESS (City, State, and ZIP Code)
Bldg. 410
Bolling AFB, DC 20332-6448

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
61102F	2303	B1	

11. TITLE (Include Security Classification)
Spectroscopic STudies of the Products of the Reactions of Electronically Excited AToms and Small Molecules (U)

12. PERSONAL AUTHOR(S)
Michael F. Golde

13a. TYPE OF REPORT
Final Report

13b. TIME COVERED
FROM 4/15/83 TO 4/14/86

14. DATE OF REPORT (Year, Month, Day)
6/16/86

15. PAGE COUNT
34

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
Energy Transfer; electronically excited noble gas atoms and nitrogen molecules; resonance fluorescence; laser-induced fluorescence.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The rate constants and products of the reactions of electronically-excited Ar, Kr, and Xe atoms and $N_2(A^3\Sigma_u^+)$ and $CO(a^3\Pi)$ molecules with several oxygen-, hydrogen- and chlorine-containing compounds have been determined, using emission spectroscopy, atomic resonance fluorescence and laser induced fluorescence measurements in discharge flow systems. As found previously for the excited noble gases, there is a strong correlation between the rate constants for quenching of $N_2(A)$ and the availability of accessible acceptor states of the

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AUG 1 3 1986
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20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION
Unclassified

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22c. OFFICE SYMBOL
NC

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. Abstract (continued)

quenching molecule, as revealed by its absorption spectrum. Consistent with this correlation, the rate constants for several inefficient quenchers are greatly enhanced in reactions with vibrationally-excited $N_2(A)$.

Energy transfer leading to molecular dissociation is the dominant mechanism, when energetically allowed, for most reactions of $N_2(A)$ studied. Similar behavior is shown by both efficient and inefficient quenchers, and the results parallel the UV photochemistry of these molecules.

In contrast to $N_2(A)$, the isoenergetic $CO(a^3\Pi)$ species is quenched very efficiently by H_2O, CH_4 and H_2. The reaction products have been investigated in an attempt to gain insight into this difference in behavior.

AFOSR-TR- 86-0504

Introduction

Good progress was made in this project, AFOSR 83-0188, in achieving the goals in the original proposal. A new apparatus was built and used extensively during the last year of the project. Our resonance-fluorescence/emission apparatus remained the work-horse for this investigation. The personnel involved in the project comprised four graduate students.

The electronically-excited species studied were the lowest metastable states of Ar, Kr, Xe, N_2 and CO. The energies and other relevant properties are listed in Table 1. The experimental techniques used are briefly reviewed in the next section, with principal emphasis on the new discharge-flow system used for the LIF studies. The results are discussed in the following sections: Section 3: analysis of products of the reactions of Ar*, Kr*, Xe* and $N_2(A^3\Sigma_u^+)$ with selected reagents, which has given new insight into the favored dissociation channels; Section 4: more specific information on this first study of dark channels in the reactions of $N_2(A)$, in which the contrasting behavior of efficient and inefficient quenchers is revealed clearly in the dependence of reactivity on the extent of vibration in $N_2(A)$; Section 5: an initial study of the important reactions of $CO(a^3\Pi)$ with H_2, CH_4 and H_2O; Section 6: the first study of vibrational excitation in the products of the dark channels of the reactions of Ar* and Xe*; and Section 7: a brief account of new observations on the kinetics of electronically-excited $NH_2(\tilde{A}^2A_1)$. Section 8 is a summary of the progress made in our understanding of the reactions of electronically-excited species as a result of this project.

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Section 2. Experimental Procedures

Two discharge-flow systems have been employed in this project: the first, which uses emission spectroscopy and atomic resonance fluorescence to detect reaction products, has been described fully;[1] and a new apparatus, designed for laser-induced fluorescence measurements, which is shown in Fig. 1. In both systems, Ar carrier gas, with small additions of N_2, Kr, or Xe as appropriate, flows through a weak dc discharge and into an observation vessel which, in the new system, is a stainless-steel block with an internal 4 cm x 4 cm square cross-section. The total pressures are in the range 0.5 to 5 Torr and the linear velocity of the gas flow as it enters the vessel is typically 3 - 5000 cm s^{-1}. Typical metastable concentrations are 5×10^9 cm^{-3} (for Xe* and Kr*) to 1×10^{11} cm^{-3} (for $N_2(A)$). Reagent gases at concentrations in the range $1 \times 10^{12} - 4 \times 10^{15}$ cm^{-3} are added either directly into the observation vessel concentrically with the main flow for product measurements (inlet A in Fig. 1), or immediately downstream of the discharge for rate constant measurements (inlet B). For the latter experiments, it is crucial to achieve rapid mixing of the flows: the simple open side-arm, shown in Fig. 1, has been found to be unsatisfactory. Because of the rapid wall loss of the metastables, an injector which protrudes into the flow cannot be used. Therefore, a new reagent inlet was designed, which comprises a wall section, 5 mm in length, containing six evenly-spaced holes of diameter 0.3 mm, through which the reagent is carried by a small Ar flow. This stainless-steel section inserts into the pyrex flow tube with rubber O-ring seals. By observing reaction flames, it has been found that complete mixing is achieved within 1 cm (0.2 ms).

LIF employs an excimer-pumped dye laser system (Lambda-Physik EMG101E, 2002). For most of this study, Sulforhodamine B dye was used in the fundamental or frequency-doubled mode. The laser pulse energy is monitored by a Gentec joule meter (ED 200). The laser baffle and light collection system (see Fig. 2), including band-pass filters in front of the photomultiplier (RCA C31034), was designed to minimize detection of scattered laser radiation and background emission from the flow tube. The signal from the pmt was detected by a gated pulse-counting system (Ortec 9315/9320), which also includes a boxcar mode. Typical gate widths are 1-10 μs in normal operation and 100 ns in the boxcar mode.

This system has allowed very sensitive and virtually background-free detection of radicals downstream of the reaction zone. Direct observation of the reaction zone has not been possible in several reactions of interest, because of large emission signals from the reaction over the same wavelength range as that of the fluorescence; these overload the photomultiplier and (at the highest levels) are detected even in gated operation. It is planned in future to gate the photomultiplier, which will alleviate the former problem, the major limitation at present.

