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# KINETICS AND MECHANISM OF $\text{NO}_2$ FLUORESCENCE

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# KINETICS AND MECHANISM OF NO<sub>2</sub> FLUORESCENCE\*

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## Abstract

NO<sub>2</sub> fluorescence experiments with steady or modulated (8 and 20 kHz), monochromatic excitation at 4000 to 6000 Å and monochromatic observation have shown the process to be interpretable in terms of a single electronically excited state undergoing vibrational relaxation at gas-kinetic rate and electronic quenching about 100 times more slowly. An apparent radiative lifetime of about 55 μsec was found, independent of excitation frequency, but the possibility of mixing with vibrationally excited ground state makes this an upper limit to the lifetime of the hypothetical unperturbed <sup>2</sup>B<sub>1</sub> state. The average amount of vibrational energy transferred per collision was found to be 1000 ± 500 cm<sup>-1</sup> based on a simplified stepladder model for the relaxation.

## Introduction

Investigation of the visible absorption and fluorescence of NO<sub>2</sub> has presented several interesting theoretical and experimental problems in recent years. As is well known, the visible spectrum of NO<sub>2</sub> is extensive

and very complicated, and only recently have parts of it been successfully analyzed. Measurements of the fluorescence decay rate have resulted in a value of the radiative lifetime more than two orders of magnitude in excess of the lifetime calculated from the integrated absorption coefficient. The complicated spectrum and the anomalously long lifetime have led to much discussion of the number of states involved in the visible transition and the possible mechanisms which could account for such a large lifetime difference. In addition, studies of the fluorescence quenching have suggested that measurable vibrational relaxation occurs in excited  $\text{NO}_2$ . Measurements of  $\text{NO}_2$  fluorescence are also of interest because of their relation to the chemiluminescent reactions of NO with O or  $\text{O}_3$  in which excited  $\text{NO}_2$  is the emitting species.

The ground state of  $\text{NO}_2$  has been well characterized by infrared and microwave spectroscopy and is reasonably well understood theoretically as well. However, the visible absorption spectrum has been a formidable problem for many years and only recently have advances been made in its interpretation<sup>1</sup>. Calculations of the low lying electronic states have been carried out using nonempirical methods by Burnelle et al.<sup>2</sup> and by Fink<sup>3</sup>. The results indicate that five states,  $^2\text{B}_1$ ,  $^2\text{B}_2$ ,  $^2\text{A}_2$ ,  $^4\text{A}_2$ ,  $^4\text{B}_2$ , lie in the energy range 2 to 4 eV above the ground  $^2\text{A}_1$  state and could be involved in the visible system; however, allowed transitions occur from  $^2\text{A}_1$  only to  $^2\text{B}_1$  and  $^2\text{B}_2$ . The calculated vertical transition energy for  $^2\text{B}_2$  is 4.1 eV, but the calculations do not appear to be sufficiently accurate at present to decide whether this state is responsible for the ultraviolet absorption between 4.8 and 5.3 eV or also contributes to the visible spectrum. For  $^2\text{B}_1$  the calculated vertical transition energy is 2.1 to 2.3 eV and the state

must contribute to the visible spectrum. Douglas and Huber's<sup>1</sup> rotational analysis of bands appearing in the absorption spectrum near 3 eV have identified the transition as  ${}^2B_1 \leftarrow {}^2A_1$ . Thus, from present evidence, it appears that the main intensity of the visible spectrum can be assigned to the transition to the  ${}^2B_1$  state, which, to account for the complicated nature of the spectrum, is most likely perturbed by interaction with the other low lying states or by interaction with the ground state itself.

In a study of  $\text{NO}_2$  fluorescence using flash excitation, Neuberger and Duncan<sup>4</sup> observed a 44  $\mu\text{sec}$  radiative lifetime independent of the excitation wavelength between 3950 and 4650 $\text{\AA}$ . The lifetime calculated from the absorption coefficient measurements of Hall and Blacet<sup>5</sup> and of Dixon<sup>6</sup> is about 0.3  $\mu\text{sec}$ , more than two orders of magnitude shorter than the observed emission lifetime. This large lifetime anomaly has led to speculation<sup>4,7</sup> that more than one electronic state may be involved in  $\text{NO}_2$  chemiluminescence and fluorescence. However, it has been pointed out by Douglas that this type of anomaly may be due to several causes, among them the interaction between vibrational levels of the excited electronic state with other states, and Hartley and Thrush<sup>9</sup> have suggested that highly excited vibrational levels of the ground electronic state may be partly responsible.

In previous experiments on  $\text{NO}_2$  fluorescence, Myers, Silver, and Kaufman<sup>10</sup> reported a large decrease in the Stern-Volmer quenching constant with increasing energy separation between exciting and fluorescent radiation; this suggested that stepwise vibrational deactivation occurs in the excited electronic state. More recently, Sakurai and Broida<sup>11</sup> have studied  $\text{NO}_2$  fluorescence using laser excitation; they observed a series of lines superimposed on what appeared to be a continuum with the resolution used. Quenching constants

obtained for the lines and the integrated continuum are somewhat uncertain but lie in the same range of values reported previously for  $\text{NO}_2$  fluorescence<sup>10,12</sup>. Relative intensity variations with  $\text{NO}_2$  pressure were interpreted in terms of collisional deactivation in the upper state.

The purpose of the present investigation was to study the vibrational deactivation of excited  $\text{NO}_2$  in more detail and to determine the possible contribution of more than one electronic state to  $\text{NO}_2$  fluorescence. A preliminary report of our results has been published<sup>13</sup>. While this work was in progress, we learned of parallel experiments on  $\text{NO}_2$  fluorescence by Schwartz and Johnston<sup>14</sup>, who used a similar experimental approach. However, the results of our measurements differ somewhat from theirs and it was thought appropriate to report them here in some detail.

In the following sections we first report the results of fluorescence experiments with steady illumination at a series of excitation and fluorescent wavelengths in the visible and near infrared regions and discuss the results in terms of a vibrational cascade model. Then, results are given of radiative lifetime measurements using modulated radiation at several excitation wavelengths and modulation frequencies.

### Experimental

The system used in these experiments is shown schematically in Figure 1. Fluorescence is excited by means of a 500 watt high pressure mercury arc (Osram HBO-500) or 900 watt xenon arc (Osram XBO-900) powered by a standard d.c. power supply with added filtering to reduce the 60 Hertz ripple below 2%. After collimation, the exciting light is modulated using a

mechanical chopper which consists of two quartz disks (Dynamics Research Corp., Stoneham, Mass.) on each of which 512 slits had been formed by metallic deposition. One of the disks is stationary; the other is rotated at a constant speed by a d.c. motor powered by a regulated voltage supply, and the two disks are mounted 0.15 mm apart. The motor speed is continuously variable up to a maximum of 5000 rpm; this provides modulation frequencies from 2 kHz up to 40 kHz. Most of the present experiments on  $\text{NO}_2$  were done at 8 or 20 kHz. For experiments with steady illumination, the modulator is removed from the light path. The wavelength of the exciting radiation is varied by means of a 1/4 meter Jarrell-Ash monochromator; 500  $\mu$  slit widths are used, giving full band widths at half height of about 30 Å. After emerging from the monochromator, the exciting light beam is collimated so that it is approximately 1 cm in diameter as it passes through the fluorescence cell. A 1P28 photomultiplier tube is used to monitor the intensity of the exciting light; it also provides the reference signal for the lifetime measurements.

Fluorescence signals are observed at right angles to the exciting beam through the side window of a glass T-shaped cell 24 cm in length with an inside diameter of 14 cm. The wavelength at which fluorescence is observed is varied by using a set of interference filters (Thin Film Products, Inc.) or Corning glass filters placed between the cell and the PMT detector. The transmission wavelengths of the interference filters are spaced at 300-600 Å intervals in the visible and near infrared; the filters have a 50-75 Å band width at half maximum transmission.

An EMR 641E photomultiplier tube is used to detect the fluorescence signal. This tube has an S-20 response with a quantum efficiency of 11% at

6300Å; for most experiments, it is operated at a gain of  $10^7$  which gives a dark current of  $3 \times 10^{-12}$  amps or 2-3 photon pulses per second when cooled. The 641E tube is housed in an evacuable metal dewar and cooled radiatively by a copper heat shield at  $-77^\circ\text{C}$ .

In the experiments using unmodulated exciting light, the 641E output is amplified (Keithley 417 picoammeter) and displayed on a strip chart recorder (Bausch & Lomb VOM5). At very low fluorescence intensities (low pressure and long excitation wavelength), the fluorescence signal is measured in digital form by means of a pulse amplifier at the 641E output, pulse height discriminator, and electronic counter. Counting times of 10 sec are adequate to obtain significant fluorescent intensity signals.

