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DEVELOPMENT OF A DIRECT, LOW PRESSURE,
LASER-INDUCED FLUORESCENCE MEASUREMENT TECHNIQUE
FOR NO₂, AMBIENT MEASUREMENTS AND
URBAN NO_x CHEMISTRY

by
LINDA ACHA GEORGE

A dissertation submitted in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY
in
ENVIRONMENTAL SCIENCES AND RESOURCES:
CHEMISTRY

Portland State University
1991

AN ABSTRACT OF THE DISSERTATION OF Linda Acha George for the Doctor of
Philosophy in Environmental Sciences and Resources: Chemistry presented March 8,
1991.

Title: Development of A Direct, Low Pressure, Laser-Induced Fluorescence Measurement
Technique for NO₂, Ambient Measurements and Urban NO_x Chemistry.

APPROVED BY THE MEMBERS OF THE DISSERTATION COMMITTEE:

Robert J. O'Brien, Chair

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John Dash

Nitrogen oxides control the global formation of ozone in the lower atmosphere and

influence the much higher levels of ozone formed in areas subjected to photochemical air pollution. As an important member of the nitrogen oxide family, NO_2 plays a significant role in serving as the only known source of ozone (through photolysis) in the lower atmosphere and as sink for HO via the formation of nitric acid. Ozone can be destroyed by reaction with another member of the nitrogen oxide family, nitric oxide (NO), to reform NO_2 . This cycle between NO, NO_2 and O_3 is known as the $\text{NO}_x\text{-O}_3$ photostationary state (PSS). Imbalances in this cycle have been used to calculate ambient levels of oxidants (such as RO_2 and HO_2) responsible for ozone production. Consequently, accurate NO_2 measurements are critical to making meaningful measurements of the imbalances in the $\text{NO}_x\text{-O}_3$ photostationary states (PSS).

A low pressure laser-excited fluorescence technique (FAGE) for the direct determination of atmospheric NO_2 has been developed. This technique has been explored with both a Nd-YAG laser (1.4 W, 532nm, 30Hz) and a Cu-vapor (1.2 W, 511nm, 5.6kHz) laser. The detection limits for these instruments, under laboratory conditions and a signal collection time of 20s (10s each signal and background), have been determined to be 450 and 350pptv NO_2 , respectively. In these systems, the background was measured by chemically reducing NO_2 with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

Ambient measurements of the $\text{NO}_x\text{-O}_3$ photostationary state (PSS) were undertaken on a rooftop monitoring site in downtown Portland, Oregon. NO_2 was monitored with the Cu-vapor system. Nitric oxide and ozone were monitored with standard instruments. Data for three days in 1990 are presented. Overall these data sets clearly show that despite daily changes in concentration of NO, NO_2 and O_3 of factors of 4-10 each, the

PSS remains relatively constant to within ~50%. This is in itself strong confirmation of the primary importance of the $\text{NO}_x\text{-O}_3$ photostationary state in controlling the concentrations of these species at these levels. In addition, these experiments also serve to demonstrate that the monitoring instruments, including FAGE- NO_2 , are not subject to serious interferences or artifacts at these concentration levels.

TO THE OFFICE OF GRADUATE STUDIES:

The members of the Committee approve the dissertation of Linda Acha George
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DEDICATION

Dedicated to the memory
of my father, E.V.George.

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TABLE OF ABBREVIATIONS

A/D	Analog to Digital Converter
CL	Chemiluminescence Instrument
CSTR	Continuous Stirred Tank Reactor
ERTC	Atmospheric Mechanism Developed by ERTC Corporation and the Environmental Protection Agency
ESR	Electron-Spin Resonance
FAGE	Fluorescence Assay with Gas Expansion
FPC	Fluorescence Photon Collection
FYP	Fluorescence Yield of Photons
$h\nu$	Energy of a Photon of Light with Frequency ν , h =Planck's Constant
HC	Hydrocarbon
LEF	Laser-Excited Fluorescence (synonymous with LIF)
LIF	Laser-Induced Fluorescence (synonymous with LEF)
Nd-YAG	Neodymium-Yttrium Aluminum Garnet
NO_x	Sum of NO (nitric oxide) and NO_2 (nitrogen dioxide)
O_x , OX	Oxidant
PAN	Peroxyacetylnitrate
PMT	Photomultiplier Tube
ppb,ppbv	Parts-Per-Billion by Volume

ppm,ppmv	Parts-Per-Million by Volume
ppt,pptv	Parts-Per-Trillion by Volume
PSS	NO _x -O ₃ Photostationary State
QVT	LeCroy (Model QVT3001) multichannel analyzer. This instrument was used in the gated charge integration mode unless otherwise noted.
SNR	Signal-to-Noise Ratio
UV	Ultra-violet portion of the electromagnetic spectrum
UVMRD	Home-made Photodiode Device Sensitive to the 300- 400nm Portion of the Solar Radiation

CHAPTER I

INTRODUCTION

Accurate measurements of global nitrogen oxide distributions are critical in assessing the impact of human activity on the troposphere. Although reliable, sensitive techniques for the direct measurement of nitric oxide (NO) have been developed, available direct techniques for the measurement of nitrogen dioxide (NO₂) suffer from interferences and/or lack of sensitivity. This investigation examines the utility of an analytic technique known as FAGE, fluorescence assay with gas expansion, in the development of a sensitive, direct method of measuring low levels of tropospheric NO₂.

IMPORTANCE OF NITROGEN OXIDES IN THE ATMOSPHERE

Nitrogen oxides play a critical role in the chemistry of the clean and polluted atmosphere. The most abundant and chemically active of the nitrogen oxides in the troposphere are NO and NO₂. Their sum concentration in the atmosphere is known as NO_x. Together, they are in large part responsible for controlling the concentration of photochemical oxidants in the atmosphere.

Photochemical oxidation of natural and anthropogenic emissions is the means by which the atmosphere maintains a near constant atmospheric composition. Evidence that increasing emissions of anthropogenic substances [Crutzen and Gidel, 1983; Khalil and

Rasmussen, 1990a, Khalil and Rasmussen, 1990b] are beginning to change this balance brings greater urgency for understanding the chemistry of the atmosphere. NO_x compounds are important in controlling the concentrations of the two primary oxidants of the troposphere, hydroxyl radical (HO) and ozone (O_3) (Figure 1).

The hydroxyl radical is the chief agent in preventing the buildup of hydrocarbons and other compounds in the troposphere. Hydrocarbon removal is usually initiated by oxidation with HO via:

where RH is a hydrocarbon. In the presence of sunlight and further reaction with HO and other compounds, oxidized hydrocarbons either are removed from the atmosphere as soluble organic compounds by wet or dry deposition or are completely oxidized to CO_2 .

Ozone also initiates the oxidation of some hydrocarbons, particularly some alkenes. It is also critical in forming HO in the clean atmosphere via reactions 2 and 3.

One of the chief environmental issues concerning tropospheric ozone is its apparent increase in remote areas of the boundary layer [Feister and Warmbt, 1987; Volz and Kley,

Figure 1. Simplified nitrogen oxide reaction scheme.

1988]. Elevated levels of ozone are detrimental to human and vegetative health as ozone causes destructive oxidation of human and plant cell tissue [Folinsbee *et al.*, 1988; Heck *et al.*, 1982].

Nitrogen oxides are released into the atmosphere both naturally and by human activity. The largest source of nitrogen oxides is nitrous oxide (N₂O) which is emitted via microbial processes in soil and natural waters. Nitrous oxide is not chemically active in the troposphere but it is an important agent in controlling stratospheric ozone.

NO_x is the principal form of chemically active nitrogen oxides in the troposphere. High temperature combustion of fossil fuel and biomass burning constitutes about 70% of the total inventoried emission sources for NO_x of which ~95% is NO and ~5% is NO₂ [Logan, 1983]. The remaining sources of NO_x emissions are due to microbial activity in soils and production of NO_x in lightning discharges [Logan, 1983]. Some recent estimates conclude that lightning could be the single largest contributor of nitrogen oxides in the global N budget [Liaw *et al.*, 1990].

Ozone in the troposphere is formed via the photolysis of NO₂ and the subsequent reaction of the released O atom with O₂. Ozone can then react with the NO newly generated or already present to reform NO₂ and O₂.

This cycle is known as the $\text{NO}_x\text{-O}_3$ Photostationary State (PSS) and has been the subject of much study and controversy [Calvert and Stockwell, 1983; Parrish *et al.*, 1986; Calvert, 1976; O'Brien, 1974; Fehsenfeld *et al.*, 1988). The occurrence of significant side reactions such as R7 or R8 involving NO_x or O_3 can alter the above null cycle resulting in the net production (R7 + R8) or loss of ozone (ozone + alkene $\rightarrow$ products). Thus measurement of the imbalance of the PSS due to side reactions is critical in understanding ozone chemistry in the troposphere.

NO_x is primarily removed from the troposphere via the production of nitric acid (HNO_3):

This is followed by the wet or dry deposition of HNO_3 . Dry deposition of NO_2 can also contribute significantly to NO_x loss processes [Logan, 1983]. NO_x is removed by these processes on the order of hours to days [Logan, 1983]. Nitric acid impacts the environment in two ways: first, its formation by R9 results in the consumption of a hydroxyl radical, which reduces hydrocarbon consumption rates and secondly, the removal

of nitric acid itself, by wet or dry deposition from the atmosphere onto land, vegetation or water, can produce environmentally undesirable results.

Although emission sources of NO_x are centered in urban areas, the production of organic nitrates via reactions such as:

have been recognized to provide a means of long range transport of reactive nitrogen from polluted to unpolluted regions [Singh and Hanst, 1981]. Peroxyacetyl nitrate (PAN) is the most abundant organic nitrate in the troposphere and contributes significantly to the total tropospheric abundance of reactive nitrogen oxides NO_y ($\text{NO}_x + \text{HNO}_3 + \text{NO}_3 + \text{organic nitrate} + \text{NO}_3 + \text{N}_2\text{O}_5 + \dots$) [Singh *et al.*, 1985; Singh, 1987; Buhr *et al.*, 1990]. With the proper meteorological conditions, transport of NO_y compounds in the range of 100's of kilometers has been observed [Hov, 1984; Moxim, 1990]. NO_y reservoir species can be converted to NO and NO_2 by the processes shown below.

If these NO_y reservoir species have been transported from a polluted region, these processes can lead to tropospheric ozone production as NO_2 is photolyzed to form O_3 , in regions remote from NO_x sources.

Concentrations of NO_x present in a given area are a strong function of the season, latitude and type of source components important there, be they anthropogenic, natural or due to transport. This results in NO_x concentrations that can vary over 4-5 orders of magnitude from mixing ratios of 10^{-12} in "very clean" environments to polluted air levels of over 10^{-8} . Increasing NO_x levels in remote areas impacted by urban emissions can have dramatic effects on remote ozone levels [Sillman *et al.*, 1990]. Consequently, accurate measurements of global tropospheric NO_x distribution are critical for predicting potential ozone production due to increasing NO_x emissions. Although reliable direct measurements of low concentrations of NO have been achieved in the last few years, direct detection of NO_2 at low mixing ratios remains a research challenge.

MEASUREMENT TECHNIQUES FOR NO_2

Tropospheric measurement of NO_2 has generally been accomplished using techniques based on NO determination. NO_x chemiluminescence (NO_x -CL) instruments, for example, monitor NO_2 by first converting the species to NO by photolytic or chemical means [Kley and McFarland, 1980; Kelly *et al.*, 1980; Ridley *et al.*, 1988a]. Nitric oxide is then measured by reacting it with excess O_3 and measuring the chemiluminescence emitted by NO_2 generated in an excited state. Nitric oxide chemiluminescence (NO-CL)

is an accurate, rapid, sensitive analytical technique which compares very well [Hoell *et al.*, 1987, Gregory *et al.*, 1990a] with more sophisticated 2-photon laser excited fluorescence (LEF) techniques [Bradshaw *et al.*, 1985]. However, NO-CL does require the subtraction of an artifact signal which is determined at night [Parrish *et al.*, 1990].

Although comparably sensitive to NO₂ and NO, CL measurement of NO₂ as NO suffers from uncertainties in the conversion efficiency, with the possibility that other members of the extensive NO_y family are partially converted as well [Fehsenfeld *et al.*, 1988; Ridley *et al.*, 1988b]. NO₂ has recently been measured [Sandholm *et al.*, 1990] by first photolyzing the molecule to produce NO, which is then measured by 2-photon LEF (utilizing three lasers) [Bradshaw *et al.*, 1985]. Direct measurement of NO₂ by other techniques (such as optical absorption, matrix-isolation/ESR) has been accomplished, but requires either long temporal [Biermann *et al.*, 1988; Mackay *et al.*, 1988; Schiff *et al.*, 1983, Mihelcic *et al.*, 1990] or spatial [Kolsch *et al.*, 1989; Platt *et al.*, 1979] averaging. Suitable averaging times are dependent on the processes being studied and on the environment in which the measurements are being made. Measurements of equilibrium atmospheric chemistry should be made with averaging times (or distances) shorter than time in which different air parcels are encountered. In urban environments this can be on the order of seconds. In order to study the kinetics of perturbation from the equilibrium state the relaxation time of the system will determine a suitable averaging time.

A recently published intercomparison of airborne NO₂ instruments [Gregory *et al.*, 1990b] compared indirect techniques, NO-chemiluminescence [Ridley *et al.*, 1988b]

and NO-LEF [Sandholm *et al.*, 1990], and one direct technique, tunable diode-laser spectroscopy (TDLAS) [Schiff *et al.*, 1990]. The intercomparison reports that there is a 30-40% level of agreement between these techniques for concentrations above 100pptv but "when the data were restricted to mixing ratios of <50pptv, little correlation among the measurements was observed". Correlations between the two indirect techniques were better than between either one with the direct technique for all concentrations reported. A recent ground-based intercomparison [Fehsenfeld *et al.*, 1990] of NO₂ measurement techniques (NO-chemiluminescence and TDLAS-NO₂), concluded that these instruments agree only for [NO₂] > 400pptv. Clearly the development of an additional direct NO₂ technique would be beneficial in understanding the discrepancies between the direct and indirect NO₂ techniques.

CHAPTER II

DEVELOPMENT OF FAGE-NO₂

FAGE PRINCIPLE

FAGE, Fluorescence Assay by Gas Expansion, is a technique that has been developed to enhance signal-to-noise ratios (SNR) for trace gas detection in the atmosphere [Hard *et al.*, 1984]. This technique involves the low pressure excitation of the target species by a light source to an upper electronic state. Excitation of the target species at low pressure reduces collisional quenching and thereby lengthens the fluorescence lifetime. To understand the superiority of this technique over ambient pressure fluorescence techniques it is beneficial to discuss the characteristics of the signal (S) and background (B).

For a fluorescence technique, the signal is due to the emission of photons of the target species after it has been excited by incident light of the appropriate wavelength(s). This signal is designated the gross signal as it includes the signal due the target species as well as the background signal. A measurement of the background is achieved by removing by some means the signal due the target species. The background signal derives from a number of sources that can be categorized into electrical, scattered photons and fluorescence of species other than the target. Interferences result when the gross signal contains significant contributions due to some source other than the target species

which is also modulated by the background subtraction technique or if the background subtraction technique corrupts the "true" background signal.