The use of the discharge-flow technique introduces much flexibility and versatility. The entire inlet assembly in each apparatus is movable, allowing the reaction zone to be positioned either in the observation zone or up to 10 cm (3 ms) upstream. An upstream observation window in the new system allows direct observation of emission from the reaction zone, while studying the reaction products downstream by LIF. The upstream inlet port (B in Fig. 1), allows addition of 'pre-reagents' to modify the distribution of metastables produced by the discharge. This was used firstly as an alternative source of $N_2(A)$ via the reaction of Ar* with N_2, and, secondly, for relaxation of the nascent vibrational distribution in the $N_2(A)$ state by addition of CF_3H, CF_4 or CH_4.[2]

The principal results reported here are total product yields and branching fractions. In all these experiments, sufficient reagent is added to drive the reaction rapidly to completion, allowing product analysis downstream by atomic resonance fluorescence or LIF. Branching fractions are deduced by comparison of the signals with those from reference reactions.[1,3,4] In a few experiments, in which nascent vibrational distributions of the products were probed, small concentrations of reagents were used. In the experiments probing the effect of vibration in $N_2(A)$ on reaction rate constant and product distribution, a large range of reagent concentration was used, including very low values such that very little reaction occurred before the observation zone.

Section 3. Dissociation channels in the reactions of electronically excited Ar, Kr, Xe and $N_2(A^3\Sigma^+)$.

Previous studies[1,3] in the lab revealed that dark channels, involving dissociation of the reagent into non-emitting states, dominate the reactions of Ar*, Kr*, and Xe* $np^5(n+1)s^1\ {}^3P_2$ metastable atoms, with many small molecules. Many novel reaction channels were discovered, including cleavage of more than one bond within a single collision event.

e.g.

$$Ar^* + H_2O \rightarrow Ar + H + OH \qquad f = 0.54 \pm 0.04 \qquad (1)$$

$$\rightarrow Ar + H + H + O \qquad f = 0.46 \pm 0.05 \qquad (2)$$

$$Xe^* + CF_2Cl_2 \rightarrow Xe + CF_2 + Cl + Cl \qquad f = 0.94 \pm .06 \qquad (3)$$

On the basis of the very large quenching rate constants and the efficient energy transfer, it was concluded[4] that energy transfer occurs at medium-to-long range with minimal distortion of the reagent molecule before energy transfer.

Additional evidence for this model was sought by investigating the reactions with NH_3 and CH_3OH in more detail, and by extending the study to N_2H_4, H_2O_2, and CH_3NH_2.

3a. $Ar^* + NH_3$.

H-atom resonance-fluorescence measurements of the reaction of Xe* with NH_3 indicated a single dominant channel

$$Xe^* + NH_3 \rightarrow Xe + NH_2 + H. \tag{4}$$

The higher-energy Ar* metastable has additional channels available, including:

$$\begin{aligned} Ar^* + NH_3 &\rightarrow Ar + NH_3^+ + e^- && (5)\\ &\rightarrow Ar + NH_2 + H && (6)\\ &\rightarrow Ar + NH + H_2 && (7)\\ &\rightarrow Ar + NH + H + H && (8) \end{aligned}$$

Chemiionization measurements yielded a branching fraction f = 0.42 ± 0.04 for channel (5), and 0.62 ± 0.04 H atoms are produced per reactive event.[3] These data imply an average of close to one H atom per dissociative reaction event, consistent with the occurrence of channel (6) <u>or</u> comparable amounts of (7) and (8). These were distinguished by measurement of the NH_2 yield by LIF via the $NH_2(\tilde{A}^2A_1 - \tilde{X}^2B_1)$ (090-000) band. The reference reaction was $Xe^* + NH_3$, and the ratio [Ar*]/[Xe*] in the two parts of the experiment was measured directly via emission intensities from the reactions:

$$Ar^* + N_2 \rightarrow Ar + N_2(C^3\Pi_u), \qquad f = 0.95 \pm 0.05 \tag{9}$$

$$Xe^* + CFCl_3 \rightarrow XeCl^* + CFCl_2, \qquad f = 0.15 \tag{10}$$

The total NH_2 yield from the $Ar^* + NH_3$ reaction was 1.0 ± 0.2. This large value is consistent with the dominance of channel (6) over (7,8), and also requires occurrence of the extremely fast secondary reaction:

$$NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2 \tag{11}$$

The observed weakness of the 2-atom elimination, channel (8), contrasts sharply with the results of the reactions of Ar* with, for instance, H_2O and CH_4, which have similar energetics. The difference is ascribed tentatively to a symmetry effect. H_2O and CH_4 can be excited to states of C_{2v} symmetry with two equivalent repulsive X-H bonds, which can break simultaneously; analogous excitation of NH_3 yields a C_{3v} configuration, with <u>3</u> weak bonds, so that cleavage of two bonds would require extensive rearrangement of the energy, which interestingly is not favored in this case. Curiously, a recent study of NH_3 photodissociation[5] at 121.6 nm revealed two-atom loss as the major process.

$$NH_3 + h\nu \rightarrow NH + 2H, \qquad f > 0.90 \qquad (12)$$

3b. Ar*, Kr*, Xe* + CH_3OH, CH_3OD.

Our previous study of these reactions revealed large yields of H atoms, implying that cleavage of the C-O bond, the weakest in the molecule, is a minor process. The present study of OH LIF, using the reactions with H_2O as reference, confirmed this conclusion: the branching fractions for OH production in the reactions with Xe*, Kr* and Ar* are respectively < 0.03, < 0.03, and 0.13 ± 0.02 (0.15 ± 0.02 for OD from CH_3OD). With these additional data, branching fractions for the allowed channels were deduced and listed in Table 2. The Ar* reaction is of particular interest. If it is assumed that 3-atom loss, to HCO + 3H, is not important, then this reaction shows at least three separate channels, each involving cleavage of two bonds:

$$Ar^* + CH_3OH \rightarrow Ar + CH_2O + H + H \qquad (13)$$

$$\rightarrow Ar + CH_3 + O + H \qquad (14)$$

$$\rightarrow Ar + CH_2 + OH + H; \qquad (15)$$

while cleavage of just one bond is apparently insignificant. In this reaction it is hard to envisage simultaneous cleavage of the two bonds; thus, sequential cleavage is more likely, the first dissociation releasing insufficient kinetic energy to prevent subsequent dissociation of the residual fragment. Qualitative evidence for production of CH_2 in eqn. (15) was obtained in the reaction of Ar* with CH_3OD, by addition of O_2 downstream of the primary reaction zone. An OH signal was produced, ascribed to the reactions:

$$CH_2 + O_2 \rightarrow CHO + OH \tag{16}$$

$$\rightarrow CO + H + OH \tag{17}$$

The H and D atom yields in the CH_3OD reaction (1.01 and 0.46 respectively per reactive event)[3] are not consistent with CH_2O as the sole product of channel (13). The relatively small D yield implies appreciable formation of CHOD, which may rearrange to CHDO.