For the lifetime measurements the pulse counting detection system is used; a schematic diagram of the experimental arrangement is shown in Fig. 2. The output of the 1P28 triggers a variable delay pulse which starts a time to amplitude converter (E.G.&G. TH200A modified to give a 130  $\mu\text{sec}$  ramp for 8 kHz modulation). A start pulse is generated once during each modulation cycle and at a known phase with respect to the exciting light as observed on a dual trace oscilloscope. After amplification and low level discrimination, the output pulses of the 641E are fed to the time to amplitude converter. The first photon pulse subsequent to the start pulse stops the ramp and the resulting voltage pulse is transmitted to a multi-channel analyzer where the fluorescent wave form is stored for later processing. For most experiments counting times of 10 minutes (real time) are sufficient to accumulate fluorescence signals with an average of 500 counts per 1.5  $\mu\text{sec}$  time channel. The time base of the analyzer is calibrated vs. a time mark generator. Using this method of detection, no



more than one fluorescence photon pulse may be counted during each cycle of the exciting light modulation; thus, distortion of the detected signal waveform will occur if the average counting rate approaches the modulation frequency. The highest counting rate used in these experiments is 600 counts per sec which is sufficiently low compared to the lowest modulation frequency (8 kHz) that distortion effects may be ignored. The phase shift introduced by the detection system itself is established by measuring the phase of scattered light with no  $\text{NO}_2$  in the cell. An electronic counter (Hewlett-Packard 5512A) is used to measure photon counting rates and the modulation frequency.

Pressures of  $\text{NO}_2$  in the range 0.5 to 500 mTorr are measured with a pressure transducer (Pace P90D) which is calibrated against a McLeod gauge using helium gas to minimize the mercury streaming effect<sup>15</sup>. The  $\text{NO}_2$  obtained from Matheson at a stated purity of 99.5% is further purified by reaction with excess oxygen gas followed by several sublimations at  $-77^\circ\text{C}$ . The purified  $\text{NO}_2$  is stored in the dark at  $-196^\circ\text{C}$ . At the start of each set of experiments, a fresh sample of  $\text{NO}_2$  is distilled from the storage bulb into a separate trap at  $-77^\circ\text{C}$  from which it is admitted to the fluorescence cell as needed. During an experimental run, the cell and one side of the pressure transducer are isolated from the remainder of the  $\text{NO}_2$  handling system by means of a stainless steel bellows valve. Typical pressure increases in the isolated cell are less than 0.1 mTorr per hour.

#### Steady Excitation

Fluorescence of  $\text{NO}_2$  was excited by steady illumination at a series of wavelengths,  $\lambda_E = 4050, 4360, 5460, \text{ and } 5780\text{\AA}$ ; for each exciting wavelength,

the fluorescent intensity was determined as a function of  $\text{NO}_2$  pressure and fluorescent wavelength out to  $7850\text{\AA}$ . The data of each experiment consist of 40 to 50 intensity vs. pressure readings over a pressure range of 0.5 to 125 mTorr. Representative Stern-Volmer plots of the results for  $4358\text{\AA}$  excitation are shown in Fig. 3, where for clarity only three fluorescent wavelengths have been included. Results at other fluorescent wavelengths lie between the curves shown. Similar curves are obtained at other excitation energies.

The Stern-Volmer<sup>16</sup> model of fluorescence quenching considers only one excited level which after formation by photon absorption may radiate or be collisionally quenched to the ground level. Under steady-state conditions, the following relation is easily obtained

$$P/F = B(1 + aP) \quad (1)$$

where  $P$  is the  $\text{NO}_2$  pressure;  $F$ , the fluorescent intensity;  $a$ , the quenching constant, defined as the ratio of the quenching rate constant,  $E$ , to the radiative rate constant,  $R$ ; and  $B$  is an experimental constant which includes such factors as the absorption cross section, the exciting light intensity, and the efficiency of the optical system used to detect the fluorescence. To facilitate comparison of experimental results at different exciting and fluorescent wavelengths,  $B$  is determined for each combination of  $\lambda_E$  and  $\lambda_F$  by linear extrapolation of  $P/F$  vs.  $P$  plots to zero pressure.

Examination of the quenching results shown in Fig. 3, where  $P/BF$  is plotted vs.  $P$ , shows that the experimental plots are linear throughout the pressure range only if the fluorescence frequency,  $\nu_F$ , is close to the exci-

tation frequency  $\nu_E$ . At low  $\text{NO}_2$  pressures, the results show increasing curvature as  $\Delta\nu = \nu_E - \nu_F$  increases. At higher  $\text{NO}_2$  pressures (above 10 to 20 mTorr) the curves become linear and it is possible to obtain an effective quenching constant from the high pressure slope. Observed quenching constants for various exciting and fluorescent wavelengths are given in Table I. As  $\Delta\nu$  increases, a sharp decrease in the magnitude of the quenching constant is observed, the variation being as large as a factor of five over the range of  $\Delta\nu$  observed. Within experimental scatter, the quenching constants are dependent only on  $\Delta\nu$  and appear to be independent of the value of  $\nu_E$  or  $\nu_F$ .

The results summarized above show that a simple Stern-Volmer description with only one excited level is not applicable to the visible fluorescence of  $\text{NO}_2$  because (1) the quenching curves (Fig. 3) deviate substantially from linearity for  $\text{NO}_2$  pressures below 20 mTorr<sup>17</sup> and (2) the observed quenching constants show a strong dependence on  $\Delta\nu$ . These observations suggest a cascade model with stepwise vibrational de-excitation in a single excited electronic state of  $\text{NO}_2$  concurrent with its electronic and radiative de-excitation. Such a vibrational cascade model may be described in terms of the following equations,

$$\begin{aligned} \frac{-d M_1}{dt} &= (R + EM + VM) M_1 - A I_e M \\ \frac{-d M_2}{dt} &= (R + EM + VM) M_2 - VM M_1 \\ \frac{-d M_i}{dt} &= (R + EM + VM) M_i - VM M_{i-1} \end{aligned} \quad (2)$$

where  $M$  is the ground state population density of the fluorescent molecule,

the  $M_i$ 's are the population densities of excited levels,  $R$  is the radiative rate constant,  $E$  is the electronic quenching rate constant,  $V$  is the vibrational quenching rate constant,  $A$  is the absorption coefficient, and  $I_e$  is the intensity of the exciting light. In Eqs. (2), a number of simplifying assumptions have been made:

- (1) The rate constants are independent of the particular level of excitation, i.e.  $R_1 = R_2 = R_i = R$ ,  $E_1 = E_2 = E_i = E$ , and  $V_1 = V_2 = V_i = V$ . This is suggested by the relative independence of the observed quenching constants on the value of  $\nu_E$  for a given  $\Delta\nu$ . For  $R_i$ , moreover, this constancy is further supported by the lifetime measurements discussed below.
- (2) The only energy transfer or loss processes important in the present case are those described by Eqs. (2). This ignores diffusive loss, radiative transfer among the excited vibrational levels, and collisionally induced vibrational excitation, all of which should be relatively unimportant compared to the rates  $R$ ,  $E$ , and  $V$ .
- (3) All the excited state levels lying within  $\Delta\nu$  of  $\nu_E$  contribute to the fluorescent intensity in proportion only to their relative population densities. This ignores the fluorescent spectral distribution which was shown to have relatively little effect on the calculated results of the simplified model by specifically including in one of the calculations a scaled spectral distribution similar to that of the  $O + NO$  emission<sup>18</sup>.

Under steady-state conditions, the population densities in the excited levels may be readily obtained:

$$M_1 = (A I_e / R) \left[ \frac{M}{1 + (a_E + a_V)M} \right]$$

$$M_i = \left[ \frac{a_V M}{1 + (a_E + a_V)M} \right] M_{i-1} \quad (3)$$

where  $a_E = E/R$  and  $a_V = V/R$  are the electronic and vibrational quenching constants. Using the above assumptions, the fluorescent intensity may be summed over all excited levels and the result is given by:

$$P/F = B (1 + a_V S P) / \{ 1 - \left[ \frac{a_V P}{1 + a_V (1+S)P} \right]^n \} \quad (4)$$

where  $F$  is the total fluorescent intensity,  $B$  is an experimental constant previously defined,  $S = a_E/a_V = E/V$ , and the ground state population density has been replaced by the corresponding pressure,  $P$ . The exponent  $n$  represents the number of excited levels which contribute to the fluorescent signal; this number depends on the average size of the vibrational quantum transferred per quenching collision,  $\Delta v_{\text{vib}}$ , and on the energy separation between the exciting and fluorescent light; i.e.,  $n$  may be written as

$$n = 1 + (v_E - v_F) / \Delta v_{\text{vib}}. \quad (5)$$

At sufficiently high pressures,  $P \gg 1/a_V$ ; Eq. (4) becomes linear in  $P$ ,

$$P/F = B a_V P S (1 + S)^n / [(1 + S)^n - 1] \quad (6)$$

and the observed quenching constants defined above and given in Table I can then be written as

$$a_{\text{obs}} = a_V S (1 + S)^n / [(1 + S)^n - 1] = a_V G(n, S) \quad (7)$$

The factor  $G(n, S)$  has been evaluated for various values of  $n$  and  $S$  and the results are given in Table II, where an increase in  $n$  for fixed  $S$  corresponds to experimentally increasing  $\Delta\nu$ . Examination of Table II shows that in order to account for the large variation in  $a_{\text{obs}}$ ,  $S$  must be 0.10 or less; that is, the vibrational quenching rate must be considerably faster than electronic quenching in excited  $\text{NO}_2$ .

