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THE EFFECT OF PRESSURE ON THE CHEMILUMINESCENT
SPECTRUM OF OXYGEN ATOMS AND NITRIC OXIDE

by

Eli Freedman
John R. Kelso

March 1969

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SPECTRUM OF OXYGEN ATOMS AND NITRIC OXIDE

Eli Freedman

John R. Kelso

Interior Ballistics Laboratory

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BRL REPORT NO. 1430

EFreedman/JRKelso/lkg
Aberdeen Proving Ground, Md.
March 1969

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SPECTRUM OF OXYGEN ATOMS AND NITRIC OXIDE

ABSTRACT

As another approach to establishing the mechanism of the chemiluminescent reaction between oxygen atoms and nitric oxide, the effect of pressure on the spectrum has been investigated. The oxygen atoms were generated by a microwave discharge, and mixed with nitric oxide in a two-stage system where the pressure could be varied from 1.0 to 0.005 torr. The spectra were obtained with a resolution of about 30 \AA with a grating monochromator. A calibrated tungsten lamp was used to correct the data for the response of the optical system. In order to compare spectra obtained at different pressures with one another, each was arbitrarily normalized to 1.0 at its peak near 6300 \AA .

Spectra obtained at pressures below 0.5 torr all show a shift towards the blue; the magnitude of the shift is roughly proportional to the decrease in pressure below 0.5 torr. This shift is almost identical with that observed in the fluorescence of NO_2 . Adding either argon or sulfur hexafluoride to the mixture at low pressures does not change the spectrum but at around 1 torr, SF_6 causes a shift similar to a decrease in pressure.

These results are shown to be consistent with a multi-step mechanism involving the formation, stabilization, quenching, and vibrational de-excitation of one excited electronic state.

TABLE OF CONTENTS

	Page
ABSTRACT	3
LIST OF ILLUSTRATIONS	7
INTRODUCTION	9
EXPERIMENTAL	11
RESULTS	16
DISCUSSION	23
ACKNOWLEDGEMENT	26
REFERENCES	27
DISTRIBUTION LIST	29

LIST OF ILLUSTRATIONS

Figure		Page
1.	Schematic Diagram of Apparatus	12
2.	The Effect of Pressure on the Chemiluminescence of O + NO.	17
3.	The Effect of SF ₆ on the Chemiluminescent Spectrum of O + NO.	18
4.	The Effect of Pressure on the Chemiluminescence of N + NO.	20
5.	Comparison of the BRL Data with those of Fontijn, Meyer, and Schiff.	21
6.	Comparison Between the Chemiluminescent Spectrum of NO + O and the Fluorescent Spectrum of NO ₂	22

INTRODUCTION

The mechanism of the chemiluminescent reaction between nitric oxide and oxygen atoms has been the subject of controversy for some time^{1-4*}. The two principal conflicting theories are a direct two-body recombination mechanism, and a more complicated three-body recombination with quenching. The former theory predicts that the chemiluminescent intensity should always depend linearly on the square of the total pressure, independent of the presence and of the pressure of any inert gas. The latter theory predicts, among other results, that at some sufficiently low pressure, the ratio I/p^2 (I = intensity, p = pressure) should show a fall-off with pressure, and that at a sufficiently low pressure, the intensity should show a linear dependence on the cube of the pressure. Most of the experimental work has consisted of attempts to determine this pressure dependence directly, which is difficult, and most of the controversy has centered over the interpretation of the results.

An investigation of the pressure dependence of the spectrum of the chemiluminescence appeared to be a different way of studying this reaction. Such a dependence has been sought twice previously, in each case incidental to another experiment. Fontijn, Meyer, and Schiff⁵ reported that there was no change in the spectral distribution down to 0.1 torr. Doherty and Jonathan⁶ likewise found no change down to 0.1 torr when observing the spectrum with a grating monochromator. Additionally they did experiments using sharp cut-off filters at pressures of 0.01 and 0.1 torr, and did not observe any change. We felt that it would be desirable to try again at pressures below 0.1 torr, and with improved resolution.

An extra incentive was provided by the results of Myers, Silver, and Kaufman⁷, who observed a change with pressure in the fluorescent spectrum of NO_2 . If no such change could be observed in the

* References are listed on page 27.

chemiluminescent spectrum, it would be evidence that at least two excited states of NO_2 were significantly concerned in the mechanism of the reaction between O and NO.

Since this work was completed, Jonathan and Petty⁸ have published a paper in which they report a new determination of the pressure dependence of the chemiluminescence. They have directly and unambiguously observed the change in order from second to third.

EXPERIMENTAL

A conventional flow system (Figure 1) was used for the production of O atoms by a microwave discharge in flowing oxygen at pressures between 0.5 and 3 torr. In our earlier work⁹ a trace of nitrogen was added to the discharge to improve the yield of O atoms, which in turn increased the signal-to-noise ratio of the measurements. Later, when the sensitivity of the apparatus was increased, the use of nitrogen was eliminated.

A small amount of this mixture was introduced into a second flow system by permitting it to effuse through a hole drilled in a Teflon plug. Depending on the pressure needed, hole diameters between 0.5 and 3 mm were used. This second flow system, which served as the observation tube, could be separately pumped down to 10^{-4} torr. This arrangement permitted observation of the chemiluminescence over an extremely wide range of pressures without having to pay any attention to the discharge; also, it permitted the same ratio of O to NO to be maintained over a series of experiments, which was a convenience although no special use was made of it.