The very small OH yields obtained in the reactions of CH_3OH with Kr* and Xe* imply that the one-atom loss channels become increasingly important as the metastable energy decreases; it is thus expected that the CH_3O and CH_2OH are born with appreciable vibrational excitation.

3c. $N_2(A)$ + CH_3OH, CH_3NH_2, N_2H_4 and H_2O_2.

These reagents all have 14 valence electrons and are further related in that the central bond (C-O, C-N, N-N, O-O) is in each case the weakest bond in the molecule. The UV photochemistry of these molecules is not fully characterized, but reveals that central-bond cleavage is dominant for H_2O_2,[6] but is apparently a minor process for the other molecules.[7-9] Our data, summarized in Table 3, qualitatively parallel the photochemistry. Thus, the large yield of OH in the reaction with H_2O_2 implies that the channel

$$N_2(A) + H_2O_2 \rightarrow N_2 + OH + OH \tag{18}$$

has a branching fraction, f = 0.87 ± 0.10. For CH_3NH_2, the very small NH_2 yield but large H-atom yield establish cleavage of a C-H and/or an N-H bond as the major process. CH_3OH shows analogous behavior. For N_2H_4, the small NH_2 yield implies a branching fraction f = 0.06 ± 0.02 for

$$N_2(A) + N_2H_4 \rightarrow N_2 + NH_2 + NH_2. \qquad (19)$$

A large H-atom resonance fluorescence signal was observed, consistent with H + N_2H_3 formation, but no quantitative result was obtained, because of very rapid removal in a secondary reaction, presumably with N_2H_4.

The findings confirm our hypothesis that a long-lived intermediate, which would be expected to favor the lowest-energy channel, is not generally involved in these reactions.

Study of the reactions of Ar* and Xe* with CH_3NH_2 and N_2H_4 has also been commenced (H_2O impurity hampers study of the interesting analogous reactions of H_2O_2). For CH_3NH_2, the yields of NH_2 are uniformily low (the possible secondary reaction, NH_2 + CH_3NH_2, was shown independently to be unimportant under our conditions). For N_2H_4, the NH_2 yield increased with metastable energy, as shown in Table 3.

Section 4. Reactions of $N_2(A^3\Sigma_u^+)$.

When this study was commenced, limited data were available on the rate constants of the reactions of $N_2(A)$,[10] and much less was known about the reaction products. Our study has revealed that the products are consistent with those for Ar*, Kr* and Xe*, extrapolated to the lower energy, 6.2 eV of $N_2(A, v = 0)$. Moreover, a clear picture is emerging of the factors determining the rate constants and their dependence on vibrational quantum number, v, in $N_2(A)$.

4a. Rate constants.

The justification for the present study was the realization that quenching rate constants for $N_2(A)$ reactions show the same correlation as those for reactions of excited Ar, Kr and Xe atoms;[2] namely that large quenching rate constants, close to the collision number, are found if the reagent has readily accessible energy levels (as revealed by its absorption spectrum) near or below the energy of the metastable atom. For the excited noble gases, this correlation was based largely on the unusual behavior of just two reagents, CF_4 and CF_3H. However, for the lower energy $N_2(A)$ state, a much greater variety of behavior is possible, and Table 4 includes available literature data,[10] showing the clear qualitative correlation between quenching rate constant and the threshold for light absorption. As yet, no quantitative correlation has been attempted, either by us or by others. Our initial measurements on other reagents further support this correlation. Thus N_2H_4, CH_3NH_2, H_2O_2 and Cl_2 have been found to be efficient quenchers, and have absorption thresholds of respectively >220 nm, 245 nm, 300 nm and ~400 nm, compared to a wavelength of 200 nm, which is the equivalent of an energy of 6.2 eV. In contrast, reaction of $N_2(A, v - 0)$ with H_2O is very inefficient, $k < 10^{-13}$ cm^3s^{-1}, in agreement with its absorption threshold of about 185 nm. The chlorofluoromethanes $CFCl_3$, CF_2Cl_2 and CF_3Cl exhibit a progressive shift in absorption threshold, from ~230 nm ($\sigma = 10^{-20}cm^2$) for $CFCl_3$ to below 200 nm for CF_3Cl, and the rate constants show a parallel trend, from 2×10^{-11} cm^3s^{-1} for $CFCl_3$ to $<10^{-13}$ cm^3s^{-1} for CF_3Cl. The only apparent exception to the correlation encountered so far is C_2H_4, an efficient quencher but with an absorption (singlet state) threshold of ~190 nm. However, triplet absorption occurs between 260 and 240 nm and triplet excited states, rather than the singlets observed more readily in absorption spectra, are expected to be important in energy transfer from $N_2(A^3\Sigma_u^+)$.

As discussed previously, we interpret the correlation as implying weak chemical forces between the excited N_2 and the reagent molecule, energy transfer occurring while the reagent molecule is not significantly distorted from its equilibrium geometry.

4b. Reaction Products

In addition to the reactions described in section 3, the products of the reactions of $N_2(A)$ with NH_3, O_2, HCl, Cl_2, $CFCl_3$, CF_2Cl_2, CF_3Cl, SO_2 and C_2H_4 have been investigated, using atomic O, H or Cl resonance fluorescence and emission spectroscopy. For the O- and H-containing compounds, absolute branching fractions were obtained, using the well-studied reactions of Ar* with O_2 and H_2 as references.[1,3] No such calibration has yet been performed for the Cl-containing reagents: $CFCl_3$ has been employed as a reference, and the following dissociation channel assumed to be dominant:

$$N_2(A) + CFCl_3 \rightarrow N_2 + CFCl_2 + Cl. \qquad (20)$$

The results are summarized in Table 5 and show that dissociation is a major channel in the reactions with NH_3, O_2, HCl, Cl_2, CF_3Cl and CF_2Cl_2. Only for O_2 is there evidence that other channels are important - see Section 5. The result for Cl_2 contrasts with a recent study[11] of the reaction with IF, which yielded strong fluorescence from excited states of IF. The behavior of CF_2Cl_2 and CF_3Cl is complicated by a strong dependence of the rate constant on vibrational quantum number in $N_2(A)$; the values are lower limits and the very large Cl-atom yield for CF_2Cl_2 suggests that a significant fraction of this reaction occurs by 2-atom loss:

$$N_2(A) + CF_2Cl_2 \rightarrow N_2 + CF_2 + Cl + Cl, \qquad (21)$$

thus paralleling the reaction of Xe* with CF_2Cl_2, equ. (3).

