## Fluorescence and Radiative Lifetime Studies of Molecules Using Laser

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**Physics** 

by

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Physical Research Laboratory Navrangpura, Ahmedabad 380 009 INDIA To my Grandma, Mom and Dad

## CERTIFICATE

I hereby declare that the work presented in this thesis is original and has not formed the basis for award of any Degree or Diploma by any university or institution.

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Certified by:

Prof. Vijay Kumar Ahmedabad. Dec, 1998.

## **Statement**

The basic aim of the present work is to measure the total fluorescence and lifetime of the excited states of  $NO_2$  in the excitation region of 399 nm (the dissociation limit) to 490 nm. Also it is intended to study their pressure dependence in the context of the problem of anomalously long lifetime and the role of quenching collisions.

The study of lifetime and quenching rates of excited states of NO<sub>2</sub> are important in the understanding of kinetics of chemi-luminescence and air afterglow occuring in the atmosphere. NO<sub>2</sub> has a few low lying excited electronic states and its first electronic absorption band is highly perturbed. The fluorescence spectrum of NO<sub>2</sub> is extensive and very complicated which extends from the dissociation limit near 399 to 800 nm. The complete identification of different vibronic bands has been extremely difficult due to the complicated and irregular fluorescence band structures which are present superimposed on a broad continuum. The observed fluorescence lifetime is anomalously large as compared to the value deduced from the absorption intensity measurements. So far, study of the pressure dependence of lifetimes of different states of NO<sub>2</sub> has not been systematically carried out in the entire visible spectrum. The present study contributes towards the understanding of the different processes involved in the fluorescence of NO<sub>2</sub> in the visible region and their pressure dependence.

Employing the technique of pulsed excitation, the measurement of total fluorescence and time resolved decay of NO<sub>2</sub> were carried out from 399 to 490 nm at target gas pressures varying from 1 to 110 mTorr. For this purpose, an experimental system was designed and fabricated in the laboratory for the measurement of lifetimes in the range 0.1 to 200  $\mu$ sec.

The excitation of the target molecule was achieved using an excimer

pumped tunable dye laser in the region 399 to 490 nm. The fluorescence signal obtained after the interaction of the laser beam with the target molecule inside the fluorescence chamber was detected perpendicular to the incident laser beam path using a photomultiplier tube. The detected signal was then digitized and stored in a fast digital storage oscilloscope which was later transferred to a PC for data processing and off-line analysis.

To estimate the fluorescence decay constants, an exponential sumfitting code was used in the present analysis of fluorescence decay curves. The autocorrelation studies of the residues were carried out for all the decay curves to validate the form of decay function being fitted to the data and to confirm whether they were physically meaningful or not. To study the pressure dependence of the observed lifetime, the Stern-Volmer study was carried out to estimate the self-quenching rate constant and the zeropressure intercept. The estimated fluorescence lifetimes, self-quenching rate constants and the zero-pressure intercepts were corrected for the systematic errors. Depending on the lifetimes being measured, the most probable error involved was estimated to be as high as  $\pm$  20.2% for  $\tau \sim 1 \ \mu$ sec to  $\pm$  3.3% for  $\tau \sim 120 \ \mu$ sec. The most probable error in the estimation of quenching rate constants and zero-pressure intercept were estimated to be as high as  $\pm$  7% and  $\pm$  5% respectively.

In the total fluorescence studies of  $NO_2$ , it was clear from the excitation spectra that the overall structure was insensitive to pressure variation but the relative intensity distribution of the banded structure changes with pressure. For excitation wavelengths near the dissociation limit 399 nm, the total fluorescence intensity was nearly zero and it sharply increases above 399 nm.

The fluorescence studies carried out at different pressures clearly show that, at low pressures ( < 5 mTorr), the fluorescence decay is exponential. This component (called the static component) was seen at all wavelength

and was found to get quenched with increasing pressure. It is seen that the observed lifetime of the static component starts decreasing as the dissociation limit was approached. In this region of excitation, the variation in lifetime was pronounced with increase in pressure. At higher pressures ( $\geq 5$  mTorr), the fluorescence decay was non-exponential at several excitation wavelengths with lifetime varying between 120  $\mu$ sec to 1  $\mu$ sec. The frequency of occurrence of the short components (1 to 4  $\mu$ sec) were found to increase with pressure. With increase of pressure, it was found that these components also get quenched. Along with these lifetime components, a very short fluorescing component ( $< 10^{-7}$ sec) has been observed in the predissociation region and above.