A more detailed comparison of the calculated and experimental quenching constants is shown in Fig. 4, where relative values of the quenching constants are plotted vs.  $\Delta\nu$ . To obtain the calculated curves, values of  $\Delta\nu_{\text{vib}}$  are chosen between 500 and 2000  $\text{cm}^{-1}$ ; and  $S$  is varied between 0.1 and 0 ( $a_E = 0$ ). For a given  $\Delta\nu_{\text{vib}}$ ,  $n$  is calculated using Eq. (5), and the relative quenching constants can then be obtained from Table II. While the best overall agreement occurs at  $\Delta\nu_{\text{vib}} = 1000 \pm 500 \text{ cm}^{-1}$ , the experimental scatter and relative insensitivity of the calculation to variation in  $S$  at low values, permit only a choice of an upper bound for  $S$ , that is,  $S \leq 0.01$ . For  $\Delta\nu_{\text{vib}} = 1000 \text{ cm}^{-1}$  and  $S = 0.01$ ,  $a_V$  can be obtained from the observed quenching constants using Eq. (7) and the values of  $G(n, S)$  in Table II. The average value of  $a_V$  obtained in this way is about 700  $\text{Torr}^{-1}$ ;  $a_E$  is then 7  $\text{Torr}^{-1}$ . Quenching rate constants may then be obtained from the definition of  $a_V$  if the radiative lifetime is known. Taking  $\tau_R = 5.5 \times 10^{-5}$  sec (see following Section),  $E = 3.9 \times 10^{-12}$  and  $V = 3.9 \times 10^{-10} \text{ cm}^3/\text{mole-sec}$ . At low values of  $S$ ,  $V$  is approximately independent of  $S$  while  $E$  varies as  $S$ ; thus for values of  $S$  less than 0.01,  $V$  differs little from the value given above.

Quenching curves calculated from Eq. (4) for  $\Delta\nu_{\text{vib}} = 1000 \text{ cm}^{-1}$  and  $S = 0.01$  are compared with experimental points in Fig. 3; the agreement is very good considering the many approximations of the model. However, the calculated curves are also insensitive to the choice of  $S$  at low values and cannot be used to determine this parameter beyond the previously established limit of  $S \leq 0.01$ .

### Fluorescence Lifetime

The lifetime of  $\text{NO}_2$  fluorescence excited at several wavelengths was determined by means of the phase-shift method<sup>19</sup>. For the lifetime experiments, modulated exciting light is used; the intensity is given by

$$I_e(t) = \bar{I}_e [1 + m \cos(\omega t - \phi_0)] \quad (8)$$

where  $\omega$  is the angular frequency of modulation,  $\bar{I}_e$  is the average exciting light intensity (d.c. level),  $m$  is the fraction of modulation defined as the ratio of maximum amplitude to the d.c. level, and  $\phi_0$  is the zero or reference phase of the system. Only the fundamental Fourier component is included in the discussion; Fourier analysis of the experimental results shows that the fundamental accounts for approximately 90% of the amplitude in both the excitation and fluorescent waveforms.

When the frequency separation between the exciting and the fluorescent radiation,  $\Delta\nu$ , is small, or for any  $\Delta\nu$  at sufficiently low pressures, only one upper level contributes to the observed fluorescent signal. At low pressure, the time variation in the fluorescent signal may be obtained by

solving Eqs. (2) for  $i = 1$  with  $I_e$  given by Eq. (8). The fluorescent signal may then be written

$$F(t) = \tilde{F} [1 + \lambda m \cos (\omega t - \Delta\phi)] \quad (9)$$

where the phase angle,  $\Delta\phi$ , by which the phase of the observed fluorescent signal is shifted with respect to  $\phi_0$ , is simply related to the lifetime,  $\tau$ , by

$$\tan \Delta\phi = \omega\tau \quad (10)$$

and

$$\tau^{-1} = \tau_R^{-1} [1 + (a_E + a_V) P]. \quad (11)$$

The fraction of modulation in the fluorescent signal is attenuated by the factor  $\lambda$ , where

$$\lambda = (1 + \omega^2 \tau^2)^{-1/2}. \quad (12)$$

Eqs. (10) and (12) show that either the phase shift or the attenuation factor can be used to measure the lifetime; however, the phase shift is the more accurately measured and this is the method used here.

A representative fluorescent waveform is shown in Fig. 5, where the counts per channel are plotted vs. time since the start trigger. To obtain the phase shift, the reference phase of the system is established by record-



ing the exciting light waveform with no  $\text{NO}_2$  in the cell. Both the fluorescent and the exciting light signals are corrected for a small dark current background and the fluorescent signal is corrected for scattered light<sup>19</sup>. Both waveforms are expanded in a Fourier series (up to the fifth harmonic) and the resulting fundamental coefficients are used to determine the phase shift by computer analysis.

Typical results of lifetime measurements using 8 kHz modulation at low  $\text{NO}_2$  pressures are shown in Fig. 6. Table III summarizes the results; the radiative lifetimes and quenching constants were obtained from a linear least squares fit of the experimental data. In experiments where  $\Delta\nu$  is large or where sharp cut filters were used in the fluorescent beam, the  $1/\tau$  vs.  $P$  plots were non-linear and  $\tau_R$  was obtained from an extrapolation of the low pressure points. Errors quoted are the standard deviations obtained from the least squares analysis. Quenching constants obtained from the steady illumination experiments (Table I) are in satisfactory agreement with these results where conditions are comparable.

#### Frequency Variation

Variation of the modulation frequency may be used to determine whether a portion of the  $\text{NO}_2$  visible fluorescence is due to emission from a state with a much shorter lifetime than 55  $\mu\text{sec}$ . If only one state contributes to the fluorescence, the observed lifetime is independent of the modulation frequency  $\omega$ ; however, if there are two or more excited states involved, the observed lifetime varies with  $\omega$ . At low  $\omega$ , the observed phase shift is due mainly to relatively long-lived states; but as  $\omega$  increases, the long-lived states cannot follow the rapid modulation and the observed phase shift is

due mainly to the short-lived states. Thus, the observed lifetime should decrease with increasing  $\omega$  if a short-lived state contributes to the  $\text{NO}_2$  fluorescence.

If emission occurs concurrently from two excited states, the following relation between the observed lifetime,  $\tau_{\text{obs}}$ , and the lifetimes of the excited states,  $\tau_1$  and  $\tau_2$ , is obtained:

$$\tau_{\text{obs}} = \frac{(1 + \omega^2 \tau_2^2) P_1 \tau_1 + (1 + \omega^2 \tau_1^2) (1 - P_1) \tau_2}{(1 + \omega^2 \tau_1^2) (1 - P_1) + (1 + \omega^2 \tau_2^2) P_1} \quad (13)$$

where  $P_1$  and  $(1 - P_1)$  represent the fraction of fluorescent intensity due to state 1 and state 2 respectively. Using the measured value of 55  $\mu\text{sec}$  for  $\tau_1$ , and for  $\tau_2$  a value of 0.25  $\mu\text{sec}$  calculated<sup>4</sup> from the absorption coefficient,  $\tau_{\text{obs}}$  as a function of  $\omega$  is shown in Fig. 7 for various values of  $P_1$ . At higher modulation frequencies the phase-shift measurement becomes sensitive to the presence of even small contributions from a relatively short-lived state; for example, with a change in frequency from 8 to 20 kHz, the observed lifetime should change by a factor of about 1.4 if 1% of the fluorescent intensity comes from a state with 0.25  $\mu\text{sec}$  lifetime.

As shown in Table III, there is no significant change in lifetime as the frequency is varied; the average observed lifetime at 8 kHz is 56  $\mu\text{sec}$ , while at 20 kHz it is 54  $\mu\text{sec}$ . This shows that the visible  $\text{NO}_2$  fluorescence originates from one excited state with a lifetime of 55  $\mu\text{sec}$ ; and as seen in Fig. 7, any contribution from a separate short-lived state must be considerably less than 1% of the total intensity.

## Discussion

The combined results of the steady and the modulated excitation experiments indicate that  $\text{NO}_2$  fluorescence involves a single electronically excited state in which efficient vibrational relaxation occurs at approximately gas kinetic rate,  $V = 3.9 \times 10^{-10}$ , compared to about  $2 \times 10^{-10} \text{ cm}^3/\text{molecule-sec}$  for the gas kinetic collision rate of ground-state  $\text{NO}_2$ . However, electronic quenching requires about a hundred collisions. The size of the vibrational quantum transferred per quenching collision,  $1000 \pm 500 \text{ cm}^{-1}$ , is in the range of the  $880 \text{ cm}^{-1}$  bending frequency of excited  $\text{NO}_2$ <sup>1</sup>. Observation of rapid collisional quenching in excited  $\text{NO}_2$  is consistent with the results of studies in  $\text{SO}_2$  fluorescence where rapid vibrational relaxation has also been reported<sup>20,21</sup>.

