Journal of Photochemistry, 6 (1976/77) 237 - 240

PRESSURE INDEPENDENCE OF THE FLUORESCENCE QUENCHING OF NO_2^*

M. BIRNBAUM, C. L. FINCHER and A. W. TUCKER

Electronics Research Laboratory, The Aerospace Corporation, El Segundo, Ca. 90009 (U.S.A.)

(Received July 16, 1976)

Summary

The results obtained demonstrate that the fluorescence yield of NO_2/N_2 mixtures of constant NO_2 concentration over the pressure range of 100 to 760 Torr is constant. Similar results were found for NO_2/air mixtures over a smaller pressure range. These results imply that fluorescence quenching by foreign gases follows a linear or Stern–Volmer quenching law.

Introduction

During the past several years, a laser fluorescence NO_2 monitor has been developed and tested [1 - 3]. A number of experiments were performed to verify features of the NO_2 fluorescence and fluorescence quenching which were important in the operation of an NO_2 fluorescence monitor. Our results were consistent with those of earlier researchers [4 - 6].

One result of these studies which was pertinent to the operation of the fluorescence monitor was that both self-quenching and foreign gas quenching showed an accurately linear pressure dependence. These linear plots are generally referred to as Stern–Volmer plots. This dependence implies that the response of our instrument in monitoring ambient NO_2 concentrations in air will be linear with the NO_2 concentration and independent of the gas pressure of the mixture over a wide pressure range.

Nevertheless, detailed investigations of NO_2 fluorescence revealed a number of features which were difficult to explain. Among these were: dependence of the radiative lifetime of electronically excited NO_2 on the wavelength of the exciting radiation [5, 6], a slight curvature in the self-quenching of NO_2 at low pressures [5, 6], and a dependence of the quenching upon the wavelength separation of the excitation and fluorescence light [4]. More recently, Braslavsky and Heicklen [7] (referred to as B & H) in a detailed study of the fluorescence quenching of NO_2 have reported that foreign gas quenching exhibited a marked deviation from linearity, but that self-quench-

*This work was supported by the U.S. Air Force under Contract No. F04701-75-C-0076.

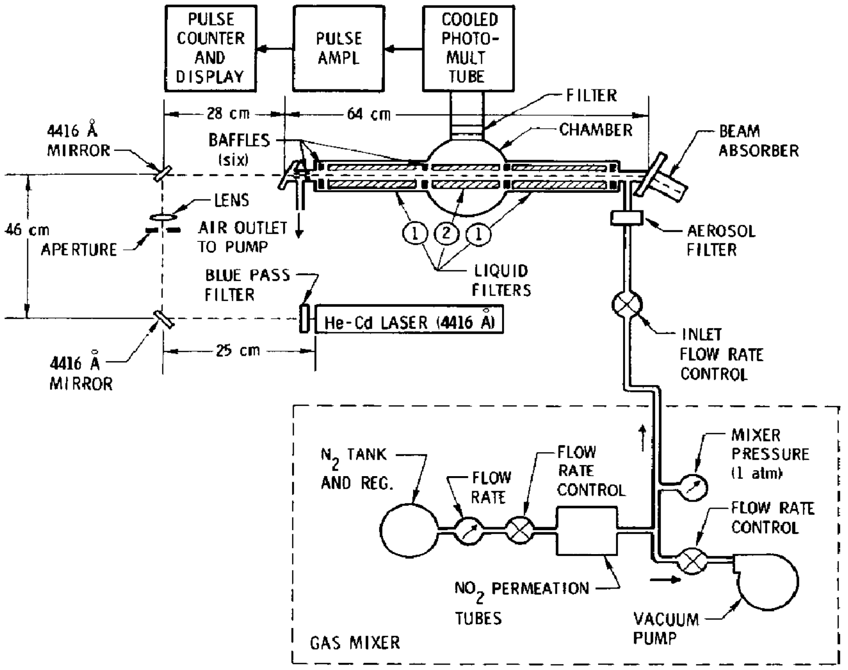

Fig. 1. Block diagram of laser NO_2 fluorescence monitor, and of system used for measurement of dependence of quenching on pressure.

ing followed a Stern–Volmer or linear dependence. In view of their results, we re-examined the calibration and performance of our laser instrument and performed several measurements specifically designed to test for possible non-linear instrument responses.