Provision was made for the introduction of oxygen or other gases at a place in the observation section just below the Teflon plug, which acted as a fine adjustment on the pressure. A stopcock near the pump was the coarse adjustment.

The radiation from the observation tube emerged from a quartz window at one end, went through a 50 Hz chopping wheel into a 3/4 meter Ebert-Fastie type recording monochromator (Leeds and Northrup), and then onto a photomultiplier. The slits on the monochromator were made from copper shim stock, and were 3 mm wide. The spectral resolution was about 30 Å. The photomultipliers used earlier were side-window 9-stage types with either S-4 or near S-20 responses. For all of the results reported here, however, an end-on 14-stage photomultiplier (EMI 9558-Q) with an S-20 response was used.

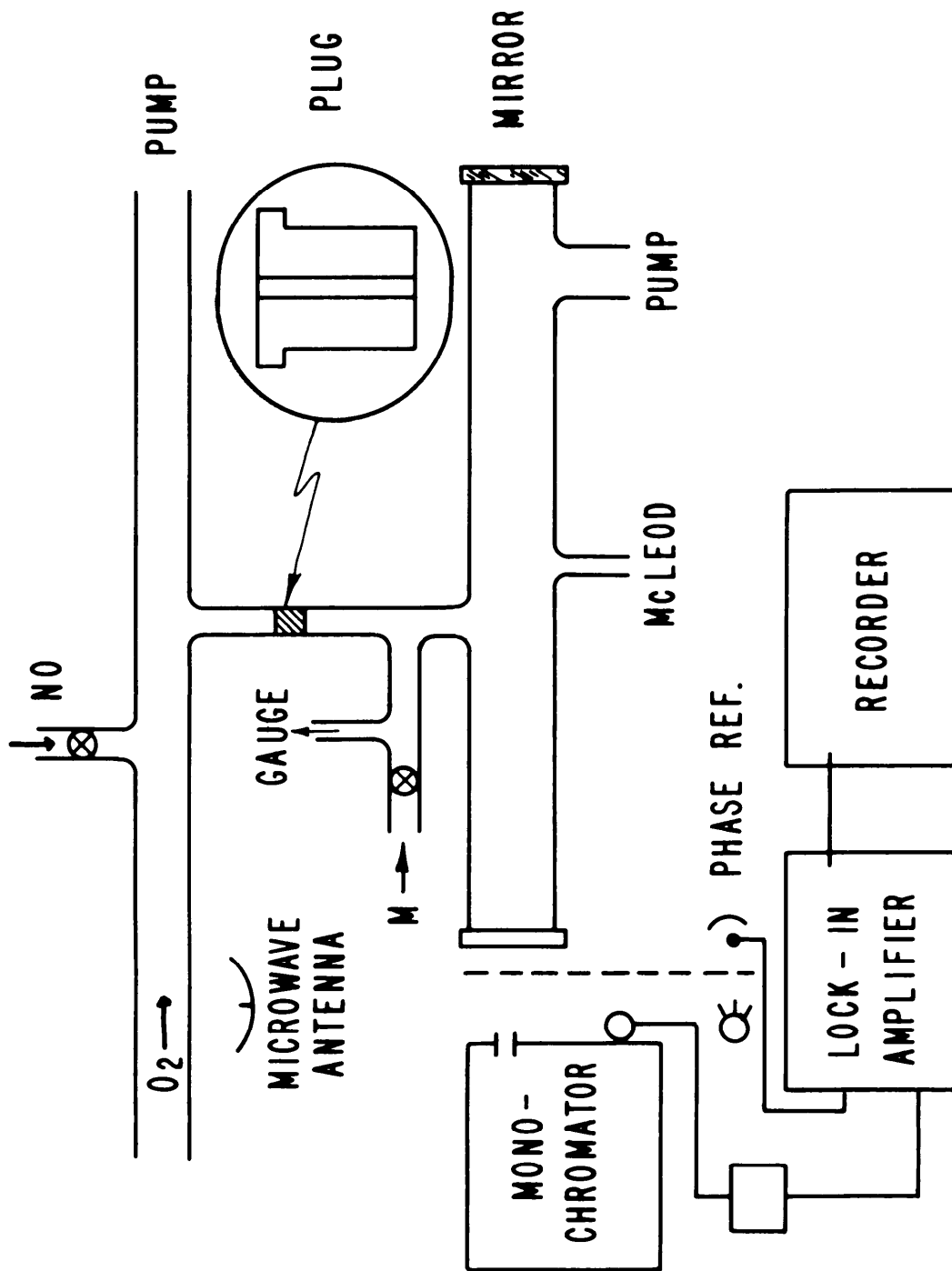


Figure 1 - Schematic Diagram of Apparatus

This tube was mounted in a holder (Pacific Photometric Instruments) that permitted the use of Dry Ice for cooling. As originally furnished, this holder had to be loaded with Dry Ice from the front end, which meant demounting the tube every time. Since a charge of Dry Ice lasted about 2 hours, a run often had to be interrupted to renew the coolant. To avoid this, the glass vacuum jacket originally supplied with the tube holder was discarded and replaced with a Styrafoam liner that was carved to make a tight fit; then a hole was cut through the side of the holder so that Dry Ice could be loaded through the side without disturbing the phototube.