SO_2 and C_2H_4 are clear exceptions, in showing small yields of dissociation products, O and H. For SO_2, this behavior contrasts with the reactions with Ar*, Kr*, and Xe*, and with SO_2 photochemistry, which shows an onset of predissociation at ~220 nm and little fluorescence at an excitation wavelength of 200 nm.6 It is concluded that energy transfer from $N_2(A)$ yields non-dissociated excited states of SO_2; only weak emission is observed, implying extensive quenching under the experimental conditions employed. It is likely that analogous triplet excitation is the major channel in the $N_2^* + C_2H_4$ reaction, analogously to the reactions of C_2H_4 with metastable ^3P states of Hg, Cd and Zn.[12]

4c. Effect of vibration in $N_2(A)$.

Vibrational relaxation within $N_2(A)$ has been studied by several groups and has been found to be very inefficient for collision partners such as the noble gases and N_2. Thus, Dreyer and Perner[13] found relaxation by N_2 to have a rate constant of 3.4×10^{-16} cm^3s^{-1} for $N_2(A, v = 1)$, but larger values for higher levels, ascribed to $\Delta v = -2$ transitions. More recently, CH_4, CF_4 and CF_3H have been shown to be more efficient at vibrational relaxation,[14] the rate constants again increasing strongly with v. We have detected small H-atom yields when CH_4 is the collision partner, indicating that vibrationally-excited $N_2(A)$ undergoes weak electronic quenching in competition with vibrational relaxation but, for CF_4 and CF_3H, electronic quenching appears to be a very minor process.

Our interest concerned, firstly, a possible v-dependence of the rate constants for electronic quenching, particularly for inefficient quenchers, and, secondly, a possible difference in quenching channels for less efficient quenchers compared to those of efficient quenchers. We have used complementary techniques: firstly, direct measurement of total quenching rate constants of $N_2(A, v)$, using emission spectroscopy, $N_2(A \rightarrow X)$, or LIF, $N_2(B \leftarrow A)$; secondly, the effect on the product distribution of inducing complete vibrational relaxation in $N_2(A)$ by the addition of CF_3H as a pre-reagent. The latter studies[2] are carried out firstly at very low concentrations of the principal reagent, Q, which gives information on the relative rate constants for $v = 0$ and $v > 0$ of the observed reaction channel; and secondly at high [Q], which gives information on the relative branching fractions for $v = 0$ and $v > 0$ of the observed channel. The initial studies have been completed for NH_3, $CFCl_3$, O_2, CH_3OH and NO; these inspired a study of the reactions with H_2O, D_2O, CF_3Cl, CF_2HCl and CF_2Cl_2, which have proved very complex and interesting and are continuing. NH_3 and $CFCl_3$ have proved to be good reference reagents: vibrational relaxation by CF_3H causes negligible changes in respectively H- and Cl-atom yields, implying that the v-dependences of rate constants and product distributions are small for these efficient quenching processes.

CH_3OH shows an approximately two-fold decrease in product H-atom signal when CF_3H is added, at low concentrations of CH_3OH; however, this effect decreases as $[CH_3OH]$ is increased, as shown in Fig. 3. Thus, for this reagent, which quenches with a rate constant, $k(v = 0) = 4.3 \times 10^{-12}\ cm^3s^{-1}$, the total quenching rate constant for $v > 0$ is more than double that for $v = 0$, but the product distribution does not change significantly with v. Similar behavior was found for N_2O, $k(v = 0) = 7.7 \times 10^{-12}\ cm^3s^{-1}$, via O-atom measurements of the channel:

$$N_2(A) + N_2O \rightarrow N_2 + N_2 + O \qquad (22)$$

For NO, the product $NO(A^2\Sigma - X^2\Pi)$ γ-band intensity increases when CF_3H is added, the increase changing little with NO concentration. It is concluded that the rate constant for quenching does not change greatly with v, but that another channel grows in at high v. If this is ascribed to NO dissociation, endothermic for $v < 1$,

$$N2(A,\ v > 2) + NO \rightarrow N2(X) + N + O, \qquad (23)$$

then the average branching fraction for this channel is $f_{23} = 0.22 \pm 0.03$.

For O_2, CF_3H reduces the O atom yield strongly at low $[O_2]$, and still significantly at high $[O_2]$ (see Fig. 3). The former result is consistent with previous studies of the total quenching rate constants,[15] while the latter implies that the O-atom yield increases with v. Using the recent results[16] concerning the <u>average</u> branching fraction for the channel

$$N_2(A) + O_2 \rightarrow N_2 + O + O, \qquad f = 0.65 \pm 0.10, \qquad (24)$$

our data imply branching fractions of 0.57 and 0.77 respectively for $N_2(A, v = 0)$ and $N_2(A, v > 0)$.

These results for quenchers of intermediate efficiency have focussed attention on those of low efficiency, particularly H_2, CH_4, H_2O, CF_3Cl and CF_2HCl. H_2 appears to have little activity towards $N_2(A)$ beyond very weak vibrational relaxation. CH_4, as discussed above, causes significant vibrational relaxation and much weaker electronic quenching. H_2O, CF_3Cl and CF_2HCl show remarkable behavior: appreciable product signals (H and OH for H_2O, Cl for CF_3Cl and CF_2HCl), which almost disappear when CF_3H is added. For none of these reagents is it possible to reach the high concentration limit at which the reaction is driven to completion (for all v) before the observation region. The data suggest that the rate constants for the observed electronic quenching channels vary from $k < 10^{-13}$ cm^3s^{-1} for $v = 0$ to $k > 1 \times 10^{-11}$ cm^3s^{-1} for high levels, $v = 4$-6. Initial studies involving direct monitoring of $N_2(A, v)$ by LIF confirm a very large change in total deactivation rate constant. There appears to be no doubt that vibration (4 to 6 quanta, equivalent to 0.7 to 1.0 eV in energy) in $N_2(A)$ is converting extremely inefficient electronic quenchers into rather efficient quenchers.

Section 5. Reactions of $CO(a^3\Pi)$

Although $CO(a^3\Pi)$ has a very similar excitation energy (6.0 eV) to that of $N_2(A^3\Sigma_u^+)$, its reactivity is very different; it is efficiently quenched by most reagents, including H_2, CH_4 and H_2O, which quench $N_2(A)$ extremely inefficiently.[17] We have thus commenced an investigation of the products of these three key reactions. In particular, we were intrigued by the possibility of an atom transfer channel:

$$CO(a^3\Pi) + RH \rightarrow HCO + R \qquad (25)$$

in competition with molecular dissociation:

$$CO(a^3\Pi) + RH \rightarrow CO + R + H \qquad (26)$$

Results to date, however, favor channel (26) as the major and possibly the dominant process.