Our results are consistent with a linear Stern–Volmer plot and disagree with the results of ref. [7]. In our work we utilized much higher gas pressures (100 to 760 Torr) which should be compared to the 30 Torr foreign gas pressure of B & H. However, the theoretical treatment of ref. [7] when extrapolated to the high foreign gas pressures of our experiments would predict a much greater departure from linearity in a Stern–Volmer plot than observed in ref. [7] at much lower pressures.

Experimental

The construction and operation of the laser NO_2 fluorescence monitor (LNFM) have been described in a number of reports [1 - 3]. However, to facilitate our discussion we include here a block diagram of the LNFM (Fig. 1). The following features of the LNFM were carefully measured. With a light-emitting diode as a source, the response of the instrument to light signals of varying intensity was tested over a wide range (which included the operating range of the LNFM). This established that the instrument response to light signals was linear as expected. Linearity of the fluorescence response of the LNFM was checked using both filtered and unfiltered air samples. The measured responses were strictly linear (Figs. 4 and 5 of ref. [1]). The above tests were all performed with NO_2 in dry nitrogen at approximately atmospheric pressure. These tests showed that the LNFM responded linearly to light signals, to NO_2 concentrations in N_2 at approximately atmospheric pressure and to the power of the laser excitation for a constant NO_2 and N_2 mixture.

If the LNFM response is linear (Stern–Volmer characteristic), then we can predict that in the atmospheric pressure régime, the fluorescence yield will be independent of pressure for a fixed volumetric concentration of NO_2. For pressures over the range of 100 to 760 Torr, eqn. (2) predicts a constant fluorescence yield. This is important in the operation of the laser fluorescence monitor since it implies that the calibration will be unaffected by changes in the barometric pressure or the greater atmospheric pressure changes that occur at high elevations.

A direct test of the quenching of NO_2 by foreign gases could be obtained by determining the fluorescence yield of NO_2 in N_2 as a function of pressure while keeping the concentration of NO_2 constant. According to Gelbwachs *et al.* [3], the quenching factor is given by:

$$Q = (1 + a_{NO_2}P_{NO_2})(1 + a_{NO_2}P_{NO_2} + \sum_x a_x p_x)^{-1} \qquad (1)$$

For trace concentrations of NO_2 in N_2, eqn. (1) reduces to:

$$Q = (1 + a_{N_2}P_{N_2})^{-1} \approx 1/a_{N_2}P_{N_2} \qquad (2)$$

According to Myers *et al.* [4] the constant $a_{N_2} \approx 44$ Torr^{-1}. The approximation of the right hand term of eqn. (2) holds to an accuracy of better than 0.02% over the pressure range 100 - 760 Torr. The fluorescence yield is proportional to the product of the concentration of NO_2 and the quenching factor, namely, $[NO_2] \times a_{N_2}P_{N_2}$. If the concentration of NO_2 is written in terms of its partial pressure, $[NO_2] = cP_{N_2}$ where c is a constant, it is clear that the fluorescence yield is constant over the pressure range for which eqn. (2) holds.

In our measurements, concentrations of NO_2 of 0.5 p.p.m. in N_2 were used. The fluorescence was measured with the instrument of Fig. 1, using a He–Cd laser operating at 441.6 nm to excite the fluorescence [1]. Details of the auxilliary apparatus used to control the flow of the NO_2/N_2 mixture and to control and measure the pressure of the gases in the fluorescence chamber are shown in Fig. 1. Although not obvious from the drawing of Fig. 1, the fluorescence chamber is identical with that of Tucker *et al.* [1].