One goal of any analytic technique is to optimize the operating parameters of the system to maximize the signal-to-noise ratio (SNR) of the instrument.

$$\text{SNR} \equiv S/\sigma_s \quad (1)$$

S is the signal and σ_s is the uncertainty in measuring S. For an instrument based on photon counting, the lower limit uncertainty of the measurement is given by Poisson statistics, where:

$$\sigma_{\text{PHOTONS}} = \sqrt{\text{PHOTONS}} \quad (2)$$

Greater uncertainty can arise due to variation in analyte concentration, fluctuations in detector response, etc.. However, systems operating under relatively low signal photon arrival rates operate with an internal variance limited by Poisson uncertainty [Currie, 1989]. A measurement of the signal (S) is made by subtracting the background (B) from the gross signal (S+B), where S and B represent the number of photons due to the signal and background respectively.

$$\text{net signal} = \text{gross signal} - \text{background}$$

$$S = (S + B) - B \quad (3)$$

The uncertainty of the measurement is a function of the total number of photons collected.

In order to measure the concentrations of analyte that may have relatively low optical densities and/or fluorescence yields, high photon excitation rates are required. This is easily achievable by laser sources. Unfortunately this results in a large background pulse due to Rayleigh, Raman and Mie scattering of the constituents of sample as well as the scattering of photons off of the components of the detection cell. Discrimination of fluorescence photons from scattered photons is difficult when the ratio of excitation photons to fluorescence photons is extremely high - resulting in poor SNR ratios. Saturation of the detection optics, such as photomultipliers, during the laser pulse is a common phenomenon further limiting SNR ratios.

FAGE takes advantage of the different temporal characteristics of the scattering and fluorescence processes. Scattered photons are emitted essentially simultaneously with the laser pulse but the fluorescence lifetime of the target species can be extended by operating at reduced pressure. By operating at lower pressure the detection system can be turned "on" some time after the laser fires. At this point the background due to scattering is greatly reduced while the signal due to fluorescence of the desired species persists. In addition, photomultiplier saturation effects are lowered due to the proportional decrease in Rayleigh and Mie scattering with pressure. Thus an effective discrimination between scattered and fluorescence photons can be achieved.

Operation at reduced pressure also proportionally decreases analyte concentration but this effect is offset, within limitations, by the change in fluorescence yield with

pressure. For a given concentration of a species in an excited state A^* , a simple fluorescence decay involves two processes:

where k_r is the rate constant for fluorescence emission, k_q is the quenching rate constant of the emitting state and M is the concentration of the quencher. The fluorescence yield of photons (FYP) from a given initial concentration of X^* can be shown to be:

$$FYP = k_r / (k_r + k_q M) A^* \quad (4)$$

The concentration of the excited species can be written as a mole fraction, x_A , times the total concentration, M , which gives:

$$FYP = k_r / (k_r + k_q M) x_A M \quad (5)$$

Since the processes considered here are in the gas-phase, pressure and concentration are directly proportional to one another. Figure 2 shows the relationship of FYP (normalized to 1) and the fluorescence lifetime to the quenching pressure. The rate coefficients for k_r and k_q used in this figure are for NO_2 . Clearly as long as $k_q M \gg k_r$ the number of emitting photons is independent of quencher concentration (or pressure) and linearly

Figure 2. Fluorescence yield and lifetime vs. quenching pressure.

dependent on the mole fraction of excited state. Thus FAGE decreases the rate of photon emission so as to achieve optimal photon recovery after the laser fires but does not decrease the total number of photons emitted.

Theoretical enhancements of SNR with FAGE can be demonstrated assuming an exponential decay for the fluorescence signal and an exponential decay plus a constant (which reflects any approximately constant background such as the dark current of the PMT or ambient (stray) light) for the background.

$$S(t) = S_0 \exp(-k_s t) \quad (6)$$

$$B(t) = B_0 \exp(-k_b t) + D \quad (7)$$

$S(t)$ and $B(t)$ represent the signal and background as function of time. S_0 , k_s and B_0 , k_b are the intensities at $t=0$ and the decay rates of the signal and exponentially decaying part of the background, respectively. For a simple fluorescence process k_s would have the form of the denominator in equation 5. D simulates the dark current of the detection device which is assumed to be constant with respect to time.

If the signal is much lower than the background at $t=0$ and the signal decays slower than the background, optimal signal recovery would be enhanced with a delay with respect to $t=0$. If the delay is too long the exponentially decaying effects of both the signal and background will have degraded the SNR (see Figure 3a). To achieve full signal recovery, an integration gate width, t_g , of infinite width would seem optimal. However, in any real detection system the signal will decay into the noise of the detection

Figure 3. Maximizing SNR with t_g and t_d .

device (represented by D). At this point the signal recovery is improving much more slowly than the increase in noise due to the influence of integrated dark current, D (see Figure 3b). Thus a finite gate width is warranted.

The integrated signal and background for time t_d (delay time) to t_d+t_g (delay plus gate width) is:

$$S_{int} = S_0/k_s[\exp(-k_s t_d) - \exp(-k_s(t_d+t_g))] \quad (8)$$

$$B_{int} = B_0/k_b[\exp(-k_b t_d) - \exp(-k_b(t_d+t_g))] + D t_g \quad (9)$$

Based on definitions in equations 1 and 2 and the propagation of error through equation 3,

$$SNR = S_{int}/(S_{int} + 2B_{int})^{.5} \quad (10)$$

For a given set of experimental conditions, S_0 , B_0 , k_s and k_b , the delay and gate width settings for maximum SNR can be predicted by setting the partial derivatives of equation 10 with respect to t_g and t_d equal to zero and solving simultaneously. SNR_{max} is calculated by substituting the optimal gate parameters, t_g , and t_d , back into equation 10. (See Appendix A for details of calculations.)

SNR_{max} is a function of the absolute values of each of the parameters, S_0 , B_0 , k_s , k_b and D. However by keeping B_0 , D and k_b constant while varying S_0 and k_s the effect of the ratios k_b/k_s and B_0/S_0 on SNR_{max} can be evaluated. As expected, the higher SNR's

are achieved when signal is stronger than background ($S_0/B_0 > 1$) and the background decays much faster than the signal ($k_b/k_s > 1$). This is seen in the steep rise in SNR_{max} in the lower right-hand quadrant of Figure 4. To compare FAGE SNR with SNR of fluorescence techniques made at atmospheric pressure (short fluorescence lifetime), SNR is calculated with full recovery of signal and background. To achieve this, t_d is set equal to zero and since lifetimes are short at atmospheric pressure, t_g need not be long. Since t_g is assumed to be short, the contribution of dark current to the total background is assumed to be negligible and set equal to zero. The net effect is to set the quantities within the brackets in equations 8 and 9 to 1. It is assumed that in order to make this comparison that equations 8 and 9 are independent of pressure. That is, the pressure difference between the high and low pressure simulation does not significantly reduce the fluorescence yield.

When signal and background conditions are favorable ($B_0/S_0 \sim < 10$), SNR enhancement, defined as the ratio of SNR_{max} computed by optimal gating to SNR without optimal gating (1 atmosphere case), is slightly greater or equal to one. On the other hand, when conditions are unfavorable ($B_0/S_0 \sim > 10$), lengthening of fluorescent lifetimes and use of optimal gating can increase SNR significantly (upper half of Figure 5). In practical terms, an enhanced SNR ratio of 5 translates into a reduction in signal averaging times of 25 to achieve the same SNR.

Summarizing, FAGE offers two important advantages over atmospheric fluorescence techniques. First, by lowering pressure for excitation, the fluorescence photon arrival rate is reduced which allows for effective temporal discrimination against

Figure 4. SNR as a function of the ratios k_b/k_s and B_0/S_0 .

Figure 5. Enhancement of SNR achieved with optimal gating as a function of k_b/k_s and B_0/S_0 .

a huge scattering pulse due the laser source. In practice this is the largest factor in improving SNR ratio. However, SNR can be further enhanced via optimal gating when background photons are higher in intensity but have faster decays than signal photons. For instance, from Figure 5, for $B_0=1000S_0$, and $k_b=50 k_s$, SNR enhancement ratio is about 4 thus indicating that a 16 times shorter averaging time can be used to achieve the same SNR. In principle, all laser-induced-fluorescence measurements that can be operated in a reduced fluorescence quenching environment should benefit from the first effect. In addition, target species with long natural lifetimes should benefit with the use of optimal gating to discriminate against unwanted fluorescence.

APPLICATION OF FAGE TO NO_2

Nitrogen dioxide absorbs in the UV and visible portion of the electromagnetic spectrum. It has a largely continuum absorption spectrum with some banded features (Figure 6). Quantum mechanical calculations predict a linear 2B_1 and a low-lying bent 2B_2 excited state [Gillespie *et al.*, 1975] (see Figure 7). Transitions involving these states and the ground state 2A_1 are complex and have been studied extensively [Donnelly and coworkers 1976,1978,1979;Hardwick, 1985] but assignment of emission lines to particular states has not been completely accomplished. There is general agreement that excitation at wavelengths above 500nm result in the electronic transition $^2B_2 \leftarrow ^2A_1$ [Hiraoka *et al.*, 1987, Schmiedl *et al.*, 1977] . The radiative lifetime of emission from the 2B_2 state based on the integrated absorption coefficient is about two orders of magnitude shorter than the

Figure 6. NO₂ absorption spectrum.

Figure 7. NO_2 energy level diagram.

observed lifetime (30-100 μ s) [Schofield, 1977]. This type of behavior is indicative of a mechanism involving forbidden transitions and energy transfer mechanisms. This effect, which has been studied extensively, results from a complicated mechanism involving perturbation of upper vibrational levels of the ground state, 2A_1 , and radiationless transitions between vibronic states [Donnelly et al, 1979]. Consequently, NO₂ has fluorescence properties that are a strong function of excitation wavelength, pressure and spectral detection region. Although the anomalous excited energy state transitions of NO₂ make it difficult to fully characterize its fluorescence properties, the extended radiative lifetime of NO₂ makes FAGE a particularly suitable analytic technique for measuring NO₂ concentration as described in the previous section.

An expression for signal recovery for FAGE-NO₂ can be derived for the measurement of NO₂. By explicitly including all known contributions to signal recovery this exercise is useful in the development of the instrument. Fluorescence photon collection is written as

$$FPC = L_p \times D_e \times F_e \times C_x \quad (11)$$

where, L_p is the number of laser photons per laser pulse at the excitation wavelength, D_e is the optical efficiency of the detection system, F_e is yield of fluorescence and C_x is the concentration of NO₂.

$$L_p = \frac{\text{average power(Watts)} \cdot \text{wavelength(meters)}}{(\text{pulse repetition rate, Hz}) \cdot 3 \times 10^8 (\text{m/sec}) \cdot 6.63 \times 10^{-34} (\text{J} \cdot \text{s})} \quad (12)$$

$$D_e = \frac{(\text{radius of optics})^2}{4 \times (\text{distance from optics to fluorescence region})^2} \cdot (Q_{ei} \cdot F_i) \cdot R \quad (13)$$

$$F_e = \sigma_\lambda (\text{cm}^2) \cdot \ell (\text{cm}) \cdot k_f / (k_f + \sum (k_{qi} M_i)) \cdot [\exp(-k_f + \sum (k_{qi} M_i) t_d) - \exp(-k_f + \sum (k_{qi} M_i) (t_d + t_g))] \quad (14)$$

The number of laser photons, L_p , is readily calculated from the average power, wavelength and pulse repetition frequency of the laser. D_e is estimated based on the solid angle of collection, photomultiplier quantum efficiency Q_{ei} over the region of emission, spectral filter overlap F_i over the region of emission, and percent reflection losses on surfaces, R . F_e is determined by the absorption coefficient at the excitation wavelength σ , path length ℓ , and fluorescence yield FYP including the integration gate width and delay.

For the FAGE- NO_2 systems, D_e is 1/16 and the length of the detection zone, ℓ , is 3 cm. Q_{ei} was determined to be 0.02 based on the quantum efficiency of the photomultiplier tube given by the manufacturer (EMI Photomultiplier Catalog, 1986) over the detected wavelength region. Reflection losses and misalignment losses give an estimated value of R of .33. The spectral filter overlap F_i was calculated to be 70% based on filter transmission and the normalized fluorescence spectrum of NO_2 measured by Donnelly and co-workers, 1979. These quantities have been used to calculate a theoretical calibration factor for the systems developed. These factors as well as other quantities pertaining to the actual FAGE systems are tabulated in Table II in Chapter IV.

CHAPTER III

DESCRIPTION OF INSTRUMENTS

INTRODUCTION

Three different laser systems were involved in the development of FAGE-NO₂. The first two systems (Figure 8), FAGE1 and FAGE2, were based on Neodymium-Yttrium Aluminum Garnet (Nd-YAG) lasers and the most recently designed instrument, FAGE3, was developed around a Cu-vapor laser. Each system contributed to a greater understanding of the limitations and potential improvements that could be made. Most of the development work was done with FAGE1. Modifications necessary and improvements made for FAGE2 and FAGE3 are elucidated below.

FAGE1

The first laser employed was a 15 year old 6Hz Nd-YAG laser (General Photonics, Model YAG-TWO-70A) used earlier in the ambient FAGE-HO measurements [Hard *et al.*, 1984]. The Nd-YAG crystal emits at 1.06μm which is frequency doubled within the laser head to emit about 30% of its power at 532nm. Typical green power of the FAGE1 laser was ~200 mW. The original detection cell was an uncoated aluminum block with 2 inch diameter ports on 5 sides to accommodate beam entrance and exit arms, vacuum and sample nozzle ports, and photomultiplier (PMT) port (see

Figure 8. FAGE1 and FAGE2 experimental setup.

Figure 8). Since the FAGE technique delays signal acquisition until some time after the laser fires, it was thought that an uncoated (semi-reflective) cell would enhance signal recovery compared to a cell which had been coated for minimum reflectivity to minimize collection of scattered light from the laser beam. Coating for maximum reflectivity is particularly effective in signal limited chemiluminescence systems [Mehrabzadeh *et al.*, 1984]. However the intensity of scattering caused by passage of the laser beam through the cell effectively saturated the PMT and its recovery was noted to last several microseconds. This was a lesson in the importance of the scattering background on the PMT even with time delayed gating. It was clear that in order to achieve an acceptable SNR, reducing the background due to scattering would be a major challenge.

One large source of scattering signal at reduced pressure comes from the laser light scatter off of the entrance and exit windows. The intensity of the scatter is a function of the laser intensity, quality of window material used and any imperfections (scratches, bubbles, etc.) or dirt on it. This light can be detected as background signal if it enters the detection cell and reflects off of the walls of the detection cell into the detection zone. The amount of window scatter reaching the detection zone was reduced by positioning baffles with circular apertures within the window arms. The size of the aperture is a compromise between the desire to minimize the scatter reaching the detection zone (reducing baffle size) and minimizing the possibility of the laser beam hitting the baffle (increasing baffle size). Likewise the position of the baffle is a compromise between reducing scattering signal reaching the detection zone (placing a

baffle close to the detection region) and reducing the effect of surfaces likely to reflect back scatter into the detection region (placing baffle further away from detection region). The optimal baffle placement and size for the Nd-Yag laser (Figure 9) were determined by peering into the detection cell at the detection port with the room lights turned off and at low cell pressure while various configurations of baffle size and placements were tried.