This study has proved difficult because the formation scheme for $CO(a^3\Pi)$ involves species which also quench this excited species. Several schemes have been investigated, including discharge of dilute mixtures of CO or CO_2 in Ar or He, and the reaction of Ar* with CO_2:

$$Ar^* + CO_2 \rightarrow Ar + CO(a^3\Pi) + O, \qquad f = 0.16 \pm 0.08 \qquad (27)$$

Total pressures were varied between 1 and 4 Torr. All the above schemes gave similar amounts of $CO(a^3\Pi)$ and most studies employed an Ar carrier, with CO_2 added before or after the discharge.

Two distinct experiments have been carried out. Firstly, relative H-atom resonance fluorescence signals were measured in the reactions with CH_4, H_2O (and NH_3), using H_2 as the reference. The ratios obtained, $I(H_2)/I(RH)$, are listed in Table 6, and are close to two, consistent with, but not proving, the dissociation mechanism, equ. (26). However, the data show significant deviations from two, suggesting at least small amounts of other quenching channels, such as (25). The relatively small H-atom yield from the NH_3 reaction was surprising and is not understood as yet.

Absolute branching fractions for the reaction with D_2O (rather than H_2O to avoid interference from a small background OH signal) were sought in the second experiment:

$$CO(a) + D_2O \rightarrow CO + D + OD \qquad (28)$$

$$\rightarrow DCO + OD \qquad (29)$$

The D_2O was added immediately downstream of the discharge (inlet B in Fig. 1), and NO_2 added through the principal reagent inlet. OD was monitored in the absence and the presence of NO_2, the change in the signal being ascribed to the fast secondary reaction:

$$D + NO_2 \rightarrow OD + NO. \qquad (30)$$

The technique was tested using the well-studied reaction Ar* + D_2O, and gave a D/OD ratio within 20% of that expected. For CO(a) + D_2O, NO_2 addition is expected to double the OD signal if channel (28) is dominant, and to have no effect if channel (27) is dominant. The measured ratio of signals with and without NO_2 was 1.96 ± 0.10.

It is thus concluded that molecular dissociation of H_2, CH_4 and H_2O is the principal channel in the reactions with $CO(a^3\Pi)$; however, other channels, including reaction to HCO, may account for up to about 20% of the reaction.

Section 6. Vibrational distributions in the products of the reactions of Ar* and Xe* with H_2O.

In the studies described so far, care was taken to ensure that the LIF measurements correctly sampled the total population of the radical, NH_2 or OH.

Because of the high Ar buffer concentration, 10^{16} - 10^{17} cm^{-3}, a thermal *rotational* distribution was expected and confirmed by measurements on the OH(A-X)(0, 0) band. Vibrational relaxation by the carrier is less rapid but the reagents used, H_2O, NH_3, etc., are expected to be efficient relaxers. All experiments covered a range of reagent concentration and included observations of vibrationally excited radicals, in particular OH, $v = 1$. It was found that vibrationally-excited OH could be relaxed completely by moderate concentrations of reagent, so that measurements of $v = 0$ were sufficient to yield the total population.

In order to observe nascent vibrational distributions of the products, vibrational relaxation must be minimized. For NH_2, such conditions could not be achieved with the present set up, due to vibrational relaxation by Ar. For OH, relaxation by Ar is slow and nascent vibrational distributions are accessible. Initial data have been obtained for the reactions Ar* + H_2O and Xe* + D_2O. The reaction of Xe* with D_2O has been studied over a ten-fold range of concentration of D_2O and with two different reaction times (movable inlet at different positions). Consistent data were obtained, yielding $[OD(v = 1)]/[OD(v = 0)] = 0.17 \pm 0.03$. The reaction Ar* + H_2O could not be studied over such a wide concentration range, because background OH emission from the primary reaction interferes with the LIF measurements at low $[H_2O]$. The data yielded $[OH(v = 1)]/[OH(v = 0)] \sim 0.14$. As a check, the *enhancement* of OH, $v = 0$ caused by vibrational relaxation of higher levels at higher concentrations of H_2O was measured. After correction of the LIF signals for quenching of the fluorescing $OH(A^2\Sigma^+)$ state at these relatively high H_2O concentrations, the data yielded $[OH(v > 0)][OH(v = 0)] \sim 0.20$.

The data thus show that only a small fraction of the large amount of energy released in these reaction channels appears as vibration in the OH(OD) product.

For Xe*, comparison can be made with measurements and calculations of photodissociation of H_2O at comparable wavelengths,[18,19] which find considerably greater vibrational excitation. For Ar*, three dissociation channels are important.

$$Ar^* + H_2O \rightarrow Ar + OH(A^2\Sigma^+) + H, \qquad f = 0.28 \pm 0.09 \qquad (31)$$

$$\rightarrow Ar + OH(X^2\Pi) + H, \qquad f = 0.26 \pm 0.10 \qquad (32)$$

$$\rightarrow Ar + O + 2H, \qquad f = 0.46 \pm 0.05. \qquad (33)$$

The low yield of vibration in $OH(X^2\Pi)$ implies that channels (32) and (33) occur by independent pathways.

Section 7. Kinetics of electronically-excited NH_2.

In using gated detection of LIF, it is important to correct for any change with conditions in the fraction of the fluorescence detected. Reagents such as H_2O, NH_3 and N_2H_4 are very efficient quenchers and affect the efficiency of LIF in two ways: firstly by reducing the quantum yield of fluorescence and secondly by shortening the effective lifetime of the emitting state, thus changing the fraction of fluorescence detected during the gate period. Where necessary, quenching rate constants were determined from the fluorescence decay rates as a function of reagent concentration, and corrections made. Effective electronic quenching rate constants were (cm^3s^{-1}): Ar: $(4.1 \pm 0.3) \times 10^{-12}$; N_2H_4: $(2.5 \pm 0.3) \times 10^{-10}$; NH_3: $(2.3 \pm 0.2) \times 10^{-10}$.

At low Ar pressures, the NH_2^* fluorescence decays appeared to show non-exponential behavior: future experiments are planned to investigate this in more detail.