The instrument was tested and calibrated over the required range. This included calibration of the flow meters and the pressure measuring instruments. The results of our measurements are shown in Fig. 2 (solid line).

In comparing our results to those of B & H, we should stress that our partial pressures of NO_2 are about 1000 times less than those used by B & H and that our quenching gas pressures are about a factor of ten greater. The constants α, β and ratio β/α (from Table 1 of B & H) increase as the partial pressure of NO_2 is decreased. We can obtain a conservative estimate of the predicted departure from linearity by utilizing the values of Table 1 [7] for the lowest partial pressure of NO_2 in N_2. If we use eqn. (III) of B & H to

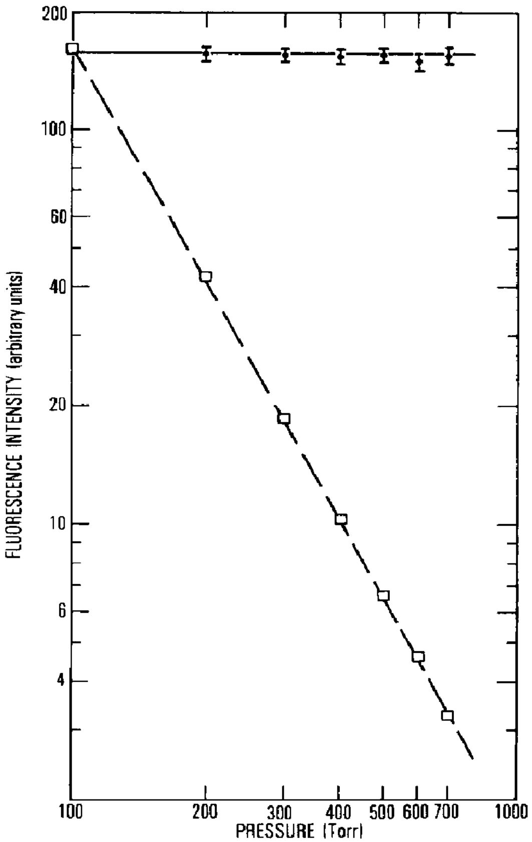

Fig. 2. Solid line shows measurements. Dashed line represents computed results using the constants given in Braslavsky and Heicklen [7].

compute the predicted fluorescence utilizing values of α and β, Table 1 (B & H) of 9.2 $Torr^{-1}$ and 15.25 $Torr^{-2}$, the broken line of Fig. 2 results. The broken line is normalized to the solid line by assuming at 100 Torr the fluorescence corresponding to that given by eqn. III (B & H) equals the measured value (solid line, Fig. 2). If account were taken of the increase in β with increased foreign gas pressure, the broken line of Fig. 2 would curve downward showing an even greater departure from the solid line. Our experiments have unambiguously demonstrated that quenching of NO_2 fluorescence by N_2 and air is accurately given by eqn. (2), and does not exhibit the non-linear quenching characteristics predicted by ref. [7]. With NO_2/air mixtures the results were similar to the solid line of Fig. 2. These tests, however, were not as extensive as the tests with NO_2/N_2.

1 A. W. Tucker, M. Birnbaum and C. L. Fincher, Appl. Opt., 14 (1975) 1418.
2 A. W. Tucker, A. B. Petersen and M. Birnbaum, Appl. Opt., 12 (1973) 2036.
3 J. A. Gelbwachs, M. Birnbaum, A. W. Tucker and C. L. Fincher, Opto-Electronics, 4 (1972) 155.
4 G. H. Myers, D. M. Silver and F. Kaufman, J. Chem. Phys., 44 (1966) 718.
5 L. F. Keyser, S. Z. Levine and F. Kaufman, J. Chem. Phys., 54 (1971) 355.
6 S. E. Schwartz and H. S. Johnston, J. Chem. Phys., 51 (1969) 1286.
7 S. Braslavsky and J. Heicklen, J. Photochem., 1 (1972/3) 203.