The output of the photomultiplier went to a lock-in amplifier with a separate high input-impedance pre-amplifier module (Princeton Applied Research Corporation model HR-8 with type A pre-amp). The pre-amplifier was designed to be operated remotely from the main chassis so that the cable connection between it and the photomultiplier could be kept as short as possible. This turned out to be a bad arrangement because the pre-amp could not be shielded sufficiently from the noise generated by the microwave discharge. The pre-amp was therefore kept inside the main chassis and placed about 1.5 m away. The connection to the phototube was made by coaxial cable (Consolidated RG-580); no significant pick-up problem was encountered with it. The required phase reference signal was generated by a separate light and a phototransistor. The amplifier contained its own detector and filter circuits; the usual mode of operation was with a filter time constant of 1 sec and roll-off of 12 db/decade. The output from this stage went to a conventional strip-chart recorder.

In order to determine the relative response of the combined monochromator-photomultiplier combination, two 1000-watt quartz-iodine tungsten lamps were obtained. One of them was calibrated and certified for emissivity by Eppley Laboratories; the other one was used as our working standard lamp. Periodically it would be compared

with the certified lamp using exactly the equipment just described. Both lamps were run at the recommended settings-- 8.3 amps at 110 v AC*. Since it was essential that the high voltage to the photo-multiplier be the same for a spectral scan as for a calibration scan, the radiation from these lamps had to be strongly attenuated to protect the photocathode from overloading. After considerable trial and error, a filter consisting of three pieces of stainless steel screening¹⁰ with holes of approximately 0.53 mm square, a neutral density filter of $D = 0.6$ (Bausch and Lomb), and a piece of tracing paper (Keuffel and Esser's "Albarene") were used. Tracing paper is not a widely used optical filter, but we found it to be useful for attenuating and diffusing the light. Diffusion was desirable because with it, the placement of the standard lamp was no longer critical. Frosted glass is generally recommended for this purpose; we found that the tracing paper had a relatively more constant absorbance than any piece of frosted glass we tested.** Two of the wire screens were rotated 45° relative to each other to minimize Moiré effects and were tied together; the third one was placed about a meter away. The absorbances of each element of this filter combination were measured in a recording spectrophotometer (Cary, model 14) and then added. The over-all absorbance varied smoothly from 4.9 at 3800 \AA to 4.69 at 8000 \AA . The metal screens were kept in place permanently in the optical path of the lamp. The tracing paper was placed in front of the monochromator slit just before each calibration scan; and the neutral density filter was placed in front of the lamp for the calibration scan only from 4200 \AA up.

* We wish to thank Mr. J. R. Hickey of Eppley Laboratories for advice on the use of these lamps.

** Details on this point will be published separately.

The spectra were obtained using the first order of the grating in the monochromator. Theoretically it was possible that second order spectra (corresponding to the wave length range from 1800 Å to 4000 Å) were also being recorded. Although this was quite unlikely, a few runs were carried out with a 4300 Å sharp cut-off filter in front of the slit to remove any second-order spectra. No difference was observed with this filter in place.

A typical run consisted of a scan of the working standard lamp, followed by a scan of the chemiluminescence. The scanning speed was usually 50 Å/min. With the recorder running at 25 mm/min, a spectrum covered about 2.1 m of paper. Since the filter circuit time constant was never set greater than 1 sec, a faster scan could probably have been used. The only disadvantage of the slow scanning speed was that a typical run required over an hour, during which time there was always a slow drift in intensity at constant wavelength. This drift arose from a combination of many factors, like changing line voltage, etc. Rather than fight it, a side-window photomultiplier was placed at the opposite end of the observation tube where it could view the glow along the length. Experiments showed that there was an exact linear relation between the reading of this monitor phototube and the reading of the 9558 tube at any wavelength. The monitor phototube current was recorded separately, and the scan data were corrected accordingly. This correction was never more than 10%; more usually it was 4 - 5%.

The records for both calibration and chemiluminescence scans were digitized by hand at intervals of 25 Å (or, infrequently, 10 Å). The numbers were recorded on punched cards and then processed in batches by an electronic computer. The monitor correction mentioned above was applied by hand while the data were being digitized; all other corrections, and the comparison with the standard lamp, were made by the computer program. Occasionally a smooth line was drawn by eye through the chart records before reading them; usually, however, they were read as recorded.

The reproducibility of the data was about 5% from month to month, but it is much more difficult to estimate their accuracy. It seems reasonable to claim $\pm 5\%$ accuracy for relative intensities within a run; nothing can be said about absolute intensities.

RESULTS

In order to permit a comparison between a spectrum at 1 torr and one at 0.005 torr, some arithmetical manipulation must be carried out on the data. Although the essential results will not be much affected by whatever operation is chosen, the details of the comparison will be affected. The method finally adopted is similar to that used by Fontijn, Meyer, and Schiff⁵; it is based on the fact that the spectra all show a peak in the neighborhood of 6300 Å. Each spectrum was normalized to 1 at its peak. This normalization is both convenient and arbitrary; a more rational normalization would require more detailed knowledge of the concentrations of O and NO, and of the concentration dependence of the glow.

Figure 2 shows the principal result of this work. The spectrum remains essentially unaffected down to a pressure around 0.5 torr. Below this pressure, a gradual shift towards the blue is observed. The magnitude of this shift is roughly proportional to the decrease in pressure below 0.5 torr, but no attempt was made to investigate this dependency quantitatively.

The "pressure" noted in the Figure is the total pressure of the observation tube; additions of either argon, helium, or sulfur hexafluoride at low pressures affected the spectrum in just the same way as addition of oxygen, neither more nor less. Around 1 torr, however, where further addition of oxygen did not affect the spectrum, replacement of part of the oxygen flowing through the side tube with a different gas did cause a change in the spectrum similar to a decrease in pressure -- a relative increase towards the blue end of the spectrum. This is shown in Figure 3.