The Stern-Volmer study of the static components was carried out in the entire excitation region. The Stern-Volmer plots were generally found to be non-linear with an upward curvature at the lower pressures. As the the predissociation region was approached, the fluctuations in the estimated valued self-quenching rate constant and zero-pressure intercept were found to increase.

The organization of this thesis is as follows. The subject of radiative and non-radiative processes in a molecule has been introduced in Chapter 1 in terms of lifetime of an excited state, followed by the discussion on the transition probabilities for these transitions to occur. This includes the discussion on the nature of electronic transitions in polyatomic molecules and the different interaction processes involved in an electronic transition. The possible schemes for anomalously long lifetime observed in certain molecules has been briefly explained. The need for lifetime studies and a brief survey of different experimental techniques for measurement of lifetime also have been discussed in Chapter 1.

A detailed discussion about the experimental setup using the pulsed excitation technique to measure the lifetime of an excited state of a molecule has been presented in Chapter 2. The type of analysis carried out to analyse the measured lifetime data and the various mathematical tools used in this analyse have been discussed in Chapter 3. An extensive discussion of the sources of systematic errors in the estimation of lifetime, selfquenching rate constants and zero-pressure interscept has been included in Chapter 4. The results obtained in the present study of total fluorescence and lifetime measurements have been discussed in detail in Chapter 5 and compared with the results reported in the literature by other workers wherever possible. In the last chapter, the conclusion of the present experimental study and the scope for future work have been discussed.

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# Contents

CERTIFICATE	i
STATEMENT	ii
ACKNOWLEDGEMENTS	vi
1 Introduction	1
1.1 Einstein Transition Probabilities	1
1.2 Transition Probability and Lifetime	4
1.3 Absorption and Emission of Radiation	6
1.3.1 Absorption Coefficient and Line Broadening	6
1.3.2 Fluorescence and Quenching	8
1.4 Electronic Transition in Molecule	10

	1.4.1 Potential Energy Surface and Their Representation	11
	1.4.2 Intensity of Vibrational and Rotational Transition	13
	1.4.3 Selection Rules	14
	1.4.4 Breakdown of Born-Oppenheimer Approximation	15
1.5	Radiative and Non-Radiative Transitions - Lifetime	17
1.6	Photodissociation and Predissociation	20
1.7	Anomalously Long Lifetime in Polyatomic	
	Molecules	21
1.8	Need for Lifetime Measurement	23
1.9	Measurement of Lifetime Using Laser	25
	1.9.1 Phase Shift Technique	25
	1.9.2 Delayed Coincidence Method	26
	1.9.3 Pulsed Excitation Technique	28
1.10	DReview of Spectral and Theoretical Information of NO $_2$ Molecule	e 29
Exp	perimental Setup	33
2.1	Sources of Excitation	35

2

		2.1.1 Excimer Laser	36
		2.1.2 Dye Laser	37
	2.2	Beam Expansion and Folding Optics	38
	2.3	Beam Splitter	39
	2.4	Fluorescence Chamber	40
	2.5	The Vacuum System	41
	2.6	Pressure Measurement System	41
	2.7	Gas Handling System	43
	2.8	Light Collection Optics	43
	2.9	Photon Detection System	44
		2.9.1 Photodiode	44
		2.9.2 Photomultiplier Tube	45
	2.10	Data Acquisition System	48
3	Met	hod and Analysis	50
	3.1	Fluorescence Excitation Spectra (FEX)	50
	3.2	Fluorescence Lifetime Measurement	51

3.3	Self Quenching Rate Constant	55
3.4	Mathematical Tools	57
	3.4.1 Exponential Sum Fitting Method	57
	3.4.2 Residual Autocorrelation Study	60
	3.4.3 Least Square Fitting	63
4 Erre	or Analysis	67
4.1	Observation Geometry	67
4.2	Bandwidth of Detection Electronics	69
4.3	Digitization Error	70
4.4	Baseline Estimation	70
4.5	Time Base	71
4.6	$NO_2 \rightleftharpoons N_2O_4$ Equilibrium Constant $\ldots \ldots \ldots \ldots \ldots \ldots$	71
4.7	Thermal Transpiration Correction	73
	4.7.1 Thermal Transpiration Effect	74
4.8	Error in Lifetime Measurement	77