No significant variation in the fluorescent lifetime was observed for excitation energies from 16,700 to 24,700  $\text{cm}^{-1}$ , which further argues against the existence of a short-lived state. If more than one state were involved, the relative contributions of the excited states may be expected to change with excitation energy and lead to a large variation in the observed lifetime. The conclusion of only one emitting state is thus supported by the frequency variation experiments, by the excitation energy experiments, and by the very direct result of Douglas<sup>8</sup> that, after sudden cut-off from steady illumination, the total fluorescence intensity decayed with a single lifetime of about 50  $\mu\text{sec}$ .

Other investigators<sup>4,8,14</sup> have also reported lifetimes from 44 to 90  $\mu\text{sec}$ . Our work is, however, in disagreement with the sharply fluctuating  $\tau_R$  (between 60 and 90  $\mu\text{sec}$ ) as function of  $\nu_E$  of Schwartz and Johnston<sup>14</sup> (SJ). As these results of SJ were obtained with a Corning 2-73 or other

sharp-cut filters in the fluorescent beam whereas ours were usually obtained with an interference filter of wavelength close to that of the exciting light, we carried out a few experiments under conditions closely matching those of SJ and corresponding to their sharp peaks of  $\tau_R$  at 5600 and 6000Å excitation. The results in Table III show no appreciable change of  $\tau_R$ . It should also be emphasized (a) that SJ's lifetimes (Fig. 3) were obtained at an  $\text{NO}_2$  pressure of 1.3 mTorr whereas ours are radiative lifetimes at zero pressure extrapolated from 20 to 30 experiments at pressures of 1 to 15 mTorr. This widens the discrepancy by about 50%, since SJ's lifetimes are to be increased by about 30% using the slopes of our  $1/\tau$  vs.  $P$  curves; (b) our lifetimes are based on a full waveform analysis of each experiment whereas SJ's are based only on the intensities of in phase and out of phase components of the fluorescence. Still, the origin of the discrepancy is unclear, but the present results, viz. the insensitivity of  $\tau_R$  to small variations of  $\nu_E$ , seem reasonable.

The magnitude of  $\tau_R$  is also affected by the size of the fluorescence cell and of the optical region of observation, because the excited molecules move an appreciable distance before radiating. The effective observation diameter used by SJ was 20 cm in a cell of 33 cm diameter whereas our observation was confined to 8 cm in a cylindrical 14 cm cell. Both SJ's (Table I) and our results with various cell sizes would suggest that this effect may increase our  $\tau_R$  by only  $\leq 10\%$ .

There is good agreement with SJ's estimate of the vibrational relaxation rate constant ( $4 \times 10^{-10} \text{ cm}^3/\text{sec}$ ) and satisfactory agreement with their electronic quenching ( $\leq 2 \times 10^{-11} \text{ cm}^3/\text{sec}$ ) and energy removed per collision ( $2000 - 4000 \text{ cm}^{-1}$ ). The latter seems too large in view of findings of chem-

ical activation experiments for larger molecules<sup>22</sup>.

Interaction of excited electronic levels of  $\text{NO}_2$  with upper vibrational levels of the ground electronic state (or of other non-radiating electronic states) is a possible explanation of the long radiative lifetime of  $\text{NO}_2$ . This type of interaction has been suggested by several authors<sup>8,9</sup> and possible mechanisms have been discussed<sup>23,24</sup>. Interaction leads to the establishment of an equilibrium between the levels (assuming that the crossing rate is greater than the deactivation rate or that the electronic states are truly mixed), and since at equal energies the density of levels is much greater in the ground than in the excited electronic state, the equilibrium assumption decreases the true radiative lifetime of the excited state by the factor  $K + 1$ , where  $K$  is the ratio of level densities of ground and excited states, because the observed radiative decay includes the continuous replenishment of excited state from vibrationally excited (non-radiating) ground state. Inclusion of this type of interaction modifies the interpretation of the observed lifetimes and quenching parameters discussed in the preceding Sections. The quantities derived from the equilibrium model may then be written in terms of the observed values as follows:

$$\tau_R(\text{eq}) = \tau_R/(K+1); a_V(\text{eq}) = a_V/(K+1); S(\text{eq}) = S/(K+1). \quad (14)$$

Using a value of  $K = 200$  which would ascribe the entire lifetime anomaly to this effect, and using the values of  $a_V$  and  $S$  obtained from the steady excitation experiments,  $\tau_R(\text{eq}) = 0.28 \mu\text{sec}$ ,  $a_V(\text{eq}) = 3.5 \text{ Torr}^{-1}$ , and  $a_E(\text{eq}) \leq 7 \text{ Torr}^{-1}$ . For this value of  $\tau_R$ ,  $V = 3.9 \times 10^{-10}$  and  $E \leq 7.8 \times 10^{-10} \text{ cm}^3/\text{molecule-sec}$ ; only an upper limit has been given for  $E$  because of the uncertainty in

S. For this high value of  $K$ , the equilibrium model results in high quenching rate constants for both vibrational and electronic quenching. However,  $K$  should be a measure of the relative degeneracy at equal energies in the excited and ground states. Estimates of this degeneracy ratio give values between about 5 and 30 over the energy range studied. Thus, the equilibrium model is unlikely to provide the sole mechanism of the lifetime lengthening. It is possible, however, that such an equilibrium exists, but that  $K$  is, say, 10 or 20, and that other explanations<sup>8</sup> bridge the remaining gap between the radiative lifetime and the integrated absorption coefficient.

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## References

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Table I. Quenching constants,  $a_{\text{obs}}$ , for steady excitation

$\lambda_F$	$\lambda_E = 4050\text{\AA}$		$\lambda_E = 4360\text{\AA}$		$\lambda_E = 5460\text{\AA}$		$\lambda_E = 5780\text{\AA}$	
	$\Delta\nu^*$	$a_{\text{obs}}, \text{Torr}^{-1}$	$\Delta\nu^*$	$a_{\text{obs}}, \text{Torr}^{-1}$	$\Delta\nu^*$	$a_{\text{obs}}, \text{Torr}^{-1}$	$\Delta\nu^*$	$a_{\text{obs}}, \text{Torr}^{-1}$
4360	1774 $\text{cm}^{-1}$	356						
4700			1656 $\text{cm}^{-1}$	247				
5090	5063	125	3300	160				
5460			4631	129				
5665	7057	107	5294	109				
5990			6252	99	1617 $\text{cm}^{-1}$	362		
6350	8961	73	7198	74	2563	238	1553 $\text{cm}^{-1}$	394
6600			7795	72	3160	207	2150	312
7000	10424	69	8661	64	4026	208	3016	272
7250			9153	63	4518	167	3508	226
7850	11971	69	10208	81	5573	148	4563	195

\*  $\Delta\nu = \nu_E - \nu_F$

Table II. Values of  $G(n,S)$ 

$n^S$	1.00	0.10	0.01	0.00
1	2.00	1.10	1.01	1.00
2	1.33	.58	.51	.50
3	1.14	.40	.34	.33
4	1.07	.32	.26	.25
5	1.03	.26	.21	.20
6	1.02	.23	.17	.17
7	1.01	.20	.15	.14
8	1.00	.19	.13	.12
9	1.00	.17	.12	.11
10	1.00	.16	.11	.10
12	1.00	.15	.089	.083
14	1.00	.14	.077	.071
16	1.00	.13	.068	.062
18	1.00	.12	.061	.056
20	1.00	.12	.055	.050

Table III. Radiative lifetime and quenching constants of NO<sub>2</sub>

$\lambda_E, \text{\AA}$	$\lambda_F, \text{\AA}$	$\omega, \text{kHz}$	$\tau_R, \mu\text{sec}$	$a_{\text{obs}}, \text{Torr}^{-1}$
4360	4700	8	$55 \pm 2$	$262 \pm 15$
4360	4700	8	$53 \pm 7$	$262 \pm 40$
4360	4700	20	$54 \pm 9$	$316 \pm 65$
4360	5990	20	$53 \pm 3$	a
4360	6350	20	$54 \pm 12$	a
5375	5990	8	$59 \pm 3$	$224 \pm 11$
5460	5990	8	$58 \pm 3$	$342 \pm 25$
5780	6350	8	$55 \pm 3$	$324 \pm 25$
5600	CS 2-58 <sup>b</sup>	8	$54 \pm 4$	a
6000	CS 2-64 <sup>b</sup>	8	$53 \pm 6$	a

<sup>a</sup>  $1/\tau$  vs.  $P$  plots curved.

<sup>b</sup> Corning sharp cut filters.