Section 8. Summary

The products of quenching of $N_2(A^3\Sigma_u^+)$ and $CO(a^3\Pi)$ are definitely comparable to those obtained previously for the higher energy metastables Xe*, Kr* and Ar*. Thus, dissociation of the reagent has been found to be the principal channel, both for efficient and less-efficient quenchers of $N_2(A)$, and in the efficient reactions of $CO(a^3\Pi)$ with H_2, CH_4, and H_2O, which quench the isoenergetic $N_2(A)$ very slowly. However, unlike the reactions with the excited noble gases, two reagents, C_2H_4 and SO_2, have been found for which reaction with $N_2(A)$ yields little dissociation, although it is energetically allowed.

The rapid reactions of $N_2(A)$ with N_2H_4 and CH_3NH_2 do not occur significantly via cleavage of the weakest bond, confirming the non-statistical nature of the energy transfer, and the close relationship to the photochemistry of these molecules. It is thus particularly interesting that the much slower reaction, $N_2(A) + CH_3OH$, $k = 4 \times 10^{-12}$ cm^{3}s^{-1}, exhibits identical behavior, showing that the mechanism of energy transfer is fundamentally unchanged, although the probability per collision is decreased, because of the reduced access to acceptor states of CH_3OH.

Despite the importance of dissociation in the unexpectedly fast reactions of CO(a) with H_2, CH_4 and H_2O, a different mechanism must be involved, as excited states of these molecules are simply not accessible without distortion of the molecule. It is thus likely that the interactions between CO(a) and these molecules are considerably more attractive than those with $N_2(A)$. Ab initio calculations of the $CO(a^3\Pi) + H_2$ system have been commenced in collaboration with Professor Ken Jordan of this department, and indicate an attractive C_{2v} approach of the C end of CO to the H_2 molecule. It is thus possible that a formaldehyde-like intermediate is involved; however, it is surprising that <u>both</u> H atoms are lost from this intermediate.

In comparable reactions of excited ^3P states of the alkaline earth metals and of Zn and Cd with H_2, similar intermediates lead to formation of MH + H products,[12,20] the M-H bond energies being comparable to that of the H-CO. However, the excited metal states do not have sufficient energy to produce

M + H + H. Thus, if these reactions are indeed comparable, HCO is expected to be at least a minor product, as appears to be indicated by some of the results reported in section 5.

This study has shown that many inefficient quenchers of $N_2(A, v = 0)$ show a large increase in rate constant with v. This is wholly consistent with our model for the reactions of $N_2(A)$, as the increased energy improves access to excited states of these molecules. The effect is thus ascribed principally to that of energy rather than to a specific effect solely of the vibrational motion. In support of this, the rate constants for electronic quenching of $N_2(A, v)$ by D_2O and CF_2HCl appear to increase only slightly between v = 0 and 1, but more strongly between v = 1 and 2.

For H_2, CF_3H, CH_4 and CF_4, however, the lowest excited states are too high in energy to be readily accessible from $N_2(A, v)$, so that little electronic quenching is observed even at high v.

Table 1

Properties of the lowest metastable excited states of Ar, Kr, Xe, N_2 and CO.

Species	State	Energy, eV	Radiative Lifetime, s
Ar	$3p^5 4s\,^3P_o$	11.7	45
	$^3P_2$	11.5	>1.3
Kr	$4p^5 5s\,^3P_2$	9.9	>1.0
Xe	$5p^5 6s\,^3P_2$	8.3	~150
N_2	$A^3\Sigma_u^+$	6.2	1.3
CO	$a^3\Pi$	6.0	7.6×10^{-3}

Table 2

Product distributions in the reactions of Ar*, Kr*, Xe* with CH_3OH

Products:	Threshold Energy, eV	Branching Fractions		
		Ar*	Kr*	Xe*
$CH_3 + OH$	4.0	~0	<0.03	<0.03
$CH_2OH + H$	4.0	~0	0.28±0.03	0.49±0.03
$CH_3O + H$	4.5	~0		
$CH_2O + 2H$	5.4	0.62±0.02	0.71±0.03	0.50±0.03
$CH_3 + O + H$	8.4	0.04±0.02	0±0.02	b
$CH_2 + OH + H$	8.6	0.13±0.02	<0.03	b
$CHO + 3H$	9.3	0[a]	0[a]	b
$CH_3OH^+ + e^-$	10.8	0.20 ± 0.01	b	b

a. Assumed value
b. Endothermic

Table 3

Product Yields in Reactions of $N_2(A)$, Ar* and Xe* with some OH- and NH_2-containing Reagents

Reaction	Product Species	Yield per reactive event
$N_2(A) + H_2O_2$	OH	1.74±0.20
$N_2(A) + CH_3OH$	OH	0.01±0.01
	H	0.88±0.07
$N_2(A) + CH_3NH_2$	NH_2	<0.03
	H	1.00±0.02
$N_2(A) + N_2H_4$	NH_2	0.12±0.03
$Xe^* + CH_3NH_2$	NH_2	<0.03
$Ar^* + CH_3NH_2$	NH_2	<0.05
$Xe^* + N_2H_4$	NH_2	0.22±0.04
$Ar^* + N_2H_4$	NH_2	0.45±0.10

Table 4

.Rate constants for quenching of $N_2(A^3\Sigma_u^+)$(energy 6.2 eV)

Reagent	Absorption Threshold[a] nm	eV	$k_Q(N_2(A))$[b] cm^3s^{-1}
H_2	110	11.3	$1.9x10^{-15}$
CH_4	144	8.6	$3.2x10^{-15}$
NH_3	210	5.9	$\sim 1.5x10^{-10}$
H_2O	185	6.7	$\sim 5x10^{-14}$
H_2S	270	4.6	$3.0x10^{-10}$
O_2	200	6.2	$(2-4)x10^{-12}$
CO_2	170	7.3	$\sim 3x10^{-14}$
N_2O	210	5.9	$7.7x10^{-12}$
OCS	250	5.0	$2x10^{-10}$
CS_2	340	3.6	$1.6x10^{-10}$
SO_2	400	3.1	$(3-5)x10^{-11}$
I_2	600	2.1	$6.9x10^{-12}$
HCl	200	6.2	$1.3x10^{-12}$
HBr	220	5.6	$7.8x10^{-11}$
HI	310	4.0	$2.8x10^{-10}$
CH_3Cl	200	6.2	$8.0x10^{-12}$
CH_3OH	200	6.2	$4.3x10^{-12}$
CH_3CN	216	5.7	$1.9x10^{-11}$
CH_3SH	280	4.4	$4.3x10^{-10}$

a Ref. 6
b Ref. 10

Table 5

Product Yields in Some Reactions of $N_2(A)$.