	4.9	Error in Self Quenching Rate Constants and Zero-Pressure intercept	. 77
5	Res	sults and Discussion	79
	5.1	Fluorescence and Lifetime Study	. 79
		5.1.1 Excitation Region 465-490 nm	. 79
		5.1.2 Excitation Region 423-462 nm	. 84
		5.1.3 Predissociation Region 399-416 nm	. 89
	5.2	Quenching Studies in the Region 399-490 nm	. 93
6	Cor	clusions And Scope For Future Work	120
	6.1	Conclusions	. 120
	6.2	Scope for Future Work	. 123
Li	st of	f Publications	126
R	efere	ences	127

# **Chapter 1**

# Introduction

Studies of emission spectra for molecules are influenced by the lifetimes of the excited states which depend on the transition probability associated with the respective molecular transition. A measurement of these excited state lifetimes yield the information about the radiative and non-radiative transition probabilities. For example, the spontaneous transition probability for radiative transitions can be estimated from the measurement of the fluorescence lifetime of an excited state. The different transition probabilities and the lifetimes involved in these transitions are discussed below for a two level system which holds good even for the polyatomic molecules.

## **1.1 Einstein Transition Probabilities**

The absorption and emission of radiation by atoms or molecules may be treated by the perturbation of an electric dipole of the system by an external electric field of radiation. Let us consider a two level system with quantized energies  $E_m$  and  $E_n$  ( $E_m > E_n$ ) in a radiation field of density  $\rho(\nu)$  which is in thermal equilibrium. There are three possible processes that

can change the state of the system from  $E_m \rightarrow E_n$  or  $E_n \rightarrow E_m$ . They are induced absorption, spontaneous and stimulated emission as illustrated in Figure 1.1.



Figure 1.1: Absorption and emission processes in a two level system in thermal equilibrium with the radiation field.

Induced absorption results from the presence of the radiation field  $\rho(\nu_{nm})$  needed to make a transition from ground state to the excited state. The probability per second that a molecule will absorb a photon,  $dP_{nm}/dt$  is proportional to the number of photons of energy  $h\nu$  ( $h\nu = E_m - E_n$ ) per unit volume expressed as

$$\frac{d}{dt}(P_{nm}) = B_{nm}\rho(\nu_{nm}) \tag{1.1}$$

The constant factor  $B_{nm}$  is called the Einstein coefficient of absorption.

If at thermal equilibrium  $N_n$  and  $N_m$  are the population densities of levels  $E_n$  and  $E_m$  respectively, the rate equation for absorption is written as

$$\frac{dN_m}{dt} = N_n B_{nm} \rho(\nu_{nm}) \tag{1.2}$$

Similarly if the system is already in an excited state, then a photon  $h\nu_{nm}$  provided by  $\rho(\nu_{nm})$  can induce the system to make a transition to the ground state. The probability dPmn/dt that one molecule emits one

induced photon per second is expressed as

$$\frac{d}{dt}(P_{mn}) = B_{mn}\rho(\nu_{nm})$$
(1.3)

where  $B_{mn}$  is known as Einstein coefficient of induced emission and the rate equation in terms of population density is given as

$$\frac{dN_m}{dt} = -N_m B_{mn} \rho(\nu_{nm}) \tag{1.4}$$

Finally, the system in the excited state can spontaneously emit a photon in the absence of the external field.

$$\frac{d}{dt}(P_{mn}^{spont}) = A_{mn} \tag{1.5}$$

where  $A_{mn}$  is called the Einstein coefficient of spontaneous emission, often called as spontaneous transition probability. In terms of population density of the excited state it can be written as

$$\frac{dN_m}{dt} = -N_m A_{mn} \tag{1.6}$$

Since this system is in thermal equilibrium, one can write

- - -

$$N_n \rho(\nu_{nm}) B_{nm} = N_m \rho(\nu_{nm}) B_{mn} + N_m A_{mn}$$
(1.7)

Using the Boltzmann expression in (1.7), rearranging terms and comparing with the Planck formula for radiation, one can derive the following relations

$$A_{mn} = \frac{8\pi h \nu_{mn}^3}{c^3} B_{mn}$$
(1.8)

$$B_{mn} = B_{nm} \tag{1.9}$$

where h is the Planck constant and c is the velocity of light.