## Figure Captions

- Fig. 1. Diagram of apparatus.
- Fig. 2. Diagram of detection system used for lifetime measurements.
- Fig. 3. Stern-Volmer plot of representative  $\text{NO}_2$  fluorescence results. Excitation wavelength is  $4360\text{\AA}$ . Theoretical curves calculated for  $S = 0.01$  and  $\Delta\nu_{\text{vib}} = 1000\text{ cm}^{-1}$ .
- Fig. 4. Comparison of calculated and experimental relative quenching constants as functions of  $\Delta\nu = \nu_E - \nu_F$ . Calculated curves obtained using Eq. (5) and Table II; reference value is at  $\Delta\nu = 1600\text{ cm}^{-1}$ . Excitation wavelength for the experimental points:  $\bullet = 4050\text{\AA}$ ,  $\circ = 4360\text{\AA}$ ,  $\Delta = 5460\text{\AA}$ , and  $\times = 5780\text{\AA}$ . Numbers next to curves indicate  $\Delta\nu_{\text{vib}}$ .
- Fig. 5. Fluorescent signal waveform; exciting wavelength =  $4360\text{\AA}$ , fluorescent wavelength =  $4700\text{\AA}$  at  $8.2\text{ mTorr NO}_2$ . Counting time, 8 minutes.
- Fig. 6. Reciprocal lifetime vs. pressure of  $\text{NO}_2$ , exciting wavelength =  $4360\text{\AA}$ , fluorescent wavelength =  $4700\text{\AA}$ ,  $8\text{ kHz}$  modulation frequency. The line through the points is the least square fit with radiative lifetime =  $55\text{ }\mu\text{sec}$  and quenching constant =  $262\text{ Torr}^{-1}$ .
- Fig. 7. Observed lifetime vs. modulation frequency; lifetime calculated using Eq. (13) with  $\tau_1 = 55\text{ }\mu\text{sec}$  and  $\tau_2 = 0.25\text{ }\mu\text{sec}$ . Numbers give fraction of total intensity due to  $55\text{ }\mu\text{sec}$  state.

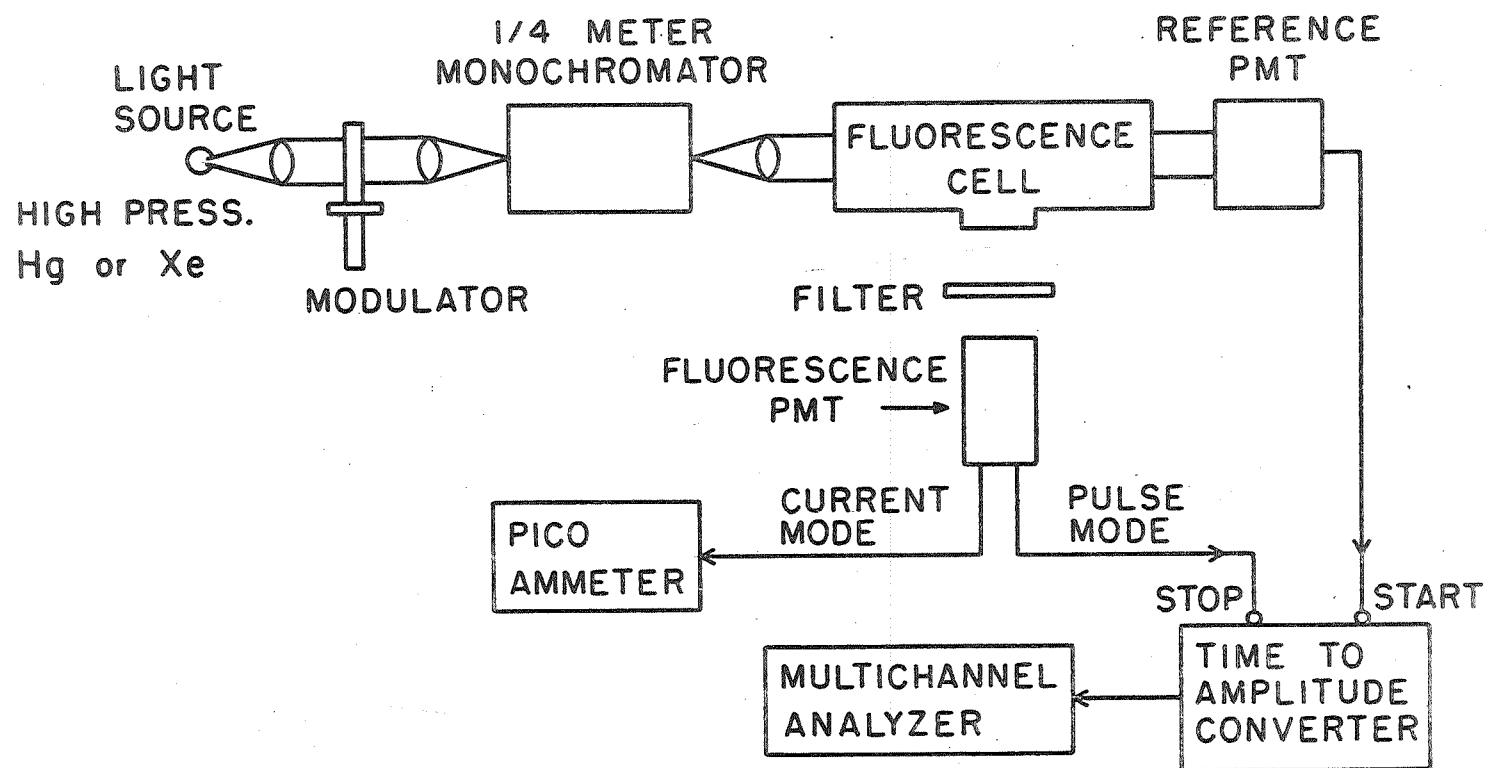


Figure 1.

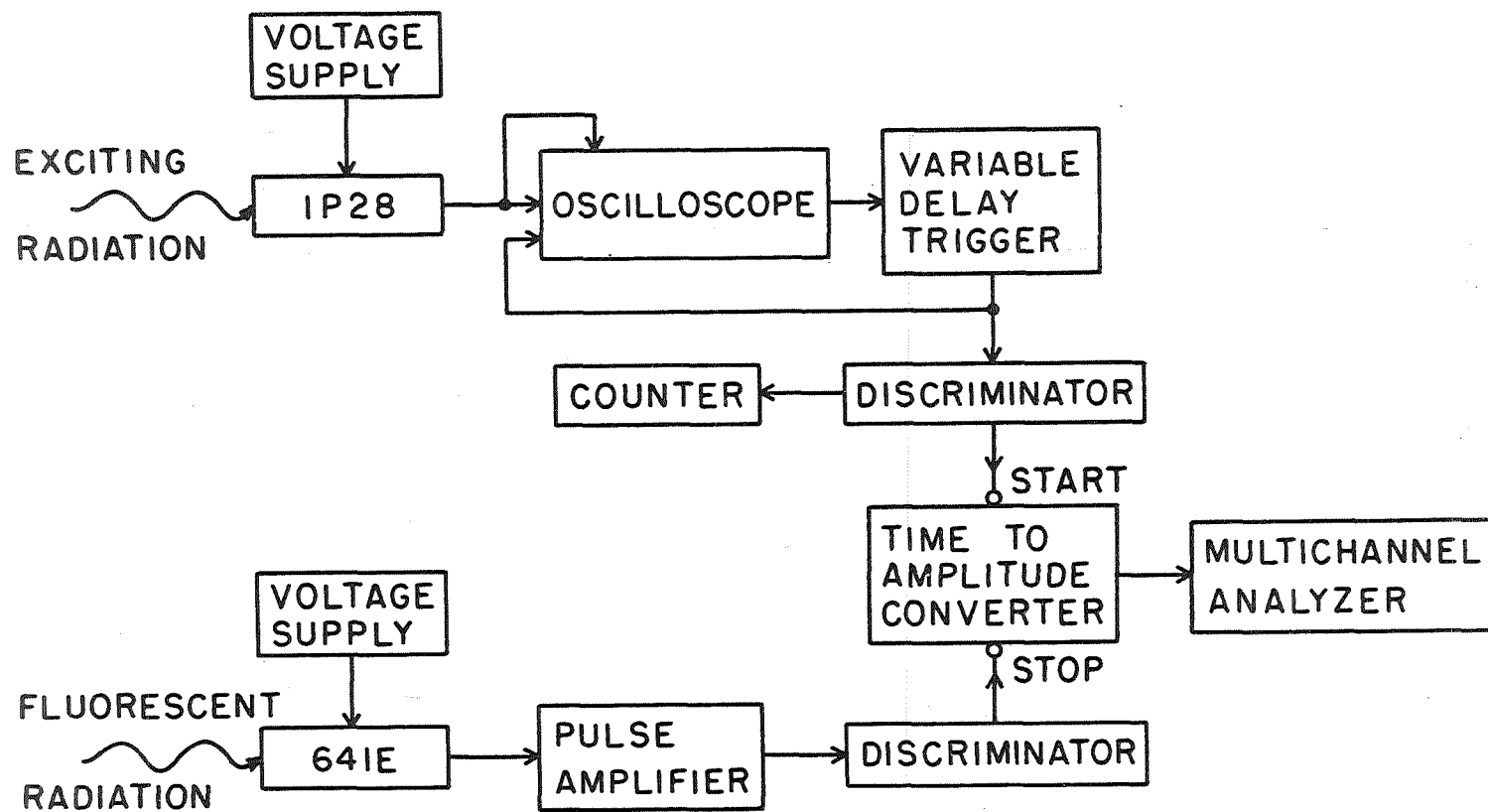


Figure 2.