Reagent	Product Species	Yield per Reactive Event
NH_3	H	1.07 ± 0.10
C_2H_4	H	0.20 ± 0.07
O_2	O	1.40 ± 0.14[a]
SO_2	O	0 ± 0.02
$CFCl_3$	Cl	1.0[b]
CF_2Cl_2	Cl	0.96 ± 0.10
CF_3Cl	Cl	>0.53[c]
Cl_2	Cl	1.82 ± 0.09[a]
HCl	Cl	1.0 ± 0.1

a. These values should be halved to obtain the branching fractions for dissociation.

b. Assumed value.

c. Reaction not complete at observation zone.

Table 6

Relative H - Atom Yields in the Reactions of CO($a^3\Pi$) with H_2, CH_4, H_2O and NH_3.

Reagent	H signal (CO(a)+RH)/H signal (CO(a)+H_2)
H_2	1.0
CH_4	0.53 ± 0.01[a]
H_2O	0.45 ± 0.02[a]
NH_3	0.41 ± 0.02[a]

a. Uncertainty given as standard deviation of the mean.

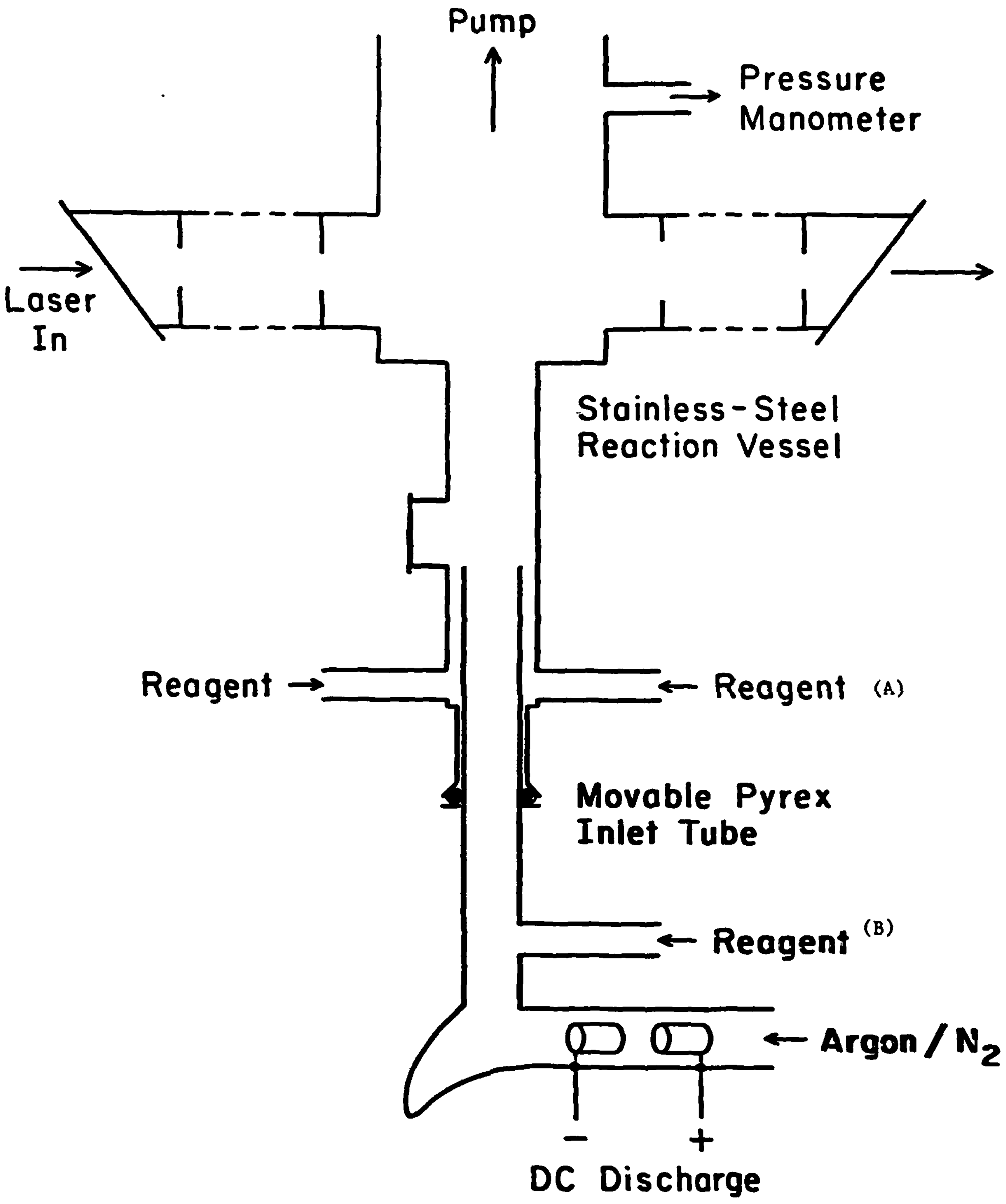

Figure 1. A schematic of the apparatus used for laser-induced fluorescence measurements.