Here the  $\nu^3$  factor plays an important role in the competition between the induced and spontaneous emission process. Since these coefficients are the intrinsic properties of the levels, the above relations are also valid when the system is not in thermal equilibrium (for example, in pulsed excitation of the molecule).

### **1.2 Transition Probability and Lifetime**

For an excited state molecule decaying spontaneously with emission of photons from the level  $E_m$  to a lower level  $E_n$ , the rate equation is given by equation (1.6) relating Einstein coefficient  $A_{mn}$  for a two level system. If the transition from  $E_m$  is to a manifold of lower levels in  $E_n$  (including ground state), the total spontaneous transition probability is given as

$$A_m = \sum_n A_{mn} \tag{1.10}$$

Integrating equation (1.6), we have

$$N_m(t) = N_{m0} e^{-A_m t}$$
(1.11)

where  $N_{m0}$  is the population density at t = 0. After a time  $\tau = 1/A_m$ , the population  $N_m$  will decrease by 1/e of its initial value at t = 0. This value of time  $\tau_m$  is the mean spontaneous lifetime of the level  $E_m$ . This definition can be realized from the concept of average time  $\tilde{t} = 1/A_m = \tau_m$ .

Apart from spontaneous emission, the level  $E_m$  can be depopulated by collision induced radiationless transitions as well. The probability of such a transition depends on the density  $N_B$  of a collision partner B and on the mean relative velocity  $\tilde{v}$  between the molecule to the collision partner and on the collision cross section  $\sigma_{mn}^{coll}$  for an inelastic collision and is given by

$$\frac{d}{dt}P_{mn}^{coll} = \tilde{v}N_B\sigma_{mn}^{coll}$$
(1.12)

When the excited molecule is left to an intense radiation field, the induced emission may become noticeable. Its contribution to the depopulation of level  $E_m$  is given by

$$\frac{d}{dt}P_{mn}^{ind} = B_{mn}\rho(\nu_{mn})\left[N_m - \frac{g_m}{g_n}N_n\right]$$
(1.13)

where  $g_m$  and  $g_n$  are the degeneracies of  $E_m$  and  $E_n$  respectively. So the total transition probability which determines the effective lifetime of a level  $E_m$  is then the sum of spontaneous, induced and collisional contribution and the mean (effective) lifetime is given as

$$\frac{1}{\tau_m^{eff}} = \sum_n \left[ A_{mn} + B_{mn} \rho(\nu_{mn}) \left( N_m - \frac{g_m}{g_n} N_n \right) + \tilde{v} N_B \sigma_{mn}^{coll} \right]$$
(1.14)

Here one can note that the effective deacy rate is the sum of the total radiative decay rate and the non-radiative (collisional) decay rate.

Hence it is evident from the above equation that the effective lifetime of a state can be written as sum of radiation and collisional lifetime

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_m^{rad}} + \tilde{v} N_B \sigma_{mn}^{coll}$$
(1.15)

For maxwellian velocity distribution,  $\tilde{v}$  can be written as

$$\tilde{v} = \sqrt{\frac{8kT}{\pi\mu}}$$

where k is Boltzmann constant and  $\mu$  is reduced mass of the colliding partners.

Using the thermodynamic equation  $P = n \times kT$ , we can rewrite the above equation as

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_m^{rad}} + bP\sigma_{mn}^{coll}$$
(1.16)

where

$$b = \sqrt{\frac{8}{\pi \mu k T}}$$

This equation is known as Stern-Volmer equation. A plot of  $1/\tau_{eff}$  versus P gives a straight line with slope =  $b\sigma_{mn}^{collo}$  and y-intercept gives the collisionless radiative lifetime. Such a plot is known as the Stern-Volmer plot.