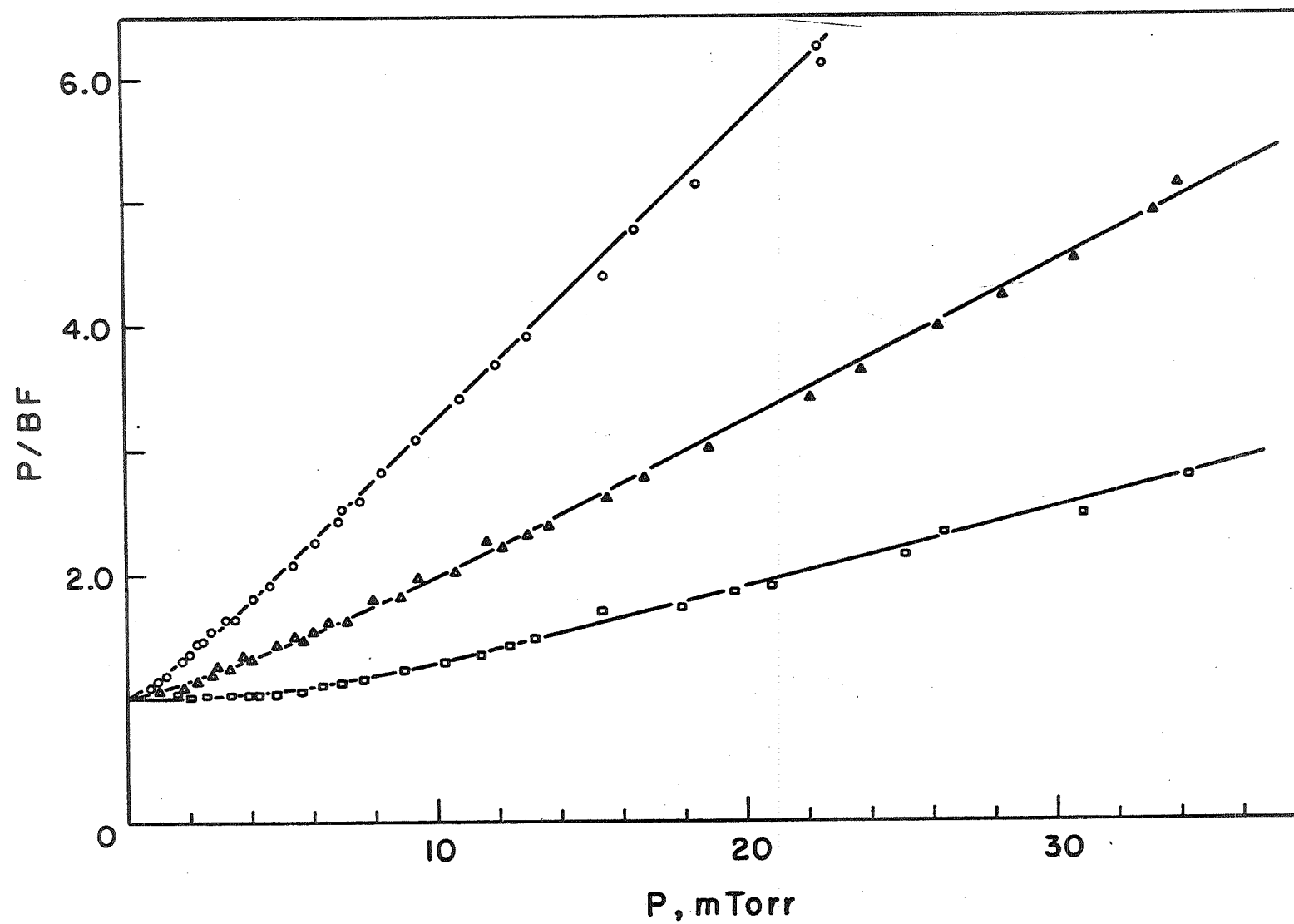


Figure 3.

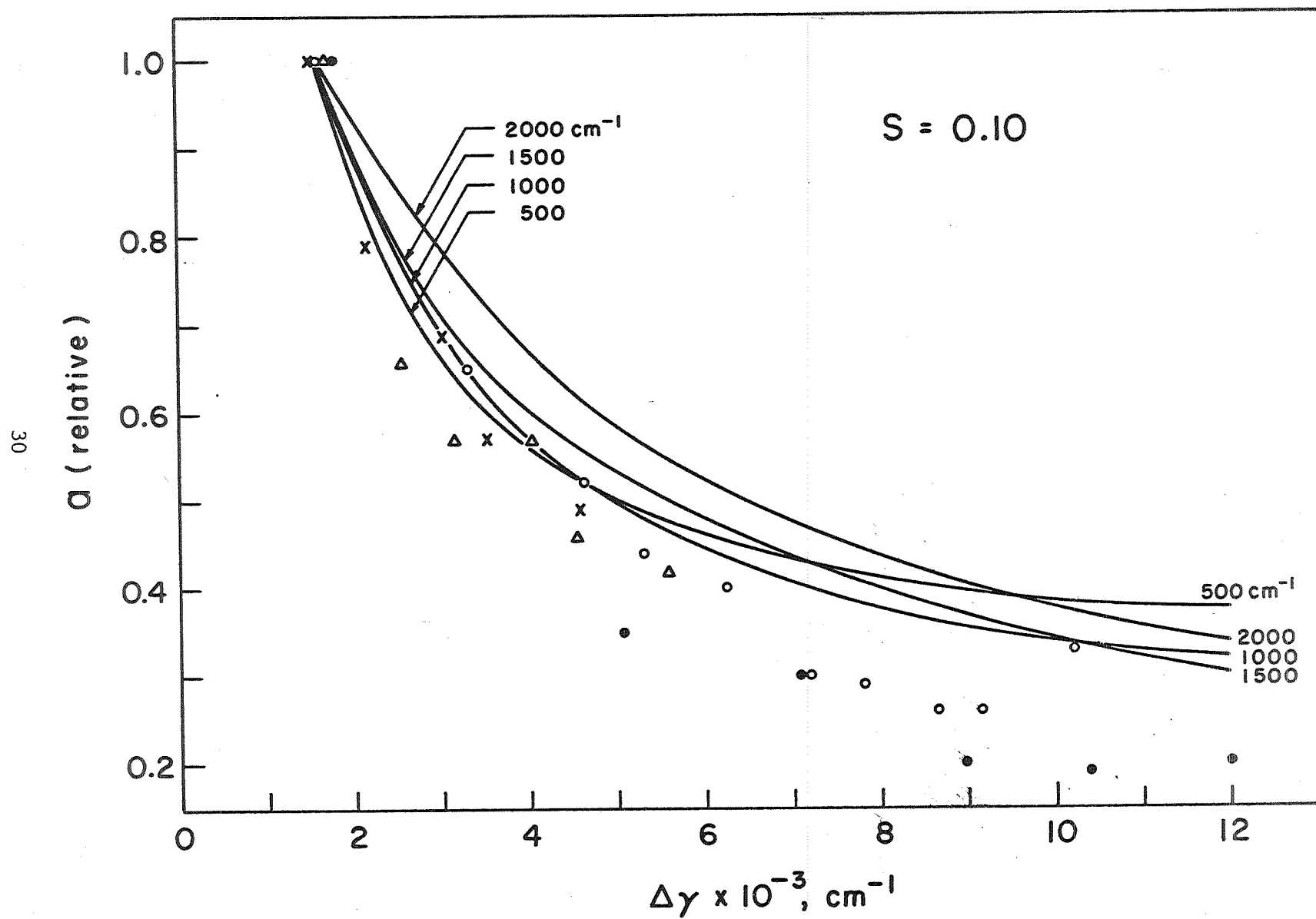


Figure 4a.