Optical imaging was also used to reduce the detection of wall-scattered photons and increase signal recovery. The design of the cell limited the minimum distance of the PMT to 3.5 inches away from the detection zone. The calculated volume collection efficiency is then 2.0%. By placing a 2 inch diameter lens 2 inches away from the detection zone the signal can be imaged onto the PMT photocathode, using a second focussing lens, to increase collection efficiency to 6.25% (equation 13). With the detection zone imaged above the cell a rectangular mask was used to further limit the amount of the scattering reaching the detector from walls outside the desired field of view (Figure 10).

While the above techniques greatly reduced the amount of unwanted scattering reaching the detection zone, spectral filters were necessary to further reduce the scattered laser photons collected. Since NO₂ fluorescence emission is red-shifted from the laser line a red cut-on filter was desirable. Wratten gel filters (No. 21, 1% transmission @532nm, Wratten filter catalog, Kodak Corp.) were initially tried but they did not have sufficient attenuation and transmission properties. We found that several

ENTRANCE ARM **EXIT ARM**

Figure 9. Optimal baffle placement.

Figure 10. Detection optics.

Schott filters (OG570) with an attenuation of 10^{-5} at 532nm placed in series (thus multiplicative attenuations) were suitable for this system.

The photon detection device was a EMI 9816QB photomultiplier tube (PMT) operating at 1900 Volts. Current from the PMT was sent to a gated charge integrator (LeCroy QVT3001) (QVT) whose binary output was connected to a home-made QVT interface device (Appendix B) which was then connected to a IBM-compatible computer. Signal acquisition was synchronized with the laser firing via a MRD trigger photodiode. A variable delay, t_d , time between laser firing and start of signal acquisition and a variable integration gate width, t_g , was accomplished using coaxial cable and the internally generated adjustable gate width of the QVT (Figure 11).

The binary output of the QVT is collected via a parallel I/O card (Metrabyte, PIO-12) in the microcomputer. The data acquisition software (Appendix C) waits for a signal from the I/O card before beginning transfer. The number transferred from the QVT is a number proportional to the charge collected from the photomultiplier for that laser shot (the proportionality constant is supplied by the manufacturer). Conversion of charge, in units of coulombs, to the number of photons was accomplished by two methods. First a histogram of the signal from the PMT with low-level light illumination is recorded. The channel with the highest number of counts is taken as the average for a single photon event. Second, a calculation was made by converting the voltage vs. time trace of the most intense curve (i.e. highest arrival rate) of a single photon observed on a 400MHz oscilloscope to charge. Since these two methods come into reasonable agreement, it is expected that direct conversion of integrated charge to

Figure 11. Timing diagram for signal acquisition.

number of photons is a valid procedure. Laser power was monitored with a digital power meter (Scientech, Model 365) and recorded by the microcomputer.

FAGE2

The experimental design of FAGE2-NO₂ was very similar to FAGE1 (Figure 8). The second Nd-YAG laser (Quintel Series YG-580) operated with a repetition rate of 30Hz and an average power of about 1.2 Watts @532nm. Improvements were made in baffle design by using adjustable metal irises for baffle apertures. This was a necessary modification since the higher power of the laser caused the paper baffles to burn within the cell. In addition the sharper edge of the metal aperture proved superior in reducing scatter (compared to the rough fibrous edge of paper) and also allowed for greater ease in optimizing baffle size. For a larger range of t_d and t_g , a home-made delay generator coupled with a pulse generator (Tektronix, PG502) was used to provide the external gate width for the gated charge integrator.

FAGE3

For FAGE3 (Figure 12) a Cu-vapor laser (Cooper Lasersonics, Model 251) was used. A larger cell was used in this setup in anticipation of the development of simultaneous measurement of other quantities of atmospheric interest. The Cu-vapor laser has a pulse frequency of 5.6kHz and a pulse width of about 30ns. Copper vapor lasers emit at two wavelengths, 578nm and 510.6nm. Laser power at 510.6nm is about 40-60% of the total emission depending on the operating pressure of the laser. The

Telescope Enlarged

Figure 12. FAGE3 experimental setup.

578nm and 510.6nm beams are separated via a dichroic mirror. The 578nm beam is used to pump a dye-laser system for use in the HO_x-FAGE apparatus.

The relatively large copper vapor laser beam diameter (~3.8cm) makes it unsuitable for use in the detection cell for a number of reasons. A large beam requires a greater field of view for the detection system and reduces the ability to physically mask undesired scattering present at the walls of the cell. In addition, a large beam also requires large entrance windows which increase the susceptibility of the detection optics to ambient light. A Galilean type telescope followed by long focal length field lenses was found to be best suited for reducing the beam diameter (Figure 12). Unfortunately super-radiant lasers, such as a Cu-vapor laser, have poor divergence characteristics which are proportionally magnified by the reduction in beam size. Therefore while every effort was made to produce a small collimated beam, an unfortunate reduction in laser power and beam stability resulted.

After telescoping, the beam is sent via reflectance coated mirrors to the FAGE cell. Baffles with adjustable irises are placed within both arms of the cell to minimize detection of light scattered by entrance and exit windows. The unavoidable expanding nature of the beam necessitated additional apertures constructed of razor blades which were placed within the main detection cell before the detection region. The baffle immediately after the detection zone was constructed with pieces cut up from a Wratten gel filter. This radiation absorbing material was found to be superior to black absorbing paper, adjustable irises or razor blades for the purposes of this baffle.

Current from the PMT is sent to the QVT capable of 3-mode analysis in the form a charge integration (Q-mode), time-to-digital conversion (T-mode) and voltage peak measurements (V-mode). T-mode data collection is most desirable since it can directly provide the number of photons collected as well as a histogram of when they arrived at the detector. This provides a simple and efficient method of determining the temporal characteristics of the signal and background. However, this mode is constrained to be only valid in environments of low photon arrival rates. Although statistical corrections can be applied, an upper limit of validity for this correction is around a 20% arrival rate. Despite this limitation T-mode data collection is a valuable tool in ascertaining the sources of background signals. When photon arrival rates are higher than can be corrected, charge integration (Q-mode) is used.

The high repetition rate of the FAGE3 laser system presented some unique problems. The data collection frequency of FAGE3 is 200 times faster than FAGE2 and 1000 times faster than FAGE1. For the same amount of net signal per unit time due to NO_2 , FAGE3 measures approximately constant background events, such as ambient light, proportionally more often. In other words, the integration sampling window is 1000-200 times longer than either FAGE1 or FAGE2. Thus background events, such as photons due to ambient light, contribute proportionally more to the gross signal than either FAGE2 or FAGE1. However, in contrast to FAGE3- HO_x [Chan *et al.*, 1990] exposure of a nozzle system to ambient light, necessary to minimize HO_x sampling loss, is not necessary to sample the relatively stable NO_2 molecule. Consequently, FAGE- NO_2 is immune from stray light entering through the nozzle into the detection cell. On

the other hand, since the measured fluorescence is visible light, room light entering through the entrance and exit windows can increase measured background signal. Acceptable reduction in the effect of room light was accomplished by attaching a long tube constructed of velvetized black paper over the exit window arm and placing an adjustable iris in front of the entrance window.

The circuitry of the QVT generates a constant current which is integrated along with the signal being measured. This provides a means of determining the zero point of the integration (called a pedestal) which is offset from zero coulombs on the QVT output. Thus each time the laser fires the measured signal from the QVT includes the current due to the pedestal of the QVT. This pedestal current is not completely constant and seems to vary as a function of instrument temperature. A drift of 1-4 QVT counts is not unusual during the course of a day, especially during field studies where temperature fluctuations are significant. In addition sudden pedestal shifts of 1-2 QVT counts were noticeable, perhaps due to electrical pickup.

Shifts in pedestal current were not particularly a problem with either FAGE1 or FAGE2 since signal due to the laser was much higher than the pedestal current. For FAGE3 the signal due to the laser is at a level much closer to the pedestal current and, since the integration sampling window is much larger, the pedestal current represents a much higher proportion of the total gross current measured. Thus drifts in the pedestal current can cause spurious signals. This problem was largely solved by introducing a baffle attached to computer-controlled stepper motor before the laser beam entered the cell. By blocking the beam periodically (every five minutes) a measurement

of the pedestal itself could be made. This modification was found to be effective in eliminating spurious signals due to pedestal drift.

The low repetition rate of FAGE1 allowed the use of a simple interpreted programming language TBASIC (Transera Corp., Provo, Utah) while the higher repetition lasers used in FAGE2 and FAGE3 demanded the use of faster compiled code. Software based on combination of QuickC (Microsoft Corp.) with inline assembly language was written for the latter two systems (Appendix C).

CHAPTER IV

INSTRUMENT OPTIMIZATION, LINEARITY AND SENSITIVITY

FAGE1

The primary goals in the development of FAGE1 were to reduce the background and to enhance net signal recovery to the extent that reasonable concentrations of NO_2 could be detected with small averaging times. The former was accomplished primarily by optimizing baffling and detection optics as discussed in the previous chapter. The latter was accomplished by exploring various NO_2 modulation techniques.

Relatively high concentrations of NO_2 were generated, for instrument development purposes, with home-made permeation tubes. These devices consisted of a pyrex bulb with a neck of glass tubing serving as a liquid NO_2 (actually N_2O_4) reservoir with a piece of Teflon tube connecting the reservoir and a pyrex cap made of tubing. The permeation rate is a function of the size of the gap between reservoir and cap, type of teflon used and temperature. A dilution system was devised with the use of mass flow controllers [Goldan *et al.*, 1986]. The linearity of the calibration system was demonstrated with the use of a chemiluminescence NO_2 analyzer (Thermoelectric, Model 14). The approximate NO_2 permeation rate could be determined by this technique.

Four different NO_2 modulation techniques were tried. Three of them were based on photolysis of NO_2 using light sources available in the lab: a flash lamp, a high

powered mercury lamp and a black light. Reduction of NO_2 to NO by photolysis is used by NO-detection instruments to measure total NO_x [Kley and McFarland, 1980; Sandholm *et al.*, 1990]. At wavelengths below 398nm NO_2 is photolyzed to NO and O atom with near unity quantum efficiency. The overall efficiency of photolyzing NO_2 contained in a given air parcel is determined by the photon flux of appropriate wavelength, the exposure time of the air parcel to the light source and pressure in the photolysis cell. The residence time of the photolysis cell was on the order of 6s. Aluminum foil surrounded the photolysis cell and light source to enhance energy transfer to the photolysis cell.

Flash lamp photolysis was the only photolytic technique to achieve a measurable modulation of the NO_2 signal. Flash lamp pulse width was measured to be $\sim 20\mu\text{s}$. Various configurations were tried to achieve maximum modulation. It was thought that by synchronizing the flash lamp firing to the laser pulse with the appropriate delay for the passage of the photolyzed air parcel, maximum modulation efficiency could be achieved. Unfortunately neither the flash lamp circuitry nor laser circuitry would accommodate synchronization. Triggering the laser with the photolysis flash lamp resulted in instabilities in the laser flash lamp trigger circuit resulting in laser shut down. Instead, the flash lamp was operated at a rate which maximized modulation independent of laser firing.

The data collection cycle for this system was to measure the NO_2 signal for 200 laser shots, turn the flash lamp on with a computer-controlled relay switch, delay for 10 seconds, then collect background for another 200 shots, turn lamp off and then delay another 10 seconds before the next collection cycle. A linearity test of the system was

performed and is shown in Figure 13. The upper data points represent the average for several repetitions of the above cycle for the gross signal phase. Similarly, the points just below the gross signal represent the average with the flash lamp firing. The net average difference is multiplied by ten for clarity and is also plotted. The error bars are the standard error of the mean. Although the data indicates that the system is generally linear, deficiencies with this system are evident.

The primary concern is the low modulation efficiency of less than 10%. Modulation efficiency is given by equation 15.

$$\frac{\text{gross signal} - \text{modulated signal}}{\text{gross signal} - \text{background ("zero" NO}_2 \text{)}} \quad (15)$$

Much larger modulations are necessary to reach acceptable detection limits. The significantly negative intercept could be explained by light from the lamp leaking into the detection zone during the photolysis mode. This would raise the background with respect to the signal and result in a negative offset. Calculated signal photon collection is ~3 photons/ppb NO₂ for a 1.1min averaging time. Signal-to-noise ratios were on the order of 5 for about 300ppb NO₂.

With further examination of the data (Figure 14) large fluctuations in the net signal are evident. This may be an indication that potentially higher modulation efficiencies are possible with proper synchronization of the laser and flash lamp. Each point here represents the signal and background summed for 200 laser shots. The

Figure 13. FAGE1 linearity with photolysis modulation.

Figure 14. Raw data from Figure 13.

averages of these points are plotted in Figure 13. The high and low modulations could be a result of a sometimes fairly good but usually poor synchronization. Another possible explanation for the "noise" in the data is interaction of electrical noise from the flashlamp with the PMT. In fact, during experiments with the flashlamp, the computer would, on occasion, "hang up" resulting in the loss of all data acquired. Because of the above considerations photolysis as modulation technique was not pursued.

Modulation of NO_2 by chemical and surface reduction to NO was widely used in CL instruments until recently [Kelly *et al.*, 1987]. These techniques include passing the sample through heated stainless steel tubing, molybdenum metal or ferrous sulfate. However chemical reduction schemes for NO_2 tend to reduce other members of the extensive NO_y family to NO as well. For this reason they are not suitable for use in instruments measuring NO [Fehsenfeld *et al.*, 1988]. Hydrated ferrous sulfate ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$) is reported to have the highest conversion efficiency for NO_2 to NO, upwards of 99%. Conversion of other species to NO is unimportant for this instrument since FAGE- NO_2 is spectrally specific for NO_2 and not NO.

A linearity test with FeSO_4 as the modulating agent was done in a experiment similar to the one utilized above. The NO_2 permeation device used in these experiments was bought commercially (VICI-Metronics) and the permeation rate certified by the manufacturer (105ng/min @30C) was used. The permeation rate was verified within 10% by constant temperature weighings over a period of one month. The cycle here was to collect gross signal for 200 laser shots, switch a three-way valve to allow air passage through a filter capsule filled with ~ 170g of FeSO_4 , wait 10 seconds, then collect

background signal for 200 laser shots. The average laser power in these experiments was ~200mW. The pressure in the fluorescence cell was 1.5 torr. In contrast to Figure 14, the background in Figure 15 is random with respect to concentration reflecting excellent conversion of NO₂. Thus with FeSO₄, unlike the photolysis experiments, the background does not appear to be limited by the conversion efficiency. Much of the variation of the background with time was due to laser beam drift and the consequent misalignment of the beam through the cell. The frequency doubler of the laser was affected by small changes in temperature which demanded frequent tuning of the crystal during an experiment as well as beam realignment.

The slope of the line through the average net signal in Figure 15 is 38.4 ± 1.6 photons/ppbv, the standard error in y is equivalent to 0.6ppbv, and the intercept is equivalent to $-0.6 \pm .6$ ppbv NO₂. The error bars in the Figure are twice the standard error in the mean. This implies a detection limit of around 0.6ppbv with a 1.1 minute averaging time. The calibration factor for FAGE1 based on the above quantities is 345 photons/(ppb min watt).