### **1.3 Absorption and Emission of Radiation**

### **1.3.1 Absorption Coefficient and Line Broadening**

When a beam of radiation with frequency  $\nu$  and initial intensity  $I_0$  is passed through a medium of length l, a fraction dI/I is absorbed by the medium. The strength of absorption is characterized by the absorption coefficient  $\alpha(\nu)$  and the absorption can be written as

$$dI = -\alpha(\nu)Idl \tag{1.17}$$

If the absorption process is linear ( $dI \propto I$ ) for a constant  $\alpha$ , we have

$$I(l) = I_0 e^{-\alpha(\nu)l}$$
 (1.18)

In the process of absorption of radiation by a molecule, the absorbed radiation is converted into the internal energies - *viz*. electronic, vibrational or rotational energies. Total radiation power 'W' absorbed per unit volume for a given transition, say  $E_n \rightarrow E_m$ , can be written as

$$\frac{dW_{nm}}{dt} = \int \alpha(\nu_{nm})I(\nu_{nm})dt = I(\nu_{nm})\int_0^\infty \alpha(\nu_{nm})d\nu$$
(1.19)

In terms of the Einstein coefficient for absorption  $B_{nm}$ , the rate of absorption can be written as

$$\frac{dW_{nm}}{dt} = N_n B_{nm} \hbar \nu_{nm} \rho(\nu_{nm})$$
(1.20)

From equations (1.19) and (1.20), the integrated absorption coefficient can be written as

$$\int_0^\infty \alpha(\nu_{nm})d\nu = N_n \frac{\hbar}{c} \nu_{nm} B_{nm}$$
(1.21)

Again,  $B_{nm}$  is related  $A_{nm}$  (equation 1.8), the spontaneous transition probability. Hence knowing the integrated absorption coefficient for a given transition, one can determine the spontaneous transition probability and hence the mean lifetime of the excited state involved in the transition.

In the process of absorption, the transitions take place between the discrete levels in accordance with the uncertainty principle,  $\Delta E \Delta t \sim \hbar$ . This uncertainty in time is a measure of the mean lifetime  $\tau$  of the excited state. The corresponding frequency spread for this state m is then given by

$$\delta\nu_{nm} \approx \frac{1}{2\pi\tau_m} \tag{1.22}$$

This is known as the natural line broadening which has a Lorentzian line shape in the absorption process for a transition. Hence the measurement of natural line width of a spectral line provides an estimate of the lifetime of the corresponding excited state with respect to the lower energy state involved in the emission process.

When the pressure of the gas is low, the natural line broadening gives a spread in energy absorbed. If the gas pressure is high, the spread in energy is further increased due to the collisions between the gas molecules called the collisional or pressure broadening. This increase in broadening is due to the collisional interactions of the molecule, whose excited state gets modified due to the formation of a quasi-molecule with the collision partner (Mitchell and Zemansky (1961)). This spread in energy is given by

$$\Delta \nu_{press} = \frac{1}{2\pi} \left( \frac{1}{\tau_m} + \frac{2}{t_c} \right) \tag{1.23}$$

where  $\tau_m$  is the natural lifetime of this excite state and  $t_c$  is the mean time between collisions. The shape of the profile is again Lorentzian as in the case of natural line broadening. These broadening processes are homogeneous in nature as they do not depend on inhomogenity factors such as the velocity distribution of the absorbers/emitters and the ambient temperature of the system.

#### **1.3.2 Fluorescence and Quenching**

The electronically excited molecules formed by the absorption of photon can undergo spontaneous transitions to various lower levels of the system with an emission of light (fluorescence). In gas phase, when the number density of the gas is increased, the fluorescence emitted from the excited state gets quenched by the ground state molecules as well as by foreign gas molecules. Assuming the steady state condition and a weak absorption ( $I_a \sim I_o \alpha l$ ), the quenching reaction for excited molecules A<sup>\*</sup> can be written as

$$\begin{array}{cccc} A & \xrightarrow{h\nu} & A^* \\ A^* & \xrightarrow{k_f} & A + h\nu' \\ A^* + A & \xrightarrow{k_q} & A + A \\ A^* + M & \xrightarrow{k_m} & A + M \end{array}$$

where  $k_f$  is the fluorescence rate constant and  $k_q$  and  $k_m$  are the self quenching rate constant and the quenching rate constant (M is a non-absorbing foreign gas molecule). Here the concentration of the excited molecule in terms of the absorbed intensity  $I_a$  can be written as

$$I_{a} = k_{f} [A^{*}] + k_{q} [A^{*}] [A] + k_{m} [A^{*}] [M]$$
(1.24)

Quenching is defined as the ratio of emitted fluorescence intensity to the total incident intensity, *i* $\dot{e}$   $Q = I_f/I_o$ . Also, the fluorescence intensity