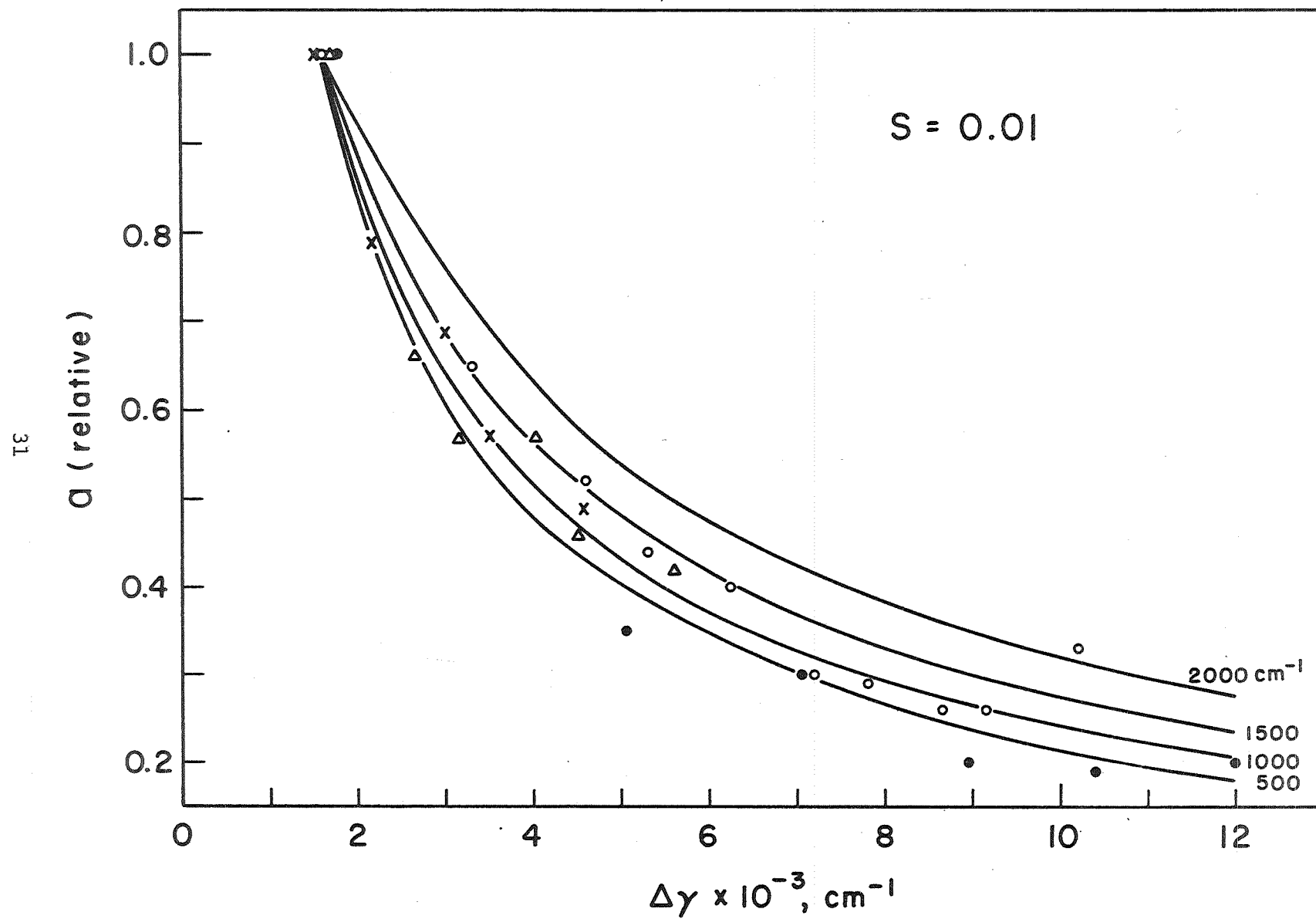


Figure 4b.

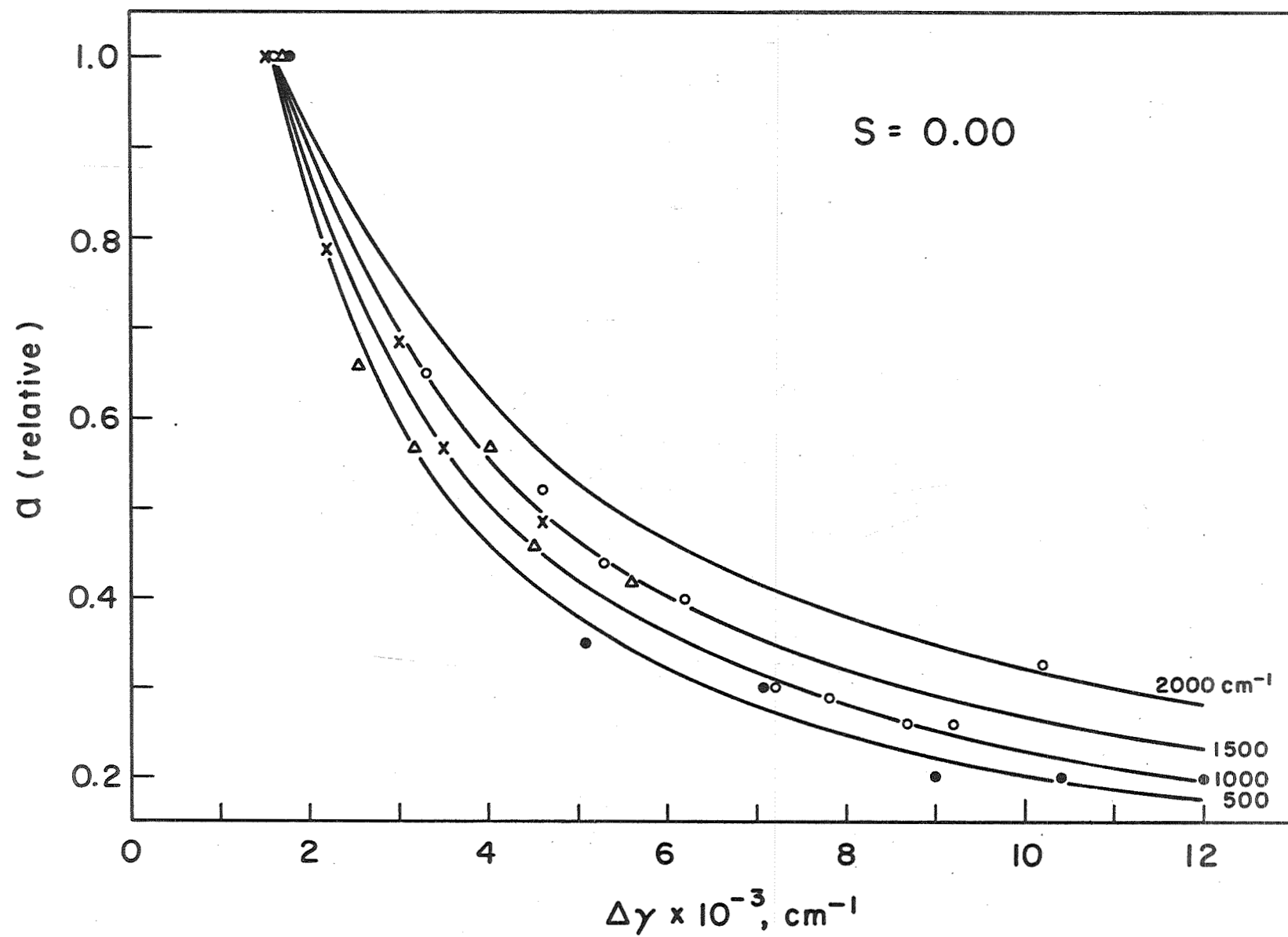


Figure 4c.

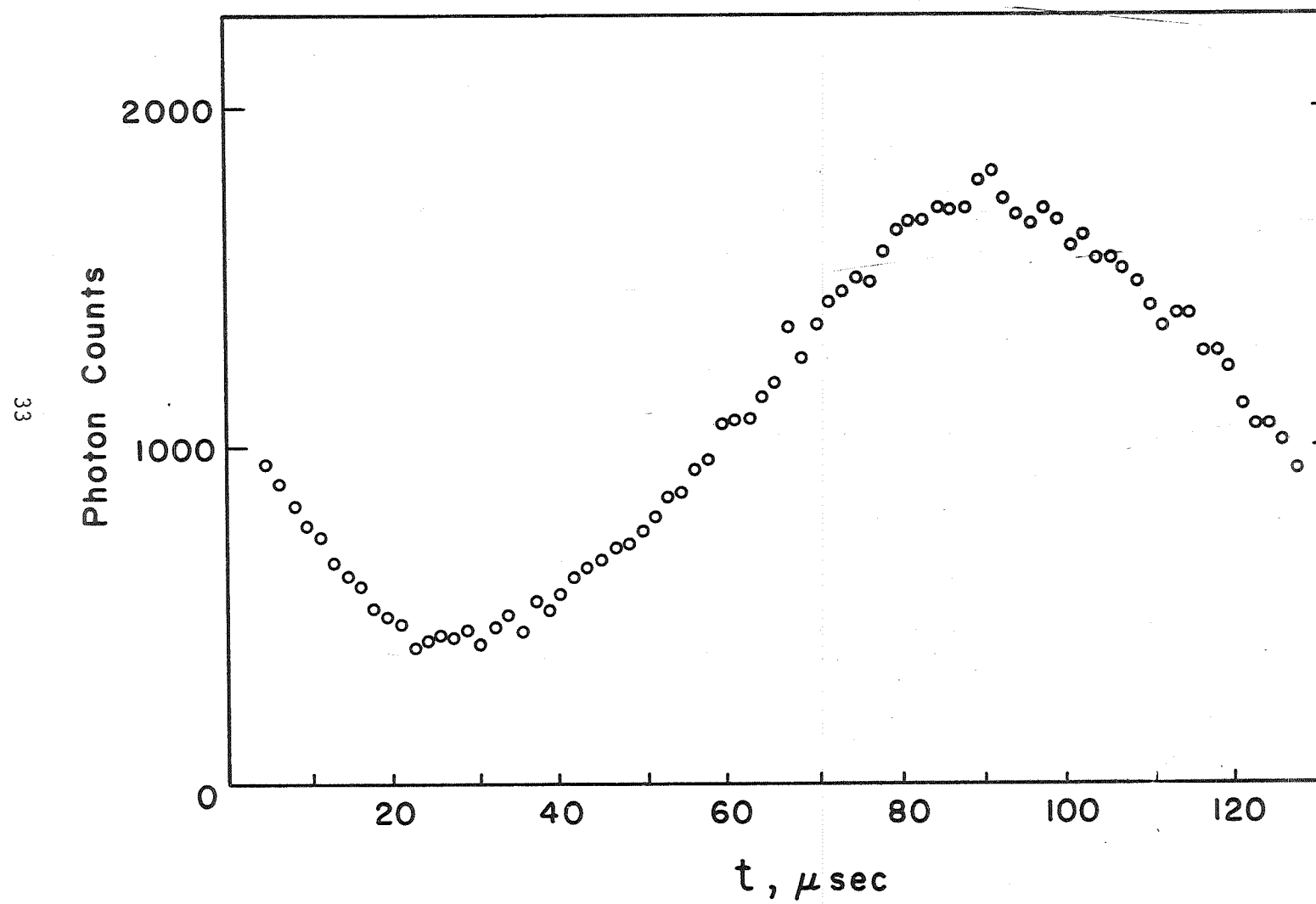


Figure 5.