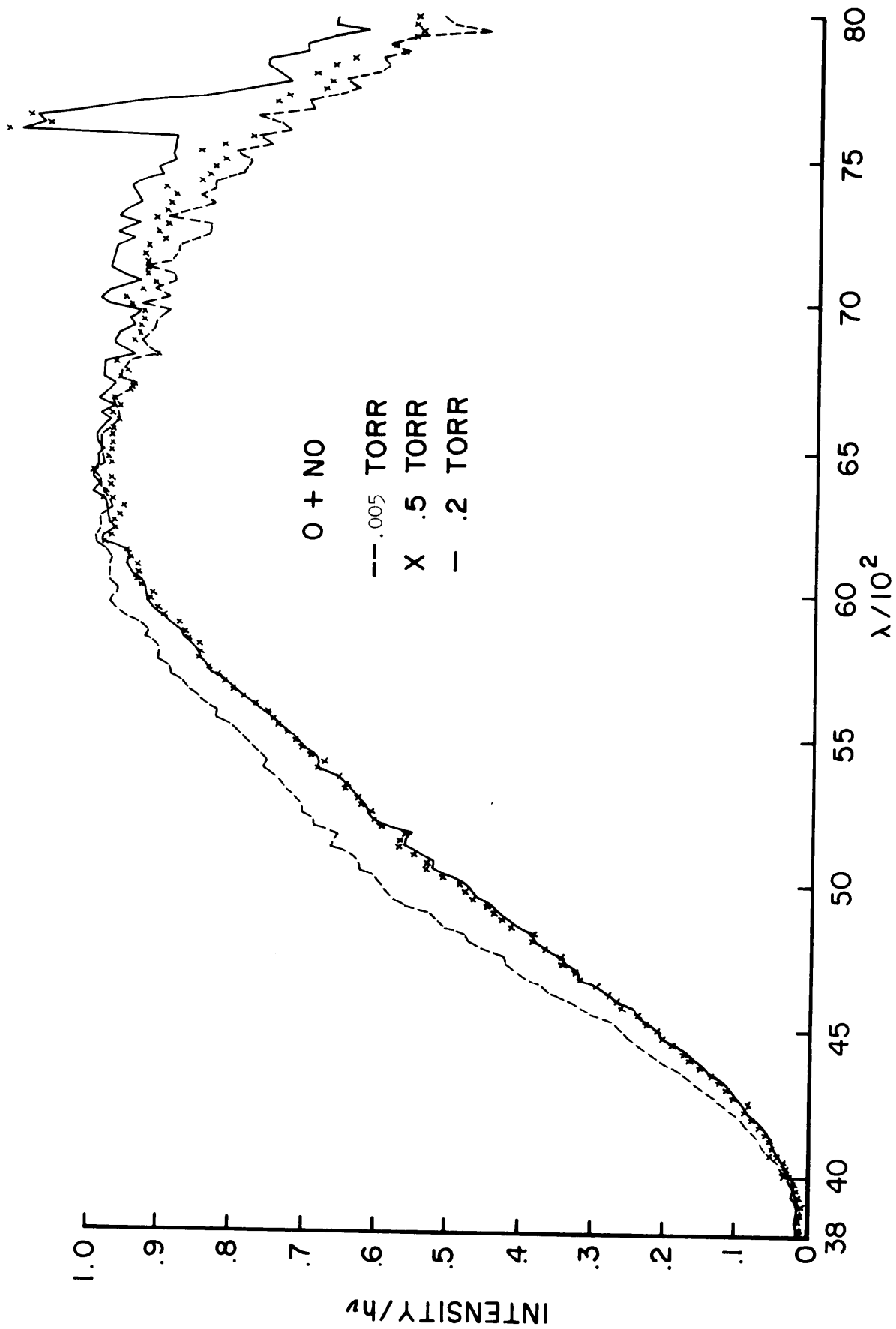


Figure 2- The Effect of Pressure on the Chemiluminescence of O + NO

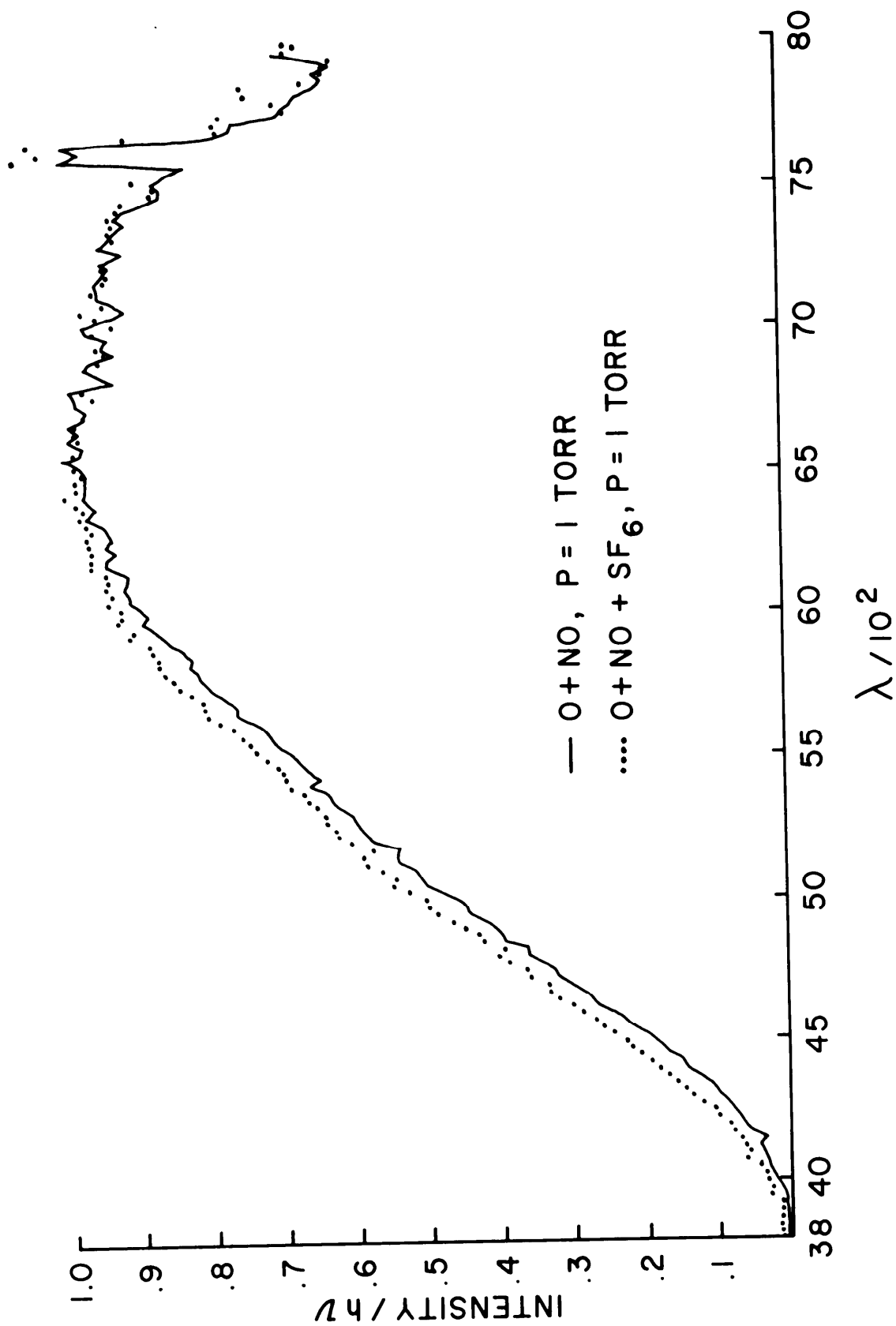
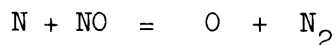


Figure 3-The Effect of SF₆ on the Chemiluminescent Spectrum of O + NO

As a further check on our results, we also prepared atomic oxygen by passing nitrogen alone through the discharge, and then mixing it with nitric oxide. The reaction



results in the formation of atomic oxygen free of molecular oxygen (but possibly containing excited nitrogen molecules). Figure 4 shows that the effect of pressure on the O + NO spectrum is essentially identical to the effect noted when atomic O was prepared by a microwave discharge in molecular oxygen.

Figure 5 shows a comparison of our data with those of Fontijn, Meyer, and Schiff⁵. In general the comparison is good, both curves being within 10% of each other at the worst.

Finally, Figure 6 shows a comparison of some of our results with those of Myers, Silver, and Kaufman on the fluorescence of NO₂. In order to make this comparison more effective, we have tried to correct their data for instrumental response. The correction was obtained by scanning the light from a 500-watt projection lamp with a flat tungsten filament, determining the temperature of the filament with an optical pyrometer, and then calculating the relative radiant output from the lamp at different wave lengths from Planck's equation and the data of DeVos¹¹ on the emissivity of tungsten. Exactly the same photomultiplier was used. The over-all similarity between the two spectra is quite marked. The rise in the fluorescence spectrum past 6000 Å is probably an artifact based on the calibration procedure.