Signals from the FAGE1 system were compared with data from a NO_x-CL analyzer in an experiment carried out in a continuous stirred tank reactor (CSTR) [Hard *et al.*, 1984]. Nitric oxide and mesitylene flowed into the teflon-film CSTR which was surrounded by UV fluorescent light. The NO_x-CL analyzer (ThermoElectron Model 14) was equipped with a heated stainless steel NO_x converter. Ozone was measured by its absorption at 254nm (Dasibi ozone analyzer). Data from the latter commercial

Figure 15. FAGE1 linearity with FeSO₄ modulation.

instruments were transferred in binary form or converted with an A/D converter to the FAGE1 computer.

Figure 16 shows NO, NO₂ and O₃ data for two cycles of photolysis and darkness. FAGE-NO₂ is plotted on this graph after application of a calibration factor determined from a linear regression of FAGE-NO₂ net photon count vs. NO₂ concentration measured by the CL instrument. The FAGE-NO₂ data is shown with a 1.1 min averaging time. The calibration factor determined in the linearity test in Figure 17 could not be used here because the signal recovery was attenuated (by reducing gate width, t_g) in this experiment to accommodate the relatively high concentrations involved. Although NO_x-Cl instruments with stainless steel converter are known to have interference in the presence of alkyl nitrates such as PAN (peroxyacetyl nitrate) a deviation from good correlation in Figure 17 is not expected in this experiment. A rough simulation of aromatic photooxidation indicates that PAN represents only about 5% of the NO₂ concentration and thus would not cause a noticeable difference between the two sets of data. This is in contrast to measurements in the remote troposphere, where low NO₂ relative to PAN is a frequent occurrence [Singh *et al.*, 1985].

FAGE2

FAGE2 involved the use of the higher-powered, more reliable Quantel Nd-YAG laser. The frequent down time and lack of beam stability limited the ability of FAGE1 to optimize FAGE-NO₂. One of the means of optimizing SNR using the FAGE technique is with optimal gating as discussed in Chapter II. Experimental optimization of the

Figure 16. FAGE1 bag calibration data.

Figure 17. Linearity of bag calibration data.

system was studied by varying the two controlling parameters of signal collection: t_d and t_g . As previously discussed, they are, respectively, the delay between the laser firing and time at which the gated charge integrator was turned on and the width of the integration gate. Average power in these experiments was around 1.4 Watts and cell pressure ~ 0.25 torr.

With gate width fixed at 2000ns, delay time was varied from 800ns to 7000ns. An NO_2 concentration of 42ppbv was used for these experiments and the PMT output was summed for 10s (300 laser shots) during each signal and background phase, with a seven second delay between each phase. Variation in SNR with t_d is shown in Figure 18 for two experiments. SNR was calculated based on equation 2. Error bars are the standard deviation of several repetitions of the same conditions. SNR is fairly constant in the region of 1000 to 1500ns but drops off beyond 1500ns. Triggering the integration gate before 1000ns results in steep decline of SNR. Triggering at times < 750 ns resulted in an overflow condition of the QVT, indicating the presence of a significant portion of the tail of the scattered laser pulse. Figure 19 shows the variation of SNR with respect to t_g . The optimal SNR could not be achieved by increasing t_g due to the limitations of the QVT. Increasing t_g , increases the zero point (or the QVT pedestal, as discussed in the previous Chapter) of the QVT which limits the dynamic range for measurements and sets an upper limit for usable t_g values. However, with the best achievable value of the parameters, t_g and t_d , using 42ppbv NO_2 , signal and background counts were 950 and 412cps respectively. This represents almost a factor of 3 improvement in calibration factor over FAGE1. This was achieved by a combination of effects, including optimization of t_g and

Figure 18. SNR versus t_d .

Figure 19. SNR versus t_g .

t_d , improved alignment of cell optics and lower cell pressure (reducing PMT saturation). Since the fluctuations in signal intensity were found to be consistent with Poisson photon counting statistics a detection limit can be extrapolated, where $SNR \equiv S/(S+2B)^{1/2}$ is calculated as unity. This calculation generates an detection limit of 450pptv for the 30s integration time employed in the experiment. Greater sensitivity would result from longer averaging times, with the improvement in SNR expected to increase as the square root of the averaging time.

These series of experiments demonstrated that the FAGE-NO₂ responds in a manner consistent with the theory presented in Chapter II. In addition, experimental optimization of gating resulted in a reasonably good calculated detection limit with a small averaging time. However, limitations of the system were also noted. The QVT-based detection system was designed for systems with low photon arrival rates per pulse and short integration gates. High photon arrival rates per pulse, as in FAGE2 (and FAGE1), integrated with a QVT, limit the effective dynamic measurement range of the instrument. In addition Figure 19 demonstrates that longer integration gates are desirable to achieve greater sensitivity.

Sensitivity is also enhanced by operating at lower cell pressures. Since the intensity of Rayleigh and Mie scattering is inversely proportional to cell pressure, decreasing pressure will reduce PMT saturation and/or recovery time (in effect, it decreases the lifetime of the background signal). The effect of cell pressure on background is seen in Figure 20. These data were taken by measuring the background signal with respect to trigger gate time. The gate width used here was kept low (250ns)

Figure 20. Background vs. cell pressure.

so that the time dependence of the signal is clear. Clearly the decay processes in the background signal are not simple and involve at least two and perhaps three different decays. Nevertheless, as expected, the decay rate is fastest at the lowest pressure. This is consistent with the idea that decreasing pressure reduces the intensity of Rayleigh scattering which decreases PMT recovery time. If a fluorescence process susceptible to collisional quenching were a major component of the background, then an decrease in fluorescence decay rate with decreasing pressure would be expected.

Optimal SNR will occur at some value of the reduced pressure if the lifetime of NO_2 increases with decreasing pressure and the lifetime of the background increases more slowly or decreases with pressure. One limit in reducing cell pressure is reached when a significant fraction of the emitting target molecules radiate (rate constant k_r) vs. undergoing quenching (rate constant k_q). This limit is related to the half-quenching pressure of the target species ($[M]_{1/2} = k_r/k_q$) (Figure 2), at which pressure half the excited molecules fluoresce while half are quenched. At this point the fluorescence signal has dropped by 1/2 relative to its value at atmospheric pressure.

Thus one parameter in the sensitivity of FAGE- NO_2 is related to k_q and k_r . Since the effective fluorescence lifetime of NO_2 is a strong function of excitation wavelength, spectral detection region and pressure regime a measurement of k_q and k_r under the operating conditions of the current system is desirable. This was accomplished by measuring the signal and background of a fairly high concentration of NO_2 (~150ppb) at various pressures as a function of trigger delay. The signal and background were acquired for 200 laser shots each with a delay of 10 seconds between phases. Multiple

measurements were made at each delay setting. FeSO_4 was used as the modulating agent. Trigger delay was measured with a 400MHz oscilloscope (Tek 2465A). As an example, the data for gross signal and background is shown in Figure 21 for the experiment done at 1 torr cell pressure.

Assuming a single exponential fluorescence decay, the net integrated signal intensity due to NO_2 from the time t_d to the time $t_d + t_g$ is given by:

$$\begin{aligned} & S/(k_r + k_q M) \{ \exp[-(k_r + k_q M) t_d] - \\ & \exp[-(k_r + k_q M) (t_d + t_g)] \} \end{aligned} \quad (16)$$

where S is essentially a proportionality constant which is a function of NO_2 concentration, k_r , and signal recovery efficiency and M is the pressure of the quencher (N_2). If the fluorescence decay rate, k_f , is defined as $k_f \equiv (k_r + k_q M)$ then equation 16 can be expressed as:

$$\text{net signal} = S/k_f \{ \exp[-k_f t_d] - \exp[-k_f (t_d + t_g)] \} \quad (17)$$

Equation 17 is the model equation with which quenching data was fitted. Each data set at a given pressure was fit using a commercial (MINSQ, MicroMath Corp.) parameter fitting (Levenberg-Marquadt algorithm) program with k_f and S as the fitted parameters. Table I gives the results of the parameter fitting. The excellent correlation of the model with the data indicates that the above model based on a single exponential fluorescence

Figure 21. Net signal and background at 1 torr.

TABLE I
RESULTS OF FITTING QUENCHING DATA
TO EQUATION 17

Pressure	S (photons)	Fitted values		1 σ error	r^2_{corr}
torr		1 σ error	k_f (nsec ⁻¹)		
0.25	9.9	0.48	2.6e-4	4e-6	.998
1.0	78.1	1.4	1.2e-3	7e-6	.999
0.5	183.8	0.8	5.3e-4	3e-6	.999
1.5	562.2	7.1	1.9e-3	2e-5	.999

decay is appropriate for the operating conditions of FAGE2. This is consistent with detailed studies of NO₂ fluorescence characteristics which indicate that single exponential decays are observed at high pressures while biexponential fluorescence decays are observed at much lower pressures ($M < 0.01$ torr) [Donnelly *et al.*, 1979]. The results in Table I of decreasing decay rate of NO₂ fluorescence intensity with decreasing pressure are in contrast to Figure 20 where decreasing pressure increases the rate of background decay.

If the fluorescence properties of NO₂ were simple, a fluorescence quenching plot of k_f or $(1/\tau)$, where $\tau \equiv$ fluorescence lifetime) vs M (Figure 22) would yield both k_r (intercept) and k_q (slope). However extrapolation of a fluorescence quenching plot obtained at relatively high pressures to zero does not give a meaningful determination of k_r for NO₂. The negative intercept (implying a negative value for k_r) of Figure 22 has been observed by others making similar measurements at comparable pressures [Kirzimis *et al.*, 1984]. Consequently, the experimental results shown in Figure 22 can only be used to determine k_q under the operating conditions of FAGE2. A linear regression of the points in Figure 22 gives $k_q = 4.0 \pm 0.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. Using the measured k_q value and reported values for k_r , $[M]_{1/2}$ is calculated to be in the range of 26 to 5 mTorr. This suggests that optimum SNR can be achieved by operating in the mTorr pressure range.

However, a second criterion in choosing an operating pressure for efficient measurement of a species with long fluorescence lifetimes requires that the emitting species remain in the detection region long enough for fluorescence to occur. This

Figure 22. Quenching of NO₂ fluorescence in N₂.

criterion can be met by suitable adjustment of flow parameters in concert with cell pressure [Mehrabzadeh, *et al.* 1984]. Figure 23 illustrates the relationship of the time the emitting species spends in the detection zone (assuming plug flow) with the fluorescence lifetime of NO_2 with respect to operating pressure. At a pressure of .1 torr, in Figure 23, given an initially excited parcel of air, 99.95% (10 fluorescent lifetimes) of this excited population is deactivated (either by radiating or by quenching) before leaving the detection zone. For the flow rates used in FAGE2 the two pressure limitations (half-pressure and fluorescent lifetime) occur at comparable pressures.

A linear increase in signal recovery is anticipated from equation 11 unless saturation effects occur. As laser intensity is increased the rate of populating the excited state also increases. Saturation occurs when the rate of populating the excited state approaches the rate of depopulating the excited state by stimulated emission. Thus increasing laser intensity at this point results in a decreased response for each excitation photon. Saturation of the excited state is potentially a concern in terms of achieving maximum signal to noise ratio. Thus saturation reduces the efficiency of the absorption - fluorescence processes and causes deviations from the implicit linearity of response with laser power. This is an important consideration for extrapolating sensitivities based on low power measurements to higher power measurements. It also necessary to understand the influence of laser power in order to normalize response variations in laser power.

Gross changes in laser power were readily controlled in FAGE2 by varying the voltage applied to the oscillator flash lamps. Small fluctuations in laser power (~5%) were present at any given setting. Figure 24 shows the effect of laser power on signal

Figure 23. Fluorescence lifetime and detection zone lifetime vs. cell pressure.

Figure 24. Signal and background vs. laser power.

recovery and the concomitant effect on the background intensity. Data collection cycle was 100 shots each for signal and background with a several second delay between them. After each change in voltage on the flash lamps, laser power was allowed to come into rough equilibrium before new data was acquired. Signal integration gate width and trigger delay were both set to 2000ns. A concentration of ~30ppb of NO₂ was generated with the VICI permeation tube for this experiment.

The fluorescence signal due to NO₂ appears to be linear with laser intensity in Figure 24 with a linear regression correlation of .999 and a slope of 1190 photons/W of laser power. A small positive offset of 11.5 is well within the 1-sigma standard error of Y of 36.8 and therefore cannot be considered a significant offset of the instrument. The log-log plot of data in Figure 25 results in a slope of 1.01 which confirms the linear correlation calculated from Figure 24. This seems indicates that over the laser power ranges used, NO₂ fluorescence is not saturated.

Figures 24 and 25 also show the relationship of the background signal to laser power. Clearly the background is not a simple linear function of laser power. The best fit line in Figure 25 gives a slope of 1.26 for the background. With a slope less than two, the contribution of two-photon processes must be minimal, if any. A slope greater than one suggests a connection between a linear scattering function and photomultiplier tube saturation.

One means of increasing sensitivity is to increase excitation power. An important limitation in this regard results from non-linear effects in either signal or background with laser power. When non-linear effects, such as $\text{slope}_{(\log S \text{ vs. } \log \text{ power})} < 1$ (excited state

Figure 25. LOG-LOG plot of data in Figure 24.

saturation) and/or $\text{slope}_{(\log B \text{ vs. } \log \text{ power})} > 1$ (photomultiplier tube saturation) , are apparent, SNR does not improve predictably or may degrade with laser power. High pulse power can also increase photochemical interference effects (discussed in Chapter VI). These effects can be minimized by reducing the laser energy per pulse while increasing average laser powers suggesting the use of a high repetition rate laser (FAGE3).

FAGE3

FAGE3 was developed with a Cu-vapor laser operating at a 5.6 kHz pulse repetition rate. The present implementation of the system was designed to make ambient measurements from the rooftop of Science Building II at Portland State University. At this point the operating parameters of the system have not been fully optimized but sensitivity was more than adequate for the ambient levels of NO_2 encountered. Calibration was achieved by the same system described earlier. A calibration factor of 292 ± 5 photons/ppb was determined with a standard error in Y of 40 photons computed with laser power of 1.2 Watts (Figure 26). One sigma error bars are plotted as horizontal bars.

Compared to FAGE2 the energy per pulse is reduced by a factor of 200 while still maintaining close to the same overall average laser power. Controlled variation in laser power is not easily achievable with the Cu-vapor laser but some characteristics of the background were determined. Using the T-mode of the QVT the effect of pressure on the background could be easily be determined. By varying the cell pressure from .14 torr to ~760 torr, the background lifetime changed from 7 μs to 3 μs . It is important to note

Figure 26. FAGE3 calibration.

that this is reversed from the situation in FAGE2 where the background decay was longer at higher pressures. The low quenching efficiency of the background implies that a gas phase background fluorescence process is not the principal background source. One possible contributor is fluorescence of the components of the detection cell resulting from excitation by Rayleigh scattered photons. However, the pressure dependence in this regard is difficult to understand. Optimization of this system will necessitate further investigation of the source of the background and the possible means of removing it.

Ambient measurements made with FAGE3 are described in the following chapter. The sensitivity of the current configuration of the system was more than adequate for making measurements in the urban environment. Typically, signal to noise ratios were in the range of 30-60 for 10s averaging time (34s cycle time). The operating characteristics of all three laser systems are summarized in Table II.