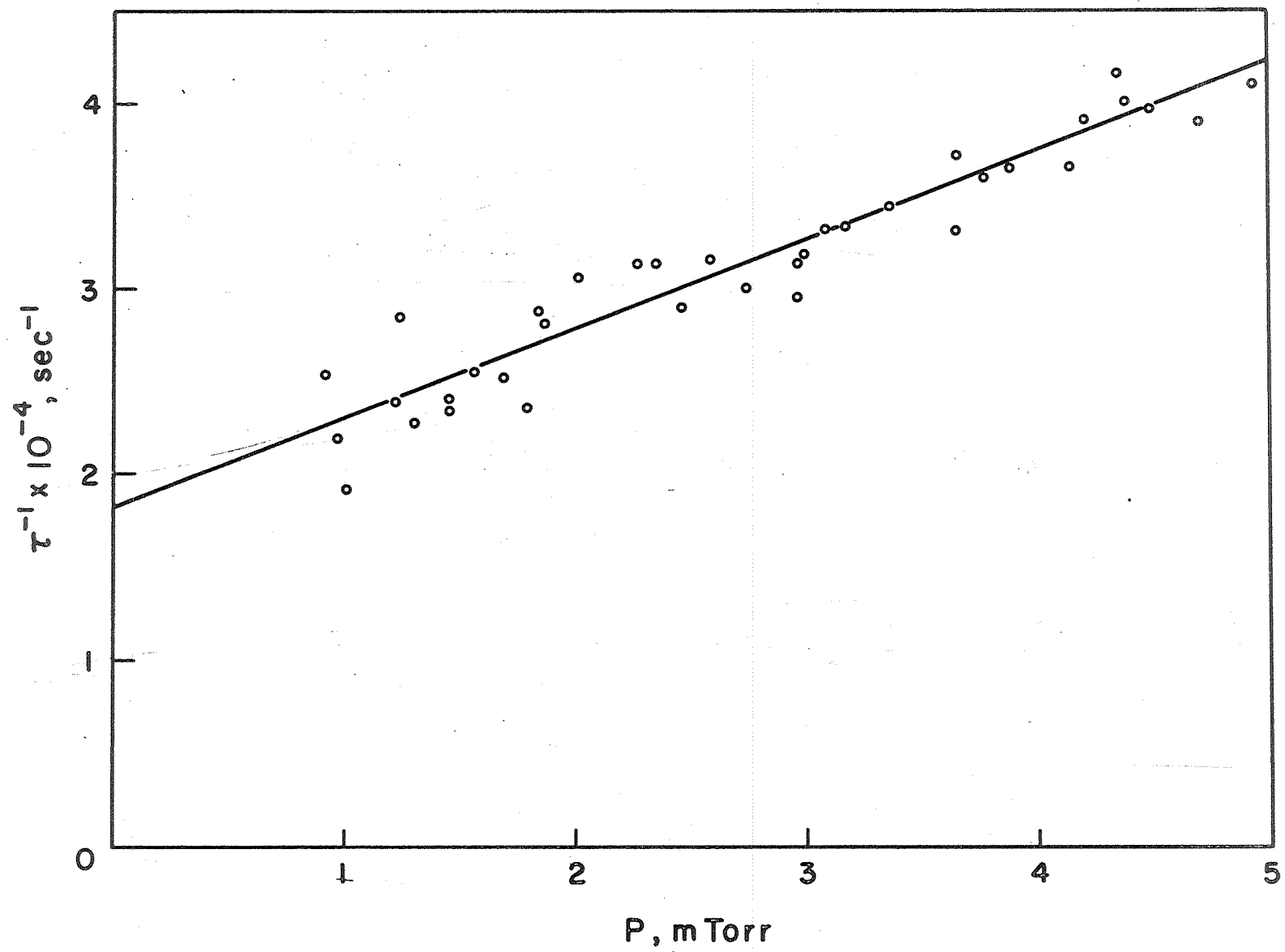


Figure 6.

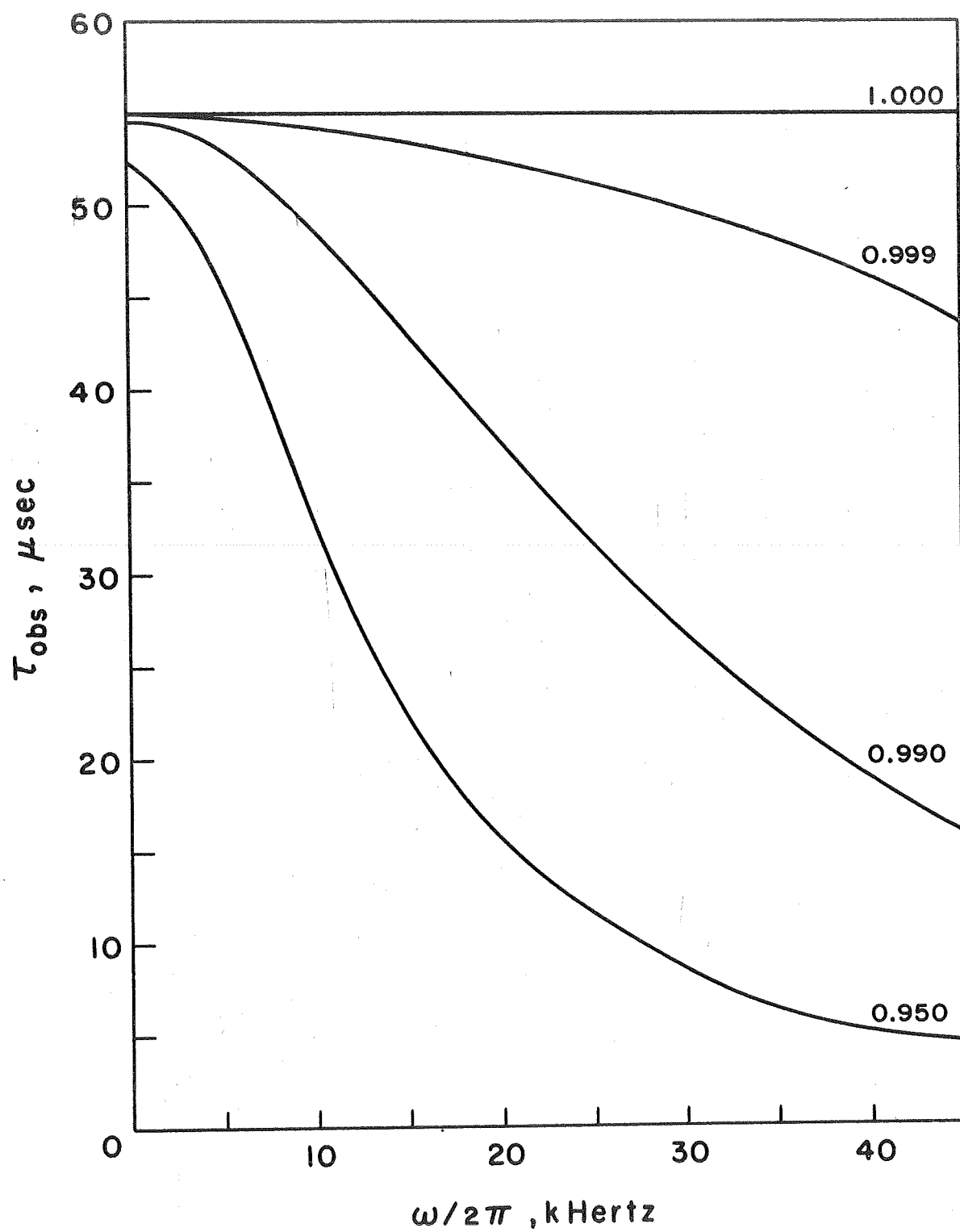


Figure 7.