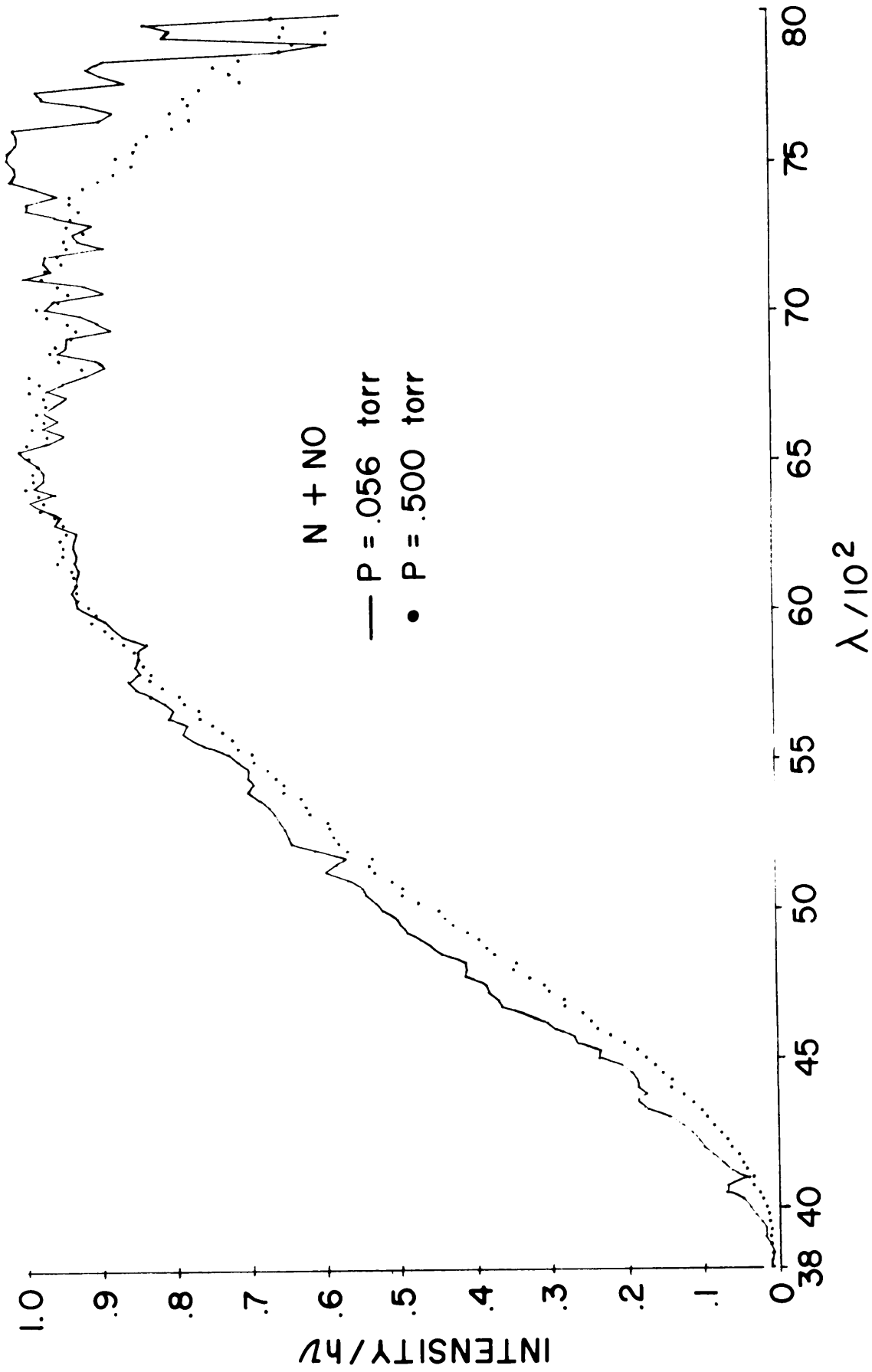


Figure 4 - The Effect of Pressure on the Chemiluminescence of N + NO

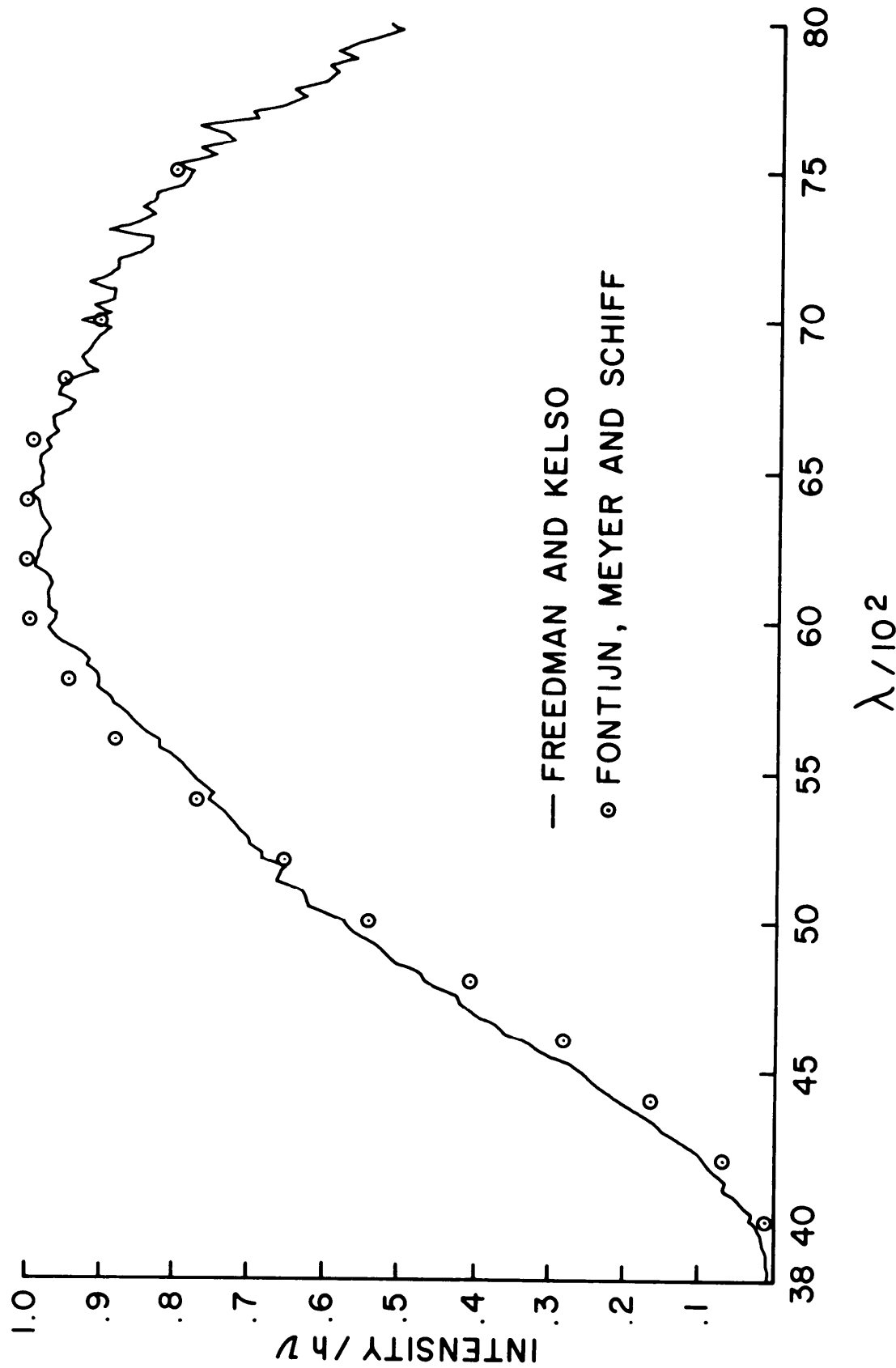


Figure 5 - Comparison of the BRL Data with those of Fontijn, Meyer, and Schiff

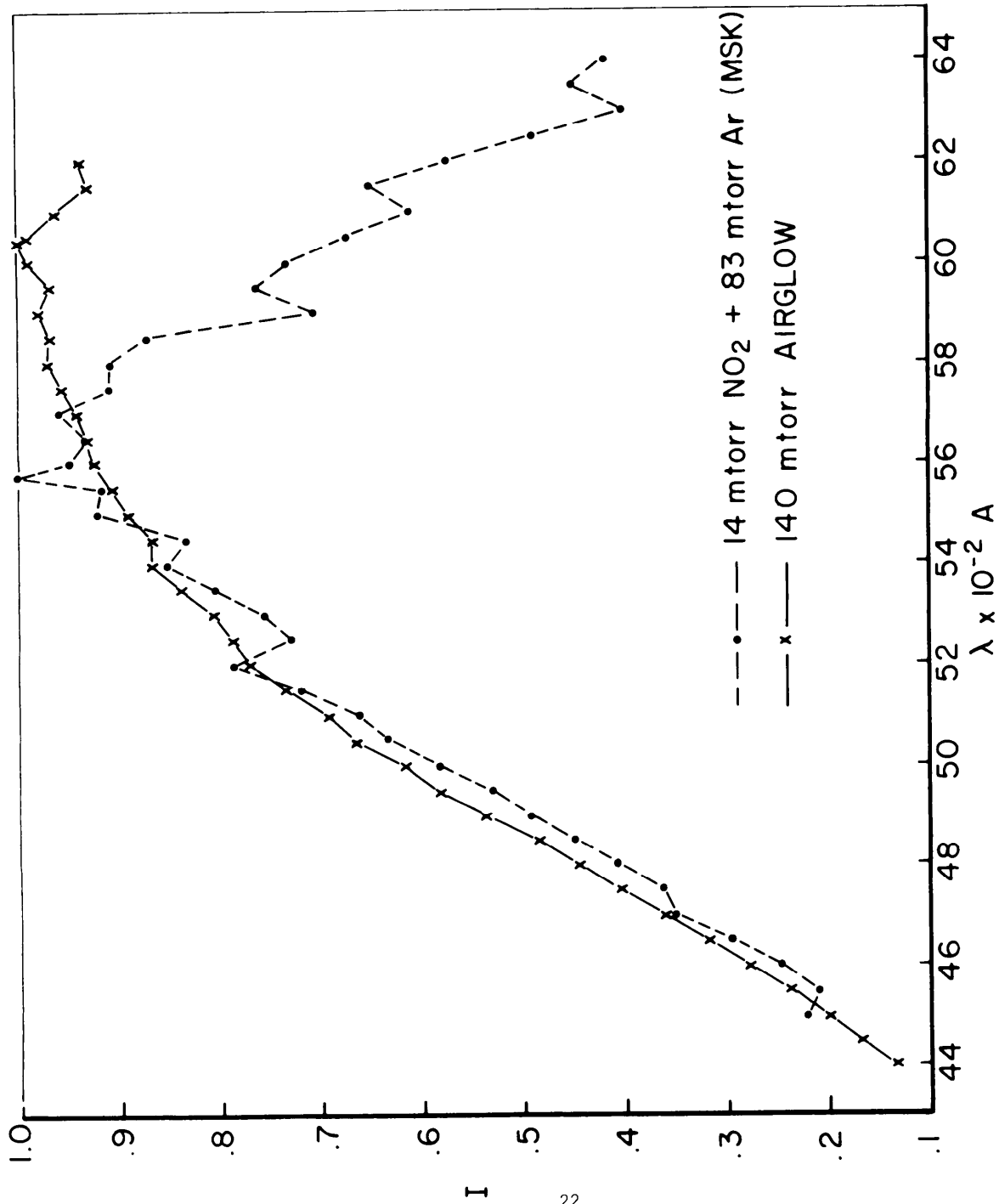


Figure 6 - Comparison Between the Chemiluminescent Spectrum of NO + O and the Fluorescent Spectrum of NO₂

DISCUSSION

Two mechanisms have been proposed for the chemiluminescent reaction between NO and O. They are the straightforward 2-body mechanism



and a three-body mechanism with quenching,



In this scheme, NO_2^* represents an excited electronic state of NO_2 . There has been considerable controversy about the nature and number of the states involved. Myers, Silver, and Kaufman,⁷ and Douglas¹³ have presented strong arguments showing that only one state is involved, namely, the state for which Neuberger and Duncan¹² found a lifetime of 44 microseconds.