TABLE II
OPERATING CHARACTERISTICS OF FAGE1,
FAGE2 AND FAGE3

Parameter	FAGE1	FAGE2	FAGE3
Laser	Nd-YAG	Nd-YAG	Cu-vapor
Excitation Wavelength (nm)	532	532	511
Pulse Repetition Rate (Hz)	6	30	5600
Beam Diameter (mm)	6	6	3
Average Power (Watt)	0.20	1.4	1.2
Pulse Energy (mJ)	33	47	.21
Detection Cell Pressure (Torr)	1.6	.25	.35
NO ₂ absorption coeff. ^a (10 ⁻¹⁹ cm ²)	1.47	1.47	2.46
Measured NO ₂ Calibration Factor (photons/(W·s·ppb NO ₂))	5.8	16	24
Theoretical NO ₂ Calibration Factor ^b (photons/(W·s·ppb NO ₂))	12	23	39
Detection Limit (ppb [NO ₂], 20s averaging time)	2.3 ^c , 1.7 ^d	.45 ^d	.35 ^c , .37 ^d

^a from Schneider *et al.*, 1987, ^b derived from equation 11 and the quantities in this table,

^c determined by calibration, ^d calculated from Poisson statistics.

CHAPTER V

ANALYSIS OF INTERFERENCES AND BACKGROUNDS

POTENTIAL INTERFERENCES

Interferences in this system are possible if the gross fluorescence signal responds to atmospheric constituents other than NO_2 and is modulated by FeSO_4 or if the modulation technique alters the "true" background signal. A review of the literature indicates that no known gas phase constituent of the troposphere both absorbs near 532 or 511nm and fluoresces [Schofield, 1977; Okabe, 1978; Finlayson-Pitts and Pitts, 1986].

The largest potential source of interference is aerosols. This was a limiting factor in previous attempts to measure NO_2 with laser-induced fluorescence at atmospheric pressure [Gelbwachs and Birnbaum, 1973]. To a large extent, aerosols should be discriminated by the temporal and spectral specificity of the FAGE system since aerosols must absorb at 532 or 511nm and fluorescence with microsecond lifetimes in order to present significant interference to the FAGE- NO_2 system. However, with heavy aerosol loading, the passage of air over the FeSO_4 crystals could potentially alter the true background fluorescence by acting as particulate filter, resulting in an interference of a positive sign. Interference problems such as these are recognizable if they alter the measured signal fluorescence lifetime relative to the known value for NO_2 . (With the low photon arrival rates associated with Cu-vapor pumping, fluorescence lifetimes may be

determined directly during ambient measurements by operating the gated charge integrator in the time mode at low NO_2 levels). It is unlikely that the fluorescence lifetime of any potential aerosol interference is pressure dependent, although this should be experimentally verified. Conversely, the fluorescence lifetime of NO_2 can be easily manipulated via the operating cell pressure. Should this approach prove unsuccessful, another (less desirable) approach would be the use of an aerosol filter before entering the sampling manifold [Tucker *et al.*, 1975]. Or it may be necessary to utilize the spectral NO_2 modulation techniques described in the literature [Kley and McFarland, 1980; Sandholm *et al.*, 1990].

Another potential source of interference is the photolysis of ambient NO_3 to NO_2 within the laser beam. NO_3 is photolyzed to NO_2 (+ O atom) with near unity quantum yield at wavelengths between 470 to 580 nm [Magnotta and Johnston, 1980]. This will result in an interference if the NO_2 produced is detected by the same or subsequent laser pulse(s). The relative magnitude of this interference will depend on the fraction of NO_3 detected as NO_2 and the relative contribution of detected NO_3 to the NO_2 signal.

NO_3 is a minor constituent of the atmosphere during the daytime as it rapidly photodissociates to form either NO_2 (90%) or NO (10%). Nighttime concentrations of NO_3 range from 9 to 500 pptv in urban areas and 6 to 30 pptv in remote environments [Finlayson-Pitts and Pitts, 1986]. In urban air where typical NO_2 concentrations are in the range of 10 to >100 ppb, the conversion of NO_3 to NO_2 will not produce a significant interference. However, at night in the remote troposphere, $[\text{NO}_3]$ is expected to be 50-70% of $[\text{NO}_2]$ [Logan, 1983] and therefore could potentially produce a significant

interference. Since NO_3 would increase the signal measured in the signal mode and would be presumably be reduced by FeSO_4 , NO_3 would be a positive interference to FAGE- NO_2 .

A simple photochemical model of the processes occurring within the laser pulse was developed to simulate NO_3 interference (see Table III). Using the values in table II, calculations indicate that the high pulse energy of the FAGE2 laser (Nd-YAG) will photolyze more than 50% of the NO_3 in the sample to produce NO_2 , 90% of which will then be detected during the same laser pulse. In the configuration of FAGE2, with a 30Hz laser, the linear velocity of the flow is sufficiently high (>1000 cm/s), that NO_2 produced, via NO_3 photolysis, by one pulse will be removed from the excitation region before the next pulse arrives. These calculations indicate that the FAGE2 system would not be suitable for nighttime clean air measurements without reductions in pulse energy. This may be accomplished by reducing overall laser power (reducing sensitivity) or by expanding the beam diameter (possibly increasing scatter off of cell windows).

Calculations done with the parameters of the Cu-vapor laser indicate that about 3% of NO_3 will be converted to NO_2 . Less than 40% of these NO_2 molecules will absorb and fluoresce within the first laser pulse. At the current operating conditions of FAGE3, based on a plug flow model, about 1/2 of the region excited by the first pulse will be traversed by the second pulse. However, even if all of the NO_2 produced via NO_3 photolysis is detected with the second pulse, the upper bound of this process represents a small interference. This small interference can be easily reduced by lowering cell

TABLE III

A SIMPLIFIED PHOTOCHEMICAL MODEL FOR FAGE-NO₂

$\text{NO}_2 + h\nu \longrightarrow \text{NO}_2^{**}$	$I\sigma_{\text{NO}_2}$
$\text{NO}_2^{**} + h\nu \longrightarrow \text{NO}_2 + 2h\nu$	$I\sigma_{\text{NO}_2}$
$\text{NO}_2^{**} + \text{M} \longrightarrow \text{NO}_2^*$	3×10^{-10}
$\text{NO}_2^* \longrightarrow \text{NO}_2 + h\nu^*$	1.6×10^4
$\text{NO}_2^* + \text{M} \longrightarrow \text{NO}_2 + \text{M}$	4×10^{-11}
$\text{NO}_3 + h\nu \longrightarrow \text{NO}_2 + \text{O}$	$I\sigma_{\text{NO}_3}$

units are: 1st order, sec⁻¹, 2nd order, sec⁻¹ cm³.

I is the intensity of the laser beam normalized to a sine wave pulse (photons cm² sec⁻¹), σ is the absorption cross-section (cm²), $h\nu$ and $h\nu^*$ are photons from the laser and from fluorescence, respectively. This mechanism (excluding NO₃ photolysis) was derived from the mechanism for NO₂ excitation and fluorescence developed by Donnelly and co-workers, 1979.

pressures (which will independently give greater sensitivity) and/or increasing the flow velocity to minimize double pulse problems.

BACKGROUND

The major source of background signal in these systems was the intense burst of scattered photons due to the laser pulse. The time-dependence of this background is related to the recovery time of the PMT and is possibly due to fluorescence of optical components (such as filters) in the cell. As the system is improved to reduce the intensity of the scattered signal (by reducing cell pressure and perhaps by finding better cell baffling), the background may be limited by other effects. These include fluorescence of species other than NO_2 (aerosols are the only known atmospheric constituents with absorption and fluorescence in this region), the dark current of the PMT and/or the efficiency of removal of NO_2 as a fluorescing species.

The signal-to-noise ratio (SNR) determines the ultimate sensitivity of an instrument. Increasing laser power is predicted to linearly increase fluorescence signal by equation 11. If the background also increases linearly with laser power,

$$\text{SNR} = \frac{S}{(S + 2B)^{1/2}} \sqrt{\text{laser power}}$$

the SNR should improve as the square root of the laser power. However, if saturation effects occur, the *improvement* in SNR with laser power will be smaller. Saturation decreases the linearity of the fluorescence response of the system.

Saturation effects in the FAGE2 and FAGE3 system were modeled with the simplified photochemical system shown in Table III. For FAGE2, these calculations indicate that at the highest laser power utilized (1.7W) the system would deviate from linearity by 7% relative to zero saturation. This result appears to be in contradiction to the experimental results shown in Figures 24 and 25 where the signal response was linear with laser power. The concentration of excited state was calculated for the laser powers used in those experiments in order to simulate the experimental results. The calculated slope_(log laser power vs log signal) of the simulated results is 0.98 with a regression coefficient of 0.9995 compared to the slope of the experimental value of 1.01 ± 0.02 . Comparing these results, it is clear that the experiment shown in Figures 24 and 25 is a necessary but not a sufficient test for saturation. In order to determine saturation levels experimentally, a greater range of laser powers must be utilized.

The calculations for FAGE3 indicate that at the average power used (1.2W), the response is deviating from linearity by ~ 0.4%. If the laser power is increased by one order of magnitude, deviations rise to 3.3%. Increased laser power is desirable for increased sensitivity or decreased averaging time, but must be weighed against increased NO₃ interference which is also linear with laser power. Overall, the FAGE3 system is superior to FAGE2 for a number of reasons: 1.) it is less susceptible to NO₃ interference - due to lower pulse energy and lower NO₃ absorption at 511nm; 2.) predicted saturation

levels are lower and 3.) detection limit is somewhat better than FAGE2 (see table II) - due largely to greater NO₂ absorption cross-section at 511nm.

CHAPTER VI

AMBIENT MEASUREMENTS AND URBAN NO_x CHEMISTRY

INTRODUCTION

In an environment that contained only NO_x and air (N₂ and O₂) the primary reaction cycle of NO_x in the presence of solar radiation would be:

Reactions of species containing nitrogen in oxidation states >4 (see Table IV) are important in the dark but will not contribute significantly in the presence of solar radiation due to the high rates of photodissociation of these species (see Table IV).

In a real or simulated atmosphere in which constituents such as hydrocarbons and water are present, the explicit chemistry of the system becomes complex. A complete set of rate expressions for NO, NO₂ and O₃ includes reactions with HO_x (HO and HO₂) and

TABLE IV
REFERENCE REACTION MECHANISM

1	RH	HO	-->	R	H ₂ O	
2	O ₃	hν	-->	O(¹ D)		
3	O(¹ D)	H ₂ O	-->	2HO		
4	NO ₂	hν	-->	NO	O	
5	O	O ₂	M -->	O ₃	M	
6	NO	O ₃	-->	NO ₂	O ₂	
7	RO ₂	NO	-->	RO	NO ₂	
8	HO ₂	NO	-->	HO	NO ₂	
9	HO	NO ₂	M -->	HNO ₃	M	
10	NO ₂	O ₃	-->	NO ₃	O ₂	
11	NO ₃	NO	-->	2NO ₂		
12	NO ₂	NO ₃	M -->	N ₂ O ₅	M	
13	N ₂ O ₅	hν	-->	NO ₂	NO ₃	
14	NO ₃	hν	-->	NO	O ₂	
15	NO ₃	hν	-->	NO ₂	O	
16	R	O ₂	M -->	RO ₂	M	
17	RO ₂	NO	-->	RONO ₂		
18	RO ₂	NO ₂	-->	ROONO ₂		
19	HO ₂	NO ₂	M -->	HNO ₄	M	
20	HNO ₄	M	-->	HO ₂	NO ₂	M
21	HO	NO	M -->	HONO		
22	HONO	hν	-->	HO	NO	
23	H ₂ CO	hν	-->	2HO ₂	CO	
24	H ₂ CO	hν	-->	H ₂	CO	
25	HO	CO	-->	HO ₂	CO ₂	
26	O ₃	alkene	-->	products		
27	O ₃	hν	-->	O	O ₂	M
28	O ₃	HO ₂	-->	HO	2O ₂	
29	CH ₄	HO	-->	CH ₃ O ₂	H ₂ O	
30	CH ₃ O ₂	NO	-->	CH ₃ O	NO ₂	
31	CH ₃ O	O ₂	-->	CH ₂ O	HO ₂	

hydrocarbons. The rate expressions below include a subset of some of these reactions (the steady-state approximation for O atoms has been made):

$$\begin{aligned} d[\text{NO}_2]/dt = & k_6[\text{NO}][\text{O}_3] + k_8[\text{NO}][\text{HO}_2] + k_7[\text{NO}][\text{RO}_2] + 2k_{11}[\text{NO}][\text{NO}_3] - \\ & k_{19}[\text{HO}_2][\text{NO}_2][\text{M}] + k_{20}[\text{HNO}_4][\text{M}] + J_{\text{NO}_{2a}}[\text{NO}_3] - J_{\text{NO}_2}[\text{NO}_2] - k_{10}[\text{NO}_2][\text{O}_3] \end{aligned} \quad (18)$$

$$\begin{aligned} d[\text{NO}]/dt = & J_{\text{NO}_2}[\text{NO}_2] - k_6[\text{NO}][\text{O}_3] - k_8[\text{NO}][\text{HO}_2] - k_7[\text{NO}][\text{RO}_2] - k_{10}[\text{NO}][\text{NO}_3] + \\ & J_{\text{HONO}}[\text{HONO}] + J_{\text{NO}_{3b}}[\text{NO}_3] \end{aligned} \quad (19)$$

$$\begin{aligned} d[\text{O}_3]/dt = & J_{\text{NO}_2}[\text{NO}_2] - k_6[\text{NO}][\text{O}_3] - k_{26}[\text{O}_3][\text{alkene}] \\ & - k_{10}[\text{O}_3][\text{NO}_2] + k_{28}[\text{HO}_2][\text{O}_3] \end{aligned} \quad (20)$$

Rate constants for reactions involving photolysis are written in terms of the species photolyzed, i.e. the rate constant for R4 is written as J_{NO_2} . Despite the seemingly complex nature of the chemistry involving these species, it was recognized in early experimental and theoretical studies of photochemical smog in smog chambers that the primary reaction cycle for O_3 and NO_x under many conditions is limited to R4-R6 [Leighton, 1961]. Inspection of the expressions 18, 19 and 20 indicates that this observation can be explained if the rates of the reactions other than R4-R6 are comparatively small in magnitude. If this condition is met, setting any of the three equations, 18, 19 or 20 to zero (steady-state for NO_2 , NO or O_3) would yield the following simple relationship :

$$p = \frac{J_{\text{NO}_2} [\text{NO}_2]}{k_6[\text{O}_3][\text{NO}]} \quad (21)$$

The right hand side of Equation 21 is known as the O_3 - NO_x photostationary state (PSS) expression. If the system is in steady-state and the contributions from reactions other than R4-R6 are exactly nil, then p is exactly unity. It follows, that under steady-state conditions, the value of p is a measure of the relative contributions of reactions other than R4-R6 to expressions 18,19 and 20. It is important to note that equation 21 can be derived from any of the expressions 18,19 or 20 but that not all of the reactions neglected are the same for each species. This has implications when considering the nature of the deviations of p from unity. When p is close to one, the relative magnitude of side reactions are small. Reversible reactions must be considered in terms of their net rate (forward-reverse) not their individual absolute rates. The net rate is the actual contribution of an equilibrium to the complete rate expression. For example, the rates of formation ($k_{19}[HO_2][NO_2]$) and destruction ($k_{20}[HNO_4]$) of peroxyntic acid (HNO_4) in expression 18 can be high but if their net reaction, net formation or destruction of NO_2 is small, p will still be close to one. Since the quantities in equation 21 have been, for the most part, more easily measured than the concentrations of other compounds appearing in expressions 18,19 and 20, this simple relationship has been an important tool in testing our understanding of the role of nitrogen oxides and ozone formation in the troposphere.