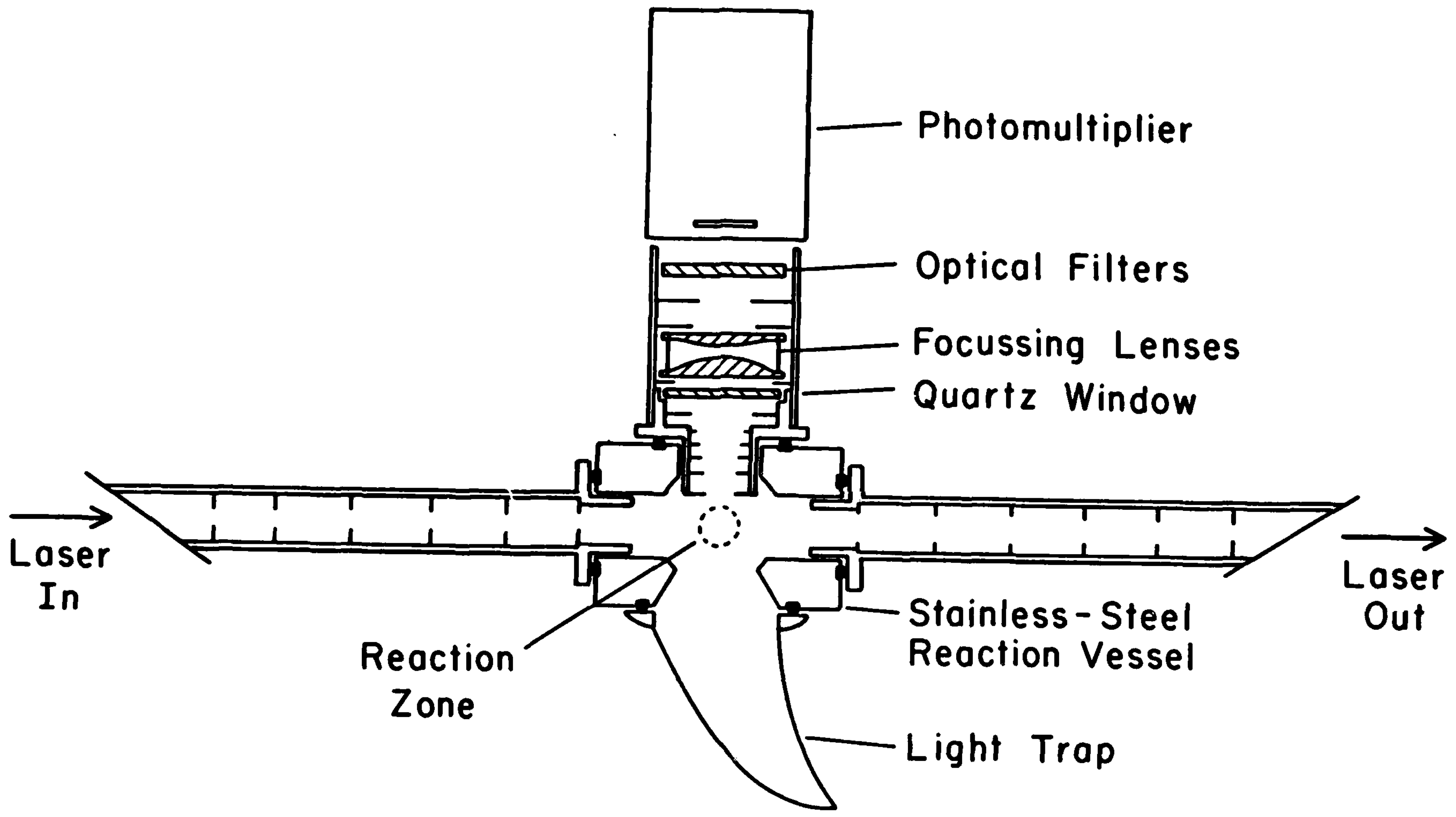

Figure 2. A cross-section through the reaction vessel showing the laser baffle and fluorescence detection systems.

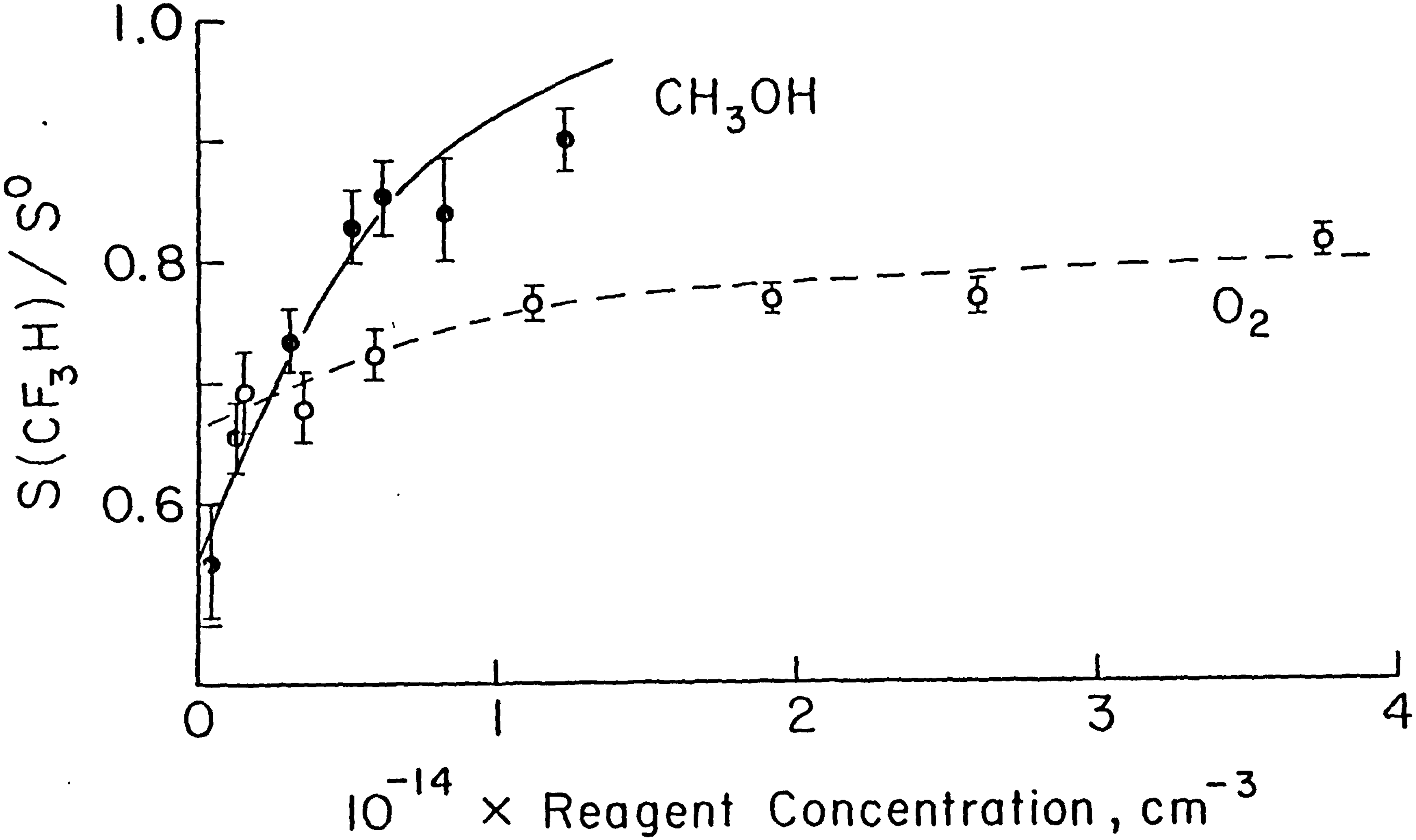

Figure 3. The effect of CF_3H addition on H- and O-atom yields in the reactions of $N_2(A)$ with respectively CH_3OH and O_2.

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Invited Seminars

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9—86