The close resemblance between our data for the effect of pressure on the chemiluminescent spectrum, and the data of Myers et al.⁷ for the effect of pressure on the fluorescence, constitutes still further evidence that the same excited state is responsible for both phenomena.

Although many of the details of this reaction can be explained using the three-body mechanism of Eqn. (2), it is not adequate for the interpretation of the present data since it does not provide any means whereby the spectral distribution can vary with pressure.

F. Kaufman^{*} has proposed a more complicated mechanism that is able to explain the present results, and a number of others as well. This mechanism supposes that there is a significant two-body reaction which

* F. Kaufman, private communication. We are indebted to Dr. Kaufman for permitting us to use these results in advance of their formal publication. Details will appear in J. Chem. Phys.

results in the formation of an intermediate complex, $[\text{ONO}]^*$. This complex is the same one postulated by Herron and Klein¹⁴ to explain their measurements of the rate of isotopic exchange between O atoms and NO and NO₂; they estimated its lifetime to be approximately 10^{-8} sec. This complex can react in three different ways: It may dissociate back to O and NO; it may be stabilized by collision with a third body, resulting in the formation of NO₂^{*}; or it may radiate and form ground state NO₂. The NO₂^{*} formed is vibrationally excited, and can undergo successive stages of vibrational de-excitation. At each state there are the possibilities that the molecule may either be quenched by collision, or it may undergo a radiative transition to the ground state. The over-all radiation is the sum of the emission from each step.

This theory predicts that the pressure dependence of the chemiluminescence should be second order at high pressure; that as the pressure is decreased, this dependence should become third order, and then second order again. Jonathan and Petty⁸ have now reported the transition from second to third order, confirming the earlier report of Kaufman and Kelso.²

The present results can now be readily interpreted. At higher pressures, say, above 0.1 torr, the rate of vibrational de-excitation is at its maximum, and there is no pressure effect. As the pressure is lowered, this rate falls off; as it does, there is an increase in the (relative) number of molecules in the higher vibrational levels. Obviously, their radiation lies more toward the blue end of the spectrum. This explains the pressure shift that we have observed.

The dependence of the high-pressure spectrum on the nature of the third body can be explained similarly, except that now it is the relative effect of the third body on the electronic quenching that is important. The more efficient the third body is as a quencher, the fewer NO₂^{*} there will be to radiate. But because the lifetime of the complex $[\text{ONO}]^*$ is so short, it is not subject to quenching; therefore its radiation will remain at a constant level, while that from NO₂^{*}

decreases. Once again the remaining radiation will be more intense in the blue region, as was observed.

This mechanism can easily be written down, and the corresponding differential equations formulated. Owing to the large number of unknown rate constants that would be involved, however, there is no point in attempting to choose a set to fit the data. This effort will become worthwhile only when information becomes available on the relative rates of quenching and vibrational de-excitation for different third bodies.

Since this theory predicts that at a sufficiently low pressure, the spectrum should become independent of the pressure, we attempted to obtain data at pressures below 5 mtorr. The signal-to-noise ratio dropped precipitously with the pressure, as was to be expected. The detector of the lock-in amplifier had provision for increasing the time constant of the filter in the output circuit up to 10 sec (and even more, if an external capacitor were used). Using the 10-sec time constant caused the recorder pen to become sufficiently sluggish to distort the spectrum, so no further efforts were made in this way. We then tried to record the spectrum statistically at a number of different wave lengths. The wave length drive on the spectrometer was turned off, but the recorder was left running, so we were able to obtain a value for the intensity at one wave length averaged over as long a time as desired (within limits).

The results were quite disappointing in that the spectra obtained did not at all resemble those obtained by continuous recording at higher pressures. We believe that this difference is not real, but the reason for it is not clear. It appears that there was background emission that was not properly taken into account in reducing the data. At the higher pressures, the only noticeable background emission had been the oxygen emission at 7600 Å. At these very low pressures, however

where the contribution of the chemiluminescence itself is so small, it may be that there is some other weak contribution, not identified, and not properly corrected for. Time did not permit us to pursue this matter further.

Tests of this new model for the reaction between NO and O will more readily be obtained from a different kind of experiment.

ACKNOWLEDGEMENT

We wish to thank Professor Frederick Kaufman of the University of Pittsburgh for permitting us to use his work on the mechanism of the reaction; and for much helpful advice throughout this project.

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13. ABSTRACT As another approach to establishing the mechanism of the chemiluminescent reaction between oxygen atoms and nitric oxide, the effect of pressure on the spectrum has been investigated. The oxygen atoms were generated by a microwave discharge, and mixed with nitric oxide in a two-stage system where the pressure could be varied from 1.0 to 0.005 torr. The spectra were obtained with a resolution of about 30 Å with a grating monochromator. A calibrated tungsten lamp was used to correct the data for the response of the optical system. In order to compare spectra obtained at different pressures with each other, each was arbitrarily normalized to 1.0 at its peak near 6300 Å. Spectra obtained at pressures below 0.5 torr all show a shift towards the blue; the magnitude of the shift is roughly proportional to the decrease in pressure below 0.5 torr. This shift is almost identical with that observed in the fluorescence of NO ₂ . Adding either argon or sulfur hexafluoride to the mixture at low pressures does not change the spectrum but at around 1 torr, SF ₆ causes a shift similar to a decrease in pressure. These results are shown to be consistent with a multi-step mechanism involving the formation, stabilization, quenching, and vibrational de-excitation of one excited electronic state.			

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