PHOTOCHEMICAL MODEL PREDICTIONS

The reactions, R4-R6, complete a null reaction cycle. For a given k_6 and J_{NO_2} the reactants NO , NO_2 and O_3 establish a photoequilibrium with no net loss or production of

NO_x or O_3 . In this case the value of p would be unity. If, for example, other reactions besides R6 are important in oxidizing NO to NO_2 , such as the reactions:

significant deviations from unity will result. Conceptually, any process that produces NO_2 without the destruction of O_3 potentially increases the ozone production rate since the primary process for producing ozone in the troposphere is through the photolysis of NO_2 . This results in a positive deviation ($p > 1$) from the photostationary state. On the other hand, if reactions such as, $\text{O}_3 + \text{alkene} \longrightarrow \text{products}$, are important in the destruction of ozone, a net destructive term for ozone would result. This would also result in positive deviation of the PSS.

In the real atmosphere, p is never exactly equal to one since the rates of the side reactions in expressions 18,19 and 20 are never zero. Measurable deviations of p from unity can provide information as to the concentrations of likely oxidants, such as HO_2 and RO_2 , present in the atmosphere. Uncertainties in the measurement of the quantities in equation 21 are a constraint on the level of deviation that can be accurately measured.

Regions in which the PSS is valid and invalid are clearly of interest in understanding the mechanisms of ozone formation. The chemistry of the atmosphere can be evaluated by computer-based kinetic modeling and direct measurement of the species of interest. These two techniques are intrinsically dependent on one another for validation

and development. A computer simulation of a reaction set simulating the chemistry of the atmosphere can indicate the regions in which the PSS is expected to be close to one and the predicted magnitude of the deviations from unity.

By varying the initial NO_x and hydrocarbon concentration (HC) the value of the PSS can be calculated for ranges of NO_x and HC concentrations and NO_x/HC ratios (Figure 27). The calculations employed the ERTC reaction mechanism (ERTC) which was developed by ERT Corporation and the Environmental Protection Agency (EPA, 1987). This mechanism incorporates a condensed reaction mechanism for hydrocarbon oxidation with detailed NO_x chemistry. The mechanism was integrated from sunrise until noon with a diurnal light intensity. The PSS values were calculated with the concentration values and light intensity reached at noon. Figure 27a shows the relationship of the calculated PSS to the initial HC and NO_x concentrations. Figures 27b, 28a,b and 29a,b show the isopleths for O_3 , NO, NO_2 , HO_2 and RO_2 concentrations, respectively, for the same simulation.

The calculated PSS shown in Figure 27 is close to 1 in the upper left-hand portion of the graph. In this region, NO_x concentrations are relatively high and HC concentrations are relatively low. As the NO_x and HC initial concentrations are lowered from 0.1ppm to 0.01ppm for NO_x and 0.25ppm to 0.025 ppm for HC, the PSS value increases. This can be understood in terms of the increasing competition between O_3 and other species in the oxidation of NO to NO_2 . As the NO level decreases, the rates of reactions involving NO are decreased proportionally. However, the levels of oxidants such as O_3 , RO_2 and HO_2 vary at different rates with respect to NO. For example in this

Figure 27. ERTC isopleths of PSS and O₃.

Figure 28. ERTC isopleths of NO and NO₂.

Figure 29. ERTC isopleths of HO₂ and RO₂.

case, the O_3 level changes from 37ppb to 100ppb while HO_2 changes from $1e6$ to $2e8$ molec/cc and RO_2 increases from $5e5$ to $1e7$ molec/cc. Summarizing, a factor of 10 decrease in both NO_x and HC results in an increase of a factor of 2.7, 20 and 200 for O_3 , RO_2 and HO_2 respectively, all measured at noon. Thus the rates of R7 and R8 contribute a greater fraction of the total oxidation rate of NO, without destroying O_3 .

Ozone production depends on the rate of cycling between NO and NO_2 via peroxy radicals such as HO_2 and RO_2 . In regions of highly reducing chemistry, ie. high NO_x or high HC, the steady-state ozone concentration will be lower (see Figure 27b). Hydrocarbons can be a net sink for ozone at high HC concentration since at low NO_x levels the rate of reaction with RO_2 and HO_2 (leading to O_3 formation) can be lower than the direct destruction of O_3 by reactions such as R28. In addition, at high HC/ NO_x ratios, NO_x can be sequestered in alkylnitrate compounds further reducing available NO_x .

The sources of deviation of the PSS from unity can be studied more carefully by analyzing the contributing rates during the course of a 1-day simulation with various initial concentrations of HC and NO_x . These simulations were carried out here earlier with a somewhat different mechanism [Calvert and Stockwell, 1983] but were found to give results similar to those of the ERTC mechanism. The initial concentrations used in the simulations are given in Table V.

In these simulations the ratios J_{NO_2}/k_6 and $[NO][O_3]/[NO_2]$ are plotted versus time of day. When the value of p in equation 21 is unity the these ratios are equal.

$$J_{NO_2}/k_6 = [NO][O_3]/[NO_2] \quad (22)$$

TABLE V
INITIAL CONDITIONS FOR PSS SIMULATIONS

Concentration, ppb for the case shown				
Species	A	B	C	D
NO ₂	25	2.5	.025	.0025
NO	75	7.5	.075	.0075
CO	100	200	100	100
ALKANE(C ₃ H ₈)	1	10	1	.1
ALKENE(C ₃ H ₆)	4	40	4	.4
O ₃	30	30	30	30
CH ₂ O	30	30	30	30
CH ₃ CHO	.1	1	.1	.01
KETONE	.05	.5	.05	.005
SO ₂	.6	6	.6	.06
CH ₄	1400	1400	1400	1400
H ₂ O	1.56E4	1.56E4	1.56E4	1.56E4
Calculated PSS value	1	1.4	1.5	1.6

Figure 30 shows the effect of changing initial concentration of hydrocarbon and NO_x on the right-hand side of equation 22. The deviations of the PSS can be studied in terms of the contributing rates to equation 18. For each case in Table V, the rates contributing to NO_2 (formation and destruction) were sorted in order of their magnitude. The largest 4 or 5 rates are plotted in Figure 31 for each case. Formation and dissociation rates of HNO_4 are small and their net rate is negligible. The net rate for NO_2 remains close to zero for all cases indicating that the steady-steady assumption is not in question.

Figure 31 demonstrates the importance of peroxy radicals in the deviations of the PSS. The relative importance of organic peroxy radicals increases with high HC concentration (case B). In addition the deviations in Figure 30 display a diurnal variation, with the highest deviation occurring at noon. Formation processes for HO_2 radicals are diurnally related since they are formed via the photolysis of formaldehyde and by the reaction of HO with CO and HC (see Table IV). Hydroxyl radical concentration is a strong function of light intensity. RO_2 radicals are formed via photolysis of aldehydes and the photooxidation of hydrocarbons.

Summarizing, these simulations combined with the results shown in Figure 27 provide some important predictions for the experimental measurement of the PSS in the real or chemically simulated atmosphere. From Figure 27, the PSS is expected to be close to 1 at high to moderate NO_x levels and low to moderate HC levels. As the NO_x decrease and/or HC levels increase, deviations from the PSS are expected. In addition, when deviations are present, these deviations are expected to have a diurnal variation (Figures 30 and 31).

Figure 30. Simulation of diurnal variation of PSS.

Figure 31. Rates contributing to deviation of PSS.

In order to test Equation 21 experimentally, simultaneous measurements of NO, NO₂ and O₃ concentrations must be made. Ideally, the photolysis rate of NO₂ should be measured on an absolute basis (chemical actinometry) but may be approximated, with limitations, based on solar irradiance calculations or by radiometric measurements (flat plate radiometers). Clearly, the accuracy with which NO, NO₂, O₃ and J_{NO2} can be measured reflects directly on our ability to assess our understanding of atmospheric chemistry based on the PSS. An propagation of error analysis of equation 21 yields:

$$\sigma_{PSS}/PSS = (\sigma_{NO}^2/NO^2 + \sigma_{NO2}^2/NO_2^2 + \sigma_{O3}^2/O_3^2 + \sigma_{k6}^2/k6^2 + \sigma_{JNO2}^2/J_{NO2}^2)^{1/2}$$

This equation indicates that in order to make a measurement of the PSS with an error of less than 1%, the quantities in equation 21 must be measurable with an accuracy of less than 1%. If this condition is not met, a deviation of 1.01 will not be distinguishable from random error.

The first laboratory determinations of the PSS were made in a smog chamber with high levels of NO_x (~250ppb) and HC (~.25 to 1ppm) [O'Brien, 1974]. The extent to which the PSS was valid was tested by varying the levels of HC. These experiments demonstrated that the PSS appeared to be valid with HC levels of about .25ppm but when HC was increased to 1ppm deviations from equation 22 were observed. These observations are qualitatively consistent with Figure 27 which shows that a level of 250ppb NO_x and 250ppb HC the PSS is close to 1. With increasing HC to 1ppm, deviations are predicted and were observed. If the deviation is assumed to be due

primarily to RO_2 , the magnitude of the deviations can be used to predict the actual level of RO_2 concentration:

$$k_8[\text{RO}_2] = J_{\text{NO}_2}[\text{NO}_2]/[\text{NO}] - k_6[\text{O}_3] \quad (23)$$

For the level of deviation measured in these experiments, an RO_2 concentration of ~ 1 ppb was calculated. This concentration of RO_2 is in rough agreement with the ERTC simulations. However, this agreement is probably fortuitous since the hydrocarbon mixture used in the actual experiment was not as complex as is present in the ERTC mechanism. These experiments were important in establishing the validity of the PSS at one NO_x level and HC level and predicting the possible cause of the deviations as HC was increased.

The actual level of RO_2 present in the atmosphere is important in determining ozone production rates. Ambient measurements of the PSS in the urban and remote environment have been made by several workers. PSS measurements in the real atmosphere can be confounded by effects of transport of air masses, local emission sources, and interferences in instrumentation.

NO_x instruments have had moderate to severe interferences in the NO_2 measurement mode [Fehsenfeld, 1988]. Generally, positive interferences were encountered resulting in measured NO_2 values that were higher than actually present. In NO-chemiluminescence instruments these interferences were due the reduction of other nitrogen oxides species such as PAN and HNO_3 to the detected NO molecule [Shetter *et*

al., 1983; Fehsenfeld, 1988]. The magnitude of this type of interference is larger at low NO_x levels since the relative magnitude of the interferants to NO_x can be quite high [Singh *et al.*, 1985]. An apparently high value of NO_2 results in a calculated PSS value that is higher than 1. Using equation 23, a calculated value of RO_2 would be higher than actually present and would indicate, erroneously, that the ozone formation rate was higher than actually present. Note that the PSS is predicted to increase as NO_x decreases, so that photochemical theory could be erroneously be "confirmed" by the presence of NO_2 artifacts.

Measurements made in urban environments are also susceptible to misleading effects of transport and mixing of local sources resulting in heterogeneity of sampled air parcels. Even if local equilibrium in a given air parcel is achieved, time averaging or, equivalently, spatial averaging results in calculating the PSS with average values of NO , NO_2 and O_3 contained in possibly several different air masses. This is not necessarily equivalent to the average value of the PSS of the air parcels encountered, which should be close to 1 if the PSS is obeyed locally in each parcel.

Theoretical studies of these effects have been undertaken with some experimental measurements confirming the results [Chock and Kumar, 1979; Janssen, 1986; Seinfeld, 1977; Bilger, 1978; Feigley, 1978]. These studies conclude that the mixing of fresh NO emissions into a background of O_3 -rich air results in a measured PSS value less than 1. Conversely, mixing of clean air (low NO and O_3) with polluted air (high NO and O_3) results in PSS values greater than 1. The extent of deviation is a function of the extent of mixing, heterogeneity and turbulence of the system.

When sources are nearby, the measured value of p can deviate from unity as the chemistry of the system reestablishes equilibrium. The relaxation time of the equilibrium:

can be determined to be:

$$\tau = \{([\text{NO}]_e + [\text{O}_3]_e)k_6 + J_{\text{NO}_2}\}^{-1}$$

assuming that the perturbation is small. $[\text{NO}]_e$ and $[\text{O}_3]_e$ are the equilibrium concentrations. When $([\text{NO}]_e + [\text{O}_3]_e)$ is $\sim 80\text{ppb}$ and J_{NO_2} is about $.5 \text{ min}^{-1}$ the relaxation time is about 22 s for the perturbation to be reduced to $1/e$ of its original value. Thus if the transit time from the source of NO, NO_2 or O_3 is less than several times the relaxation time of the equilibrium, a deviation from p will be measured.

PREVIOUS PSS MEASUREMENTS

Several workers have made ambient measurements of the PSS in both the urban and remote environments. Figure 32 shows measurements made in environments remote from urban areas. Figure 33 shows previous measurements of the PSS made in urban environments. Most of these measurements are expressed in terms of equation 21 or 22. In Figure 32a, the deviations are attributed to an oxidant $[\text{OX}]$, whose value is calculated as equivalent ozone via,

Figure 32. Previous urban air determinations of PSS.

Values of [OX] plotted as a function of time of day for the summertime. These data were collected between June 1 and August 31 of 1981, 1983, and 1984 during clear sky conditions. Only data with f_{NO_2} greater than 10^{-2} s^{-1} are included.

Values of the photostationary state number P calculated from measured values of NO , NO_2 , O_3 , and $f(\text{NO}_2)$, for April 14, 1979, at Niwot Ridge.

Figure 33. Previous clean air determinations of PSS.

$$[\text{OX}] = J_{\text{NO}_2}[\text{NO}_2]/k_6[\text{NO}] - [\text{O}_3]$$

This is similar in form to equation 23 except that the rate constant for the oxidation of NO by OX is assumed to be k_6 and OX is left as an unidentified oxidant.

Urban measurements clearly show the effect of inhomogeneity of sampled air parcels. Except for Figure 33a, the urban measurements are characterized by deviations that do not appear to be diurnally related. The fluctuations in the calculated PSS result in values less than and greater than one as predicted by the discussion above.

Measurements made under clean air conditions display a strong diurnal variation (Figure 32). Figure 32b shows data acquired with an instrument later demonstrated to have significant interferences [Ridley *et al.*, 1988a] in the remote environment. This data is included to demonstrate the effect of known interferences on the PSS measurements. Figure 32a shows data acquired with an instrument that does not suffer from the same interferences encountered in Figure 32b. Deviations here are predominantly positive. Assuming the deviation is due to oxidation of NO by compounds other than O_3 , the level of oxidant [OX] can be calculated. The authors calculate a value for [OX] that is higher than predicted for the conditions of their site. Clearly, the simultaneous determinations of oxidants, HO_2 and RO_2 , and the PSS parameters, NO, NO_2 , O_3 and J_{NO_2} would be beneficial in understanding the true nature of the deviations encountered.

PSS MEASUREMENTS WITH FAGE3

Ambient measurements of the PSS were made from the rooftop of Science

Building II (SBII) at Portland State University. For these measurements an insulated, air-conditioned instrument enclosure was constructed on the south side of the rooftop. The Cu-vapor laser beam was directed to the enclosure through a pipe connecting the roof and the Laser Lab located on the 4th floor of SBII (Figure 34). One other pipe was used to feed gas supply lines, sample lines and power lines. Once in the enclosure, the two wavelength components of the laser beam were separated with a dichroic mirror. The 511nm and 578nm beams were directed into the FAGE-NO₂ and FAGE-HO_x instruments, respectively.

The nitric oxide instrument was located in the Laser Lab to minimize the possibility of vacuum pump fumes affecting the measurements. Ozone was monitored by its absorption at 254nm with a Dasibi ozone analyzer. Environmental parameters such as wind speed, direction, temperature and pressure were monitored with a weather station (Heathkit, Model 4001). Relative ultra-violet light intensity was measured with a homemade device (UVMRD) consisting of a photodiode (MRD500) with a 300-400nm bandpass filter. All instruments were interfaced to and controlled by a microcomputer (Appendix C).

All measurements except NO were averaged for ~1 minute intervals and recorded. The design of the NO instrument introduced a ~40s dead time when switching between zero and measure modes. Consequently only one net measurement was calculated and recorded every 40s (instead of an average for that time) in order to decrease collection cycle time. NO₂ concentrations were calculated based on the calibration factor described in Chapter IV. Calibration for the nitric oxide instrument was determined by diluting a

Figure 34. Location of PSU monitoring site.

measured volume of pure NO with pure air into a large reaction vessel of known volume. The ozone instrument was not calibrated (due to instrument failure at the end of these experiments) but did not indicate any positive offset in the presence of zero air. Absolute calibration errors would result in an offset of the PSS from its true value but could not contribute time dependence to the calculated PSS (such as the diurnal variation predicted by the simulations described above). The effect of light intensity measurements on the PSS is discussed below.

In addition to calibration, all three concentrations were corrected for reaction during transit in the sample lines. Since k_6 is $26.8 \text{ ppm}^{-1} \text{ min}^{-1}$ (at 298K, 760 torr), the $1/e$ lifetime of NO in the sample line is ~40 seconds with 50ppb of O_3 . The delays in the NO, NO_2 and O_3 sample lines were determined to be 4 sec, 4 sec and .6 sec, respectively. This loss is most significant when either NO or O_3 is low in concentration. The maximum correction term was ~10% when O_3 was about 50 times higher than NO. The rate constant for R6 was calculated using the recorded ambient temperature ($k_6 = 2.0 \times 10^{12} \text{ EXP}(-1400/T) \text{ cm}^3 \text{ sec}^{-1}$, DeMore *et al.*, 1989).

Since actinometric measurements of J_{NO_2} were not made, the photolysis rate was estimated based on the UV measurements made by the UVMRD and the results of an irradiance model [Madronich, 1990]. Irradiance models are best suited for calculating photolysis rates with clear sky conditions. In the presence of cloud cover or aerosols it is difficult to quantify the attenuation and albedo characteristics. On the other hand, flat plate detectors, such as the UVMRD, respond correctly to overhead isotropic radiation produced by scattering due to aerosols but produce a non-linear response curve with

respect to the direction of the incoming solar beam [Madronich, 1990].

An error in the measurement of J_{NO_2} that has a time dependence (such as an incorrect response with respect to zenith angle) will result in an apparent deviation from the PSS that has a time dependent characteristic - unlike systematic errors in calibration. In order to correct for these effects, irradiance model calculations and UVMRD data were fit with an empirical equation with data from a day with clear sky conditions, July 13, 1990. With minimal ambiguity due to aerosol scatter, an empirical fit between the irradiance model and UVMRD should correct for the response of the direct solar beam on the UVMRD. When the best fit equation is applied to days where haze and cloud cover were present, the results seem reasonable between the hours of 10am and 4pm. However, the corrected intensities in the early morning and late afternoon hours seem anomalously high. On the other hand, UVMRD data does appear to have some additional features during these hours not apparent in the clear sky case of July 13th. It is difficult to ascertain whether or not the calculated intensities of the early morning and early afternoon hours (10H>Time>16H) are real effects of aerosol scatter or due to the inadequacy of the fitting equation in this region.

Complete data sets for three days, July 13, Sept 5 and Sept 21, 1990 (hereinafter referred to as J13, S5 and S21) are shown in Figures 35, 37 and 39. (Figures 36, 38 and 40 represent these data sets with a 5 minute running average). The key to Figures 35, 37 and 39 is given in Table VI. The data in these figures, with one exception, are shown without any signal averaging in order to show the magnitude and frequency of fluctuations. Wind direction data are presented with a 5 minute running average in order

TABLE VI

KEY TO FIGURES 35,37 AND 39

Figure 35: July 13,1990 - clear and sunny all day

Figure 37: Sept 5, 1990 - morning haze, clearing in afternoon

Figure 39: Sept 21, 1990 - early morning haze

Graph A PSS

solid line - UVMRD empirical fit (normalized)

dashed line - irradiance model (normalized)

dotted line - PSS calculated with UVMRD fit

Graph B CONCENTRATION

solid line - NO, ppb

dashed line - NO₂, ppb

dotted line - O₃, ppb

open diamonds - UVMRD, normalized

Graph C ENVIRONMENTAL

solid line - Temperature ÷ 10, °C

dotted line - Wind Speed, miles/hr

Graph D ENVIRONMENTAL

solid line - North, South wind component

dotted line - East, West wind component

Figure 35. Complete data set for July 13,1990.

Figure 36. Averaged data for July 13, 1990.

Figure 37. Complete data set for Sept 5,1990.

Figure 38. Averaged data for Sept 5, 1990.

Figure 39. Complete data set for Sept 21,1990.

Figure 40. Averaged data for Sept 21, 1990.

to emphasize trends in wind direction.

Nitric oxide sources in an urban environment derive primarily from high temperature combustion products, such those emanating from auto exhaust. Consequently, the NO measured at an urban site is a strong function of its proximity to traffic areas and the direction of the wind transporting air parcels to the monitoring instrument.

The rooftop monitoring site at PSU is closely bounded to the west by a major freeway (Figure 34). Air parcels coming from this direction are likely to contain fresh exhaust emissions containing NO, NO₂ and hydrocarbons. This effect is vividly seen in Figure 39 at ~19H. At this time the wind direction shifts sharply from its generally easterly trend to a westerly direction carrying along with it fresh emissions from the freeway. Over one order of magnitude change in NO concentration is evident. The effect of westerly transport to the monitoring site is evident in the other data sets as well. On the other hand, the NO concentration appears to be largely independent of the north-south component of the wind direction, reflecting similar source components in these directions.

Comparing graphs B and C in Figures 35,37 and 39 the variation in NO concentration appears related to fluctuation in wind speed, with large velocity fluctuations resulting in a "noisier" NO signal. This behavior is predicted by the formulation of the distribution of a pulse of emission after entering a flow, where velocity fluctuations have a Gaussian probability distribution [Seinfeld, 1986]. The average standard deviations for wind velocity in 9 minute periods are plotted versus the average relative standard deviation in NO, NO₂ and O₃ in Figure 41. The lowest fluctuation in NO occurs with the

Figure 41. Fluctuations in ambient concentrations vs. fluctuations in wind velocity.

lowest wind fluctuation (S5). Instrument noise for NO is estimated at 2ppb. The average fluctuations for NO₂ and O₃ appear less coupled to wind fluctuations consistent with source dominance by NO. NO₂ represents about 5% of the NO_x produced in car exhaust [Seinfeld, 1986]. If this was the primary source of the observed NO₂, NO/NO₂ would be on the order of 20. However, the observed levels of NO₂ and NO in the data sets are similar. This indicates that the observed levels of NO₂ are the result of its production by the oxidation of NO present or the transport of NO₂ from other regions. Thus, car exhaust cannot be a significant direct source of NO₂ and therefore is not expected to exhibit the higher fluctuations seen in source driven NO levels.

Graphs A in Figure 35,37 and 39 show the calculated PSS using the ambient NO,NO₂ and O₃ values along with the UVMRD corrected light intensity. Since absolute values of J_{NO2} were not measured, the photolysis rates were scaled to give an approximately average PSS value of 1. The values used were consistent within 10% of the clear sky irradiance model calculations for this latitude (46°N) and time of year for each data set.

Figures 36,38 and 40 show averaged data of Graph A and B of Figures 25,37 and 39. Smoothing with a 5 minute running average reduces the higher frequency fluctuations so that the relationship between the PSS and the chemical quantities measured can be more easily seen. PSS is shown calculated with both the UVMRD fit and the irradiance model. Overall these data sets clearly show that despite daily changes in concentration of NO, NO₂ and O₃ of factors of 4-10 each, the PSS remains relatively constant to within ~50%. This is in itself strong confirmation of the primary importance of the NO_x-O₃

photostationary state in controlling the relative concentrations of these species at these concentrations. In addition, these experiments also serve to demonstrate that the monitoring instruments, including NO₂-FAGE, are not subject to serious interferences or artifacts at these concentration levels.

However, large positive spikes and some negative spikes in the PSS are noted in all three data sets. Large positive spikes correlate with low NO values unaccompanied by concomitant changes in either NO₂ or O₃. These low NO values may be indicative of the transport of "cleaner" air into the vicinity. Deviations of this nature have been discussed as being possibly caused by sampling of clean air parcels with urban air. Conversely, negative spikes can be understood as due to sampling and averaging of air parcels containing fresh NO emissions with those of background air. These spikes are indicative of cases where the sampled averaged value of NO is higher than the average value of the PSS in the air samples encountered. In Figures 36,38 and 40 note that negative spikes usually correspond to peaks in NO.

The wind speed characteristics, concentration fluctuations and constancy of the PSS for the S5 data indicate a greater homogeneity of the downtown Portland air mass for that date. These factors facilitate a computer simulation of the results with fewer ambiguities caused by rapid changes in concentration due to transport or emission. In order to simulate the results of S5 the measured NO concentration at 1 minute intervals were input into a numerical integration routine using the ERTC atmospheric reaction set. Between each 1 minute data point the NO concentration was interpolated to its next experimentally measured value. The values of [O₃] and [NO₂] were determined as the

result of the computer integration of the reaction set. Since the hydrocarbon concentration was not measured, a sequence of initial hydrocarbon concentrations was tried. The Department of Environmental Quality (DEQ) measured the HC concentration at a site about 2 miles from the PSU monitoring site during the years 1982-1988 [DEQ, 1988]. These measurements suggest a value of ~200ppbC of HC. The results of these simulations are shown in Figure 42 along with the results of the actual measurements.

The simulation utilizing 100ppb HC demonstrates an exceptionally good correlation to the measured data of NO_2 and O_3 . As an algebraic relationship, equation 22 does not require that NO_2 and O_3 be held at any particular values given the $[\text{NO}]$, k_6 and J_{NO_2} . Only the ratio of NO_2 to O_3 is constrained by equation 22 when the PSS is valid. The simulations shown in Figure 42 demonstrate that the quantities measured are not only consistent with the PSS being approximately valid but that the concentrations measured are also consistent with the entire reaction mechanism of over 150 reactions simulated.

The measurement of the PSS in the above downtown urban environment in which its value is expected to be close to one can be thought of as a test of the instruments making the measurements. Overall, the ambient measurements made of the PSS in Portland confirm model predictions that the NO_x - O_3 photostationary state is obeyed at the observed levels of NO_x (<150ppb). This relationship is generally obeyed despite several-fold changes in concentration of NO , NO_2 and O_3 during the course of a day. Thus these first ambient studies utilizing the FAGE- NO_2 instrument indicate that this instrument is capable of making meaningful ambient measurements at these concentration levels.

Figure 42. Computer simulation of Sept 5, 1990 measurements.

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APPENDIX A

DETAILS OF SNR CALCULATION

Details of SNR Calculation

Equation 1 is the expression for signal-to-noise ratio (SNR) based on Poisson photon counting statistics for an integrated signal with exponential decays for the signal and background with magnitudes S_0, B_0 and decay rates of k_s and k_b , respectively. A constant background signal d_0 is also included. To optimize SNR with respect to delay time (t_g) and gate width (t_d) the partial derivative of equation 1 was symbolically computed (SolverQ, University of Wisconsin) with respect to t_g and t_d , equations 2 and 3, respectively.

$$\text{SNR} = S_0/k_s(\text{EXP}(-k_s t_d) - \text{EXP}(-k_s(t_d + t_g)))$$

$$/((S_0/k_s(\text{EXP}(-k_s t_d) - \text{EXP}(-k_s(t_d + t_g))) + 2(t_g d_0 + B_0/k_b(\text{EXP}(-t_d k_b) - \text{EXP}(-k_b(t_d + t_g))))))^{0.5} \quad (1)$$

$$d(\text{SNR})/d(t_g) =$$

$$S_0 / ((S_0/k_s \text{EXP}(-k_s t_d) - S_0/k_s \text{EXP}(-(k_s t_d + k_s t_g))) + 2B_0/k_b \text{EXP}(-t_d k_b) - 2B_0/k_b \text{EXP}(-(t_d k_b + k_b t_g))) + 2d_0 t_g)^{0.5} \text{EXP}(-(k_s t_d + k_s t_g)) - S_0/k_s d_0 \text{EXP}(-k_s t_d) + S_0/k_s d_0 \text{EXP}(-(k_s t_d + k_s t_g)) - S_0/k_s B_0 \text{EXP}(-k_s t_d) \text{EXP}(-(t_d k_b + k_b t_g)) + S_0/k_s B_0 \text{EXP}(-(k_s t_d + k_s t_g)) \text{EXP}(-(t_d k_b + k_b t_g)) - 0.5 S_0^2/k_s \text{EXP}(-k_s t_d) \text{EXP}(-(k_s t_d + k_s t_g)) + 0.5 S_0^2/k_s \text{EXP}(-(k_s t_d + k_s t_g))^2 \quad (2)$$

$$d(\text{SNR})/d(t_d)=$$

$$\begin{aligned} & S_0/k_s / (S_0/k_s (\text{EXP}(-k_s t_d) - \text{EXP}(-k_s(t_d+t_g))) + 2(d_0 t_g + B_0/k_b (\text{EXP}(-t_d k_b) - \text{EXP}(-k_b(t_d+t_g))))^{0.5} (- \\ & k_s \text{EXP}(-k_s t_d) + k_s \text{EXP}(-k_s(t_d+t_g))) - 0.5 S_0/k_s (S_0/k_s (-k_s \text{EXP}(-k_s t_d) + k_s \text{EXP}(-k_s(t_d+t_g))) + 2B_0/k_b (- \\ & k_b \text{EXP}(-t_d k_b) + k_b \text{EXP}(-k_b(t_d+t_g)))) (\text{EXP}(-k_s t_d) - \text{EXP}(-k_s(t_d+t_g))); \end{aligned} \quad (3)$$

Solving simultaneously, with equations 2 and 3, the optimal values for t_d and t_g can be computed (SEQS, Provo, Utah) given values for k_s, k_b, S_0, B_0 and D .

APPENDIX B

ELECTRONIC CIRCUIT

Summary of data flow of the QVT-Computer interface (circuit diagram on following page):

After each laser pulse fires, the QVT integrates signal from the photomultiplier tube (see Figure 11). Digital output of charge acquired appears at rear interface of QVT - pins A-L. When data is ready at the interface, SEL (pin S, QVT rear interface) goes low for 300ns. This signal is captured by the 74ALS244 buffer/line driver. The line driver then signals the two 74ALS374, D-Type Flip-flops to store the data. The SEL signal is also sent to the parallel port to initiate a parallel strobe of data in the computer from the flip-flop. This simple interface acquires data after each laser pulse and therefore must be used in conjunction with software interfaces that collect data at the necessary repetition rate. The circuit was tested extensively before and during actual field use.

APPENDIX C

COMPUTER PROGRAMS

APPENDIX C

2qvt.c - program to control data acquisition from LeCroy QVT:
only main program, qvt and stepper motor subroutines are printed

```

#include <stdio.h>
#include <conio.h>
#include <bios.h>
#include <time.h>
#include <graph.h>
#include <string.h>
#include <math.h>

void qvt( double ,unsigned long *,unsigned long *);
int fnckey(void);
void delay(unsigned);
void delaysec(unsigned);
void chemlum(float,float *,float *,float *);
float oz(void);
void initialize(void);
double pwrin();
int initgraf(void);
void viewq(int,int,int,int);
void windowq(double,double,double,double,double,double);
void movetoq(double,double);
void linetoq(double,double);
void plotpointq(double,double);
void endgraf();
void testkey();
void initmoto();
void motomove(int,int,int);
void motobrake(int);
float rtime(void);
void clearqvt();
void findpdt(double);

double shots,cycle;
float fs,coul,pdt,xtra=0;
FILE *fp1,*fp2;
time_t initime;
unsigned valvedelay;
double xw1,xw2,yw1,yw2,xwa,ywa;

```

```

unsigned vx1q,vx2q,vy1q,vy2q,xwq,yhq;
float pyq,pxq;

struct videoconfig screen;
double wx1q,wylq;
main ()
{
unsigned long chargesum,q1,q2;
double qvt1,qvt2,pwr=0,a[]={0,0,0};
int i,j,k,l;
int dbas=768;
float no,no2,o3,realtime,pdtime;
time_t nowtime;
char buffer[100];
int v[2]={32,0};

initialize();
initgraf();
initmoto();
motobrake(1);
viewq(20,90,20,90);
_setcolor(5);
windowq(xw1,xw2,yw1,yw2,xwa,ywa);
realtime=rtime();
delaysec(1);
findpdt(shots);
pdtime=realtime;
    for (i=1;i<cycle;i++)
    { testkey();
      for (j=1;j<3;j++)
      {
        outp(dbas+2,v[j-1]);
        delaysec(valvedelay);
        qvt(shots,&q1,&q2);
        chargesum=q1;
        a[j-1]=(chargesum-pdt*shots)/coul;
        chemlum(fs,&no,&no2,&o3);
        sprintf(buffer,"%4.1f
%4.1f",pdt,(float)(chargesum/shots-pdt));
        _settextposition(24,30);
        _outtext(buffer);
        sprintf(buffer,"%d",i);
        _settextposition(1,2);
        _outtext(buffer);
      }
    }
}

```

```

        _settextposition(1,30+j*13);
        sprintf(buffer,"%1.4le",a[j-1]);
        _outtext(buffer);
        pwr=pwrin()*1000;
        sprintf(buffer,"%4.1f",pwr);
        _settextposition(1,7);
        _outtext(buffer);
    }
    time(&nowtime);nowtime-=initime;
    _setcolor(3);
    sprintf(buffer,"%3.3f",realtime);
    _settextposition(24,15);
    _outtext(buffer);
    a[2]=0;
    if (a[0]+a[1]>0)
        a[2]=(a[0]-a[1])/sqrt(a[0]+a[1]); /* SNR */
    sprintf(buffer,"%4.1le %2.1le",a[2],a[0]-a[1]);
    _settextposition(24,55);
    _outtext(buffer);
    realtime=rtime();
    if (realtime>(pdtime+.10))
    {
        findpdt(shots);
        pdtime=realtime;
    }
    plotpointq(realtime,a[0]-a[1]);
    fprintf(fp2,"%f %le %le ",realtime,a[1],a[0]-a[1]);
    fprintf(fp2,"%f %4.1lf %f\n",pdt,pwr,xtra);
    fcloseall();
    fp2=fopen("c:out.dat","at");
}

while(!kbhit());
getche();
endgraf();
}

void clearqvt()
{
    outp(0x312,6);delay(10000);
    outp(0x312,5);delay(10000);
}

void findpdt(double hits)
{

```

```

    unsigned long q1,q2;
    clearqvt();
    motomove(1,25,0);
    delaysec(2);
    qvt(hits,&q1,&q2);
    pdt=(float)(q1/hits);
    motomove(1,25,1);
}

void qvt( double cyc,unsigned long *q1,unsigned long *q2)
{
    unsigned sum2,q1l=0,q1h=0,q2l=0,q2h=0;
    unsigned int cyc1,cyc2;
    double test,sxtn=65536.0;

    outp(0x313,0x91);delay(10000); /* control word */
    outp(0x311,0Xff);outp(0x311,0xdb);delay(10000);
    outp(0x311,0xff);outp(0x311,0xed);delay(50000);
0    outp(0x312,0xff);outp(0x312,0x5f);
    test=cyc/sxtn;
    cyc1=0;
    cyc2=cyc-65536*(int)test; /* cyc2 counter for
cyc<=65535 */
    while(test>=1)          /* cyc1 counter for
cyc>=65536 */
    {
        cyc1++;
        cyc-=sxtn;
        test=cyc/sxtn;
    }
    _asm \
    {
        mov dx,312h      ;initialize variables
        mov cx,310h
        mov ax,0ffh      ;clear resets
        out dx,ax        ;****
        L1:in al,dx       ;test portc
        test al,8         ;test for data present at pc2
        jnz L1
        mov ax,0bfh
        out dx,ax        ;select qvt 1
        in al,dx          ;input higher byte data pc0 & pc1
        and al,3          ;
        mov ah,al         ;

```

```

        mov dx,cx
        in al,dx      ;input lower byte data pa0-pa7
        add q1l,ax
        adc q1h,0
        mov dx,312h
        mov ax,7fh
        out dx,ax     ;reset qvt 1
        mov ax,0efh
        out dx,ax     ;select qvt 2
        in al,dx      ;input higher byte data pc0 & pc1
        and al,3      ;
        mov ah,al     ;
        mov dx,cx
        in al,dx      ;input lower byte data pa0-pa7
        add q2l,ax
        adc q2h,0
        mov dx,312h
        mov ax,0dfh
        out dx,ax     ;reset qvt 2
        dec cyc2
        jnz L1
        add cyc1,0
        jz L2
        dec cyci
        mov cyc2,65536
        jmp L1
L2:
    }
    *q1=q1l+q1h*65536;*q2=q2l+q2h*65536;
}
void initmoto()
{
    int mco=748,mpc=744,j;
    outp(mco,192);/*motor control word*/
    outp(mpc,5); /*enable motor board*/
}
void motomove(int motor,int sts,int dir)
{
    int i,z,mpa=736,mpb=740,s1,s0,mcw;
    motor=(int)pow(2,motor);
    dir=dir*motor*16;
    s0=dir;s1=dir+motor;
    mcw=(~(motor&15)&15);
    outp(mpb,mcw);

```

```
    for(i=1;i<=sts;i++)
    {
        outp(mpa,s1);
        for(z=1;z<=300;z++){;}
        outp(mpa,s0);
        for(z=1;z<=300;z++){;}
    }
}

void motobrake(int motor)
{
    int mpb=740,mcw;
    motor=(int)pow(2,motor);
    mcw=(~(motor&15)&15)+240;
    outp(mpb,mcw);
}
```

/* envir.c program to acquire environmental parameters, only routines related to data acquisition are shown */

```

#define PI 3.14159265359
#include <stdio.h>
#include <conio.h>
#include <bios.h>
#include <time.h>
#include <graph.h>
#include <string.h>
#include <math.h>

int fnckey(void);
void delay(unsigned);
void delaysec(unsigned);
float oz(void);
void initialize(void);
int initgraf(void);
void viewq(int,int,int,int);
void windowq(double,double,double,double,double,double);
void movetoq(double,double);
void linetoq(double,double);
void plotpointq(double,double);
void endgraf();
void testkey();
void weasm(void);
void weathin( float *,float *,float *,float*);
void dash8(float *,int);
void d8io(int);
float rtime(void);

extern  unsigned short parma; /* wind  direction */
extern  unsigned short parmb; /* wind speed */
extern  unsigned short parmc; /* temperature */
extern  unsigned short parmd; /* pressure */
float fs,coul,pdt,xtra=0;
FILE *fp1,*fp2;
time_t initime;
unsigned savetime;

unsigned vx1q,vx2q,vy1q,vy2q,xwq,yhq;
float pyq,pxq;
struct videoconfig screen;

```

```
double wx1q,wylq;
```

```
main ()
{
int i,j,k,l;
int dbas=0x300;
int p1bas=0x308;
int p2bas=0x310;
float no,no2,o3,nobertha,nozero=0,nosig=0;
float mrd,dew,od;
float sno,sno2,so3,snob=0,lsod=0,lsnob=0,lso3=0,rtl;
double cwdir,swdir,cwdirsum=0,sdirsum=0;
time_t nowtime;
char buffer[100];
int v[2]={ 32,0},sig=1,iostat=0;
float wdir,wvel,ambtemp,ambpres;
float swvel,sambtemp,sambpres;
float smrd,sdew,sod,jno2;
float now,nowhr,ptime=0,swtch_nx=0,realtime;
float d8[]={ 0,0,0,0,0,0,0,0};
float cnt;

initialize();
initgraf();
rtl=rtime();
viewq(20,90,20,90);
_setcolor(5);
windowq(0,28,0,5,3,1);
i=0;
swdir=0;cwdir=0;sambpres=0;sambtemp=0;
while(!kbhit())
{
smrd=0;sdew=0;sod=0;so3=0;
time(&nowtime);nowtime-=initime;
nowhr=(float)(nowtime/3600.0);
while ((float)nowtime<ptime+savetime)
{
testkey();
i++;
time(&nowtime);nowtime-=initime;
nowhr=(float)(nowtime/3600.0);
dash8(d8,iostat);
o3=oz();
```



```

weathin(&wdir,&wvel,&ambtemp,&ambpres);
realtime=rtime();
if((float)nowtime>swtch_nx+40)
{
    if(sig==1)
        {nosig=d8[2]*2;iostat=128;d8io(iostat);
        sig=0;swtch_nx=(float)nowtime;
        }
    else
        {nozero=d8[2]*2;iostat=0;d8io(iostat);
        sig=1;swtch_nx=(float)nowtime;
        }
}
sprintf(buffer,"%4.5f %4.5f %4.5f %4.5f\n",
wdir,wvel,ambtemp,ambpres);
_settextposition(1,2);
_outtext(buffer);
sprintf(buffer,"%4.5f %u\n",rtime(),i);
_settextposition(24,15);
_outtext(buffer);
sprintf(buffer,"%3.2f %3.3f %3.3f %3.3f\n",o3,d8[3],d8[4],
d8[5]);
_settextposition(1,40);
_outtext(buffer);
sprintf(buffer,"%3.2f %3.2f %3.2f\n",nosig,nozero,nosig-nozero);
_settextposition(2,40);
_outtext(buffer);
if (d8[0]<=0){ d8[0]=-10;}
s p r i n t f ( b u f f e r , " % 2 . 2 f % 2 . 3 f % 3 . 3 f
%3.3f\n",d8[0],d8[1],d8[1]/d8[0],d8[1]+d8[0]);
_settextposition(3,40);
_outtext(buffer);
nobertha=nosig-nozero;
cwdir+=cos((double)(wdir/360.0*2*PI));
swdir+=sin((double)(wdir/360.0*2*PI));
snob+=nobertha;
sno+=d8[1];sno2+=d8[0];so3=so3+o3;
smrd+=d8[3];sdew+=d8[4];sod+=d8[5];
swvel+=wvel;sambpres+=ambpres;sambtemp+=ambtemp;
cnt=(float)i;
}
ptime=(float)nowtime;
swdir/=cnt;cwdir/=cnt;swvel/=cnt;sambtemp/=cnt;sambpres/=cnt;
sdew/=cnt;smrd/=cnt;sod/=cnt;

```

```

        snob/=cnt;so3/=cnt;
        sno/=cnt;sno2/=cnt;
/*file printing*/
fprintf(fp2,"%f %2.4f %2.4f %3.4f %3.1f %.3f %.3f %3.2f %3.1f %3.3f\n",
rtime(),sdew,smr,so3,swvel,swdir,cwdir,sambpres,sambtemp,snob);
fcloseall();
fp2=fopen("c:out.dat","at");
/*plot routine */
        plotpointq(realtime,smrd);
        so3/=10;
        movetoq(rtl,lso3);linetoq(realtime,so3);lso3=so3;
        sambtemp/=10;
        plotpointq(realtime,sambtemp);
        snob/=2;
        movetoq(rtl,lsnob);linetoq(realtime,snob);lsnob=snob;
        rtl=realtime;
        i=0;swdir=0;swvel=0;sambpres=0;sambtemp=0;snob=0;
    }
    endgraf();
}

float oz(void)
{
    int pbas=0x310,o3a,o3b;
    float o3;
    outp(pbas+3,0x92);
    do
    {
        o3a=inp(pbas);o3b=inp(pbas+1);
    }while((o3b&31)>9);
    o3=(int)(o3a/16)*10+o3a%16+(int)(o3b/16)*1000+o3b%16*100;
    return o3;
}

void dash8(float *d8,int iostat)
{
    int dbas=0x300,ch,chandio;

    for (ch=0;ch<8;ch++)
    {
        iostat=iostat&255;
        chandio=iostat<ch;
        outp(dbas+2,chandio);
        outp(dbas+1,0);
    }
}

```

```

        while(inp(dbas+2)>=128)
            {;}
        d8[ch]=inp(dbas)/16.0+inp(dbas+1)*16.0;
        d8[ch]=d8[ch]*10/4096-5;
    }

void d8io(int state)
{
    int dbas=768;
    outp(dbas+2,state);
}

void weathin(float *wdir,float *wvel,float *ambtemp,float *ambpres)
{
    float          direct[16]={0,22.5,67.5,45,157.5,125,90,112.5,337.5,
                               315,270,292.5,180,202.5,247.5,225};
    outp(0x30b,0xbe);
    weasm();
    *wdir=360-direct[parma];
    *wvel=parmb;
    *ambtemp=parmc;
    *ambpres=parmd/100.;
}

void delay(unsigned a)
{
    unsigned i;
    for(i=1;i<a;i++)
    {;}
}

float rtime(void)
{
    char buffer[9];
    unsigned hr,min,sec;
    long l;
    float time;
    _strtime(buffer);
    sscanf(buffer,"%u:%u:%u",&hr,&min,&sec);
    time=(float)hr+(float)min/60+(float)sec/3600;
    return (time);
}

void delaysec(unsigned a)

```

```
{  
time_t time1,time2;  
unsigned diff;  
time(&time1);  
do  
    {  
        time(&time2);  
        diff=time2-time1;  
    }while(diff<a);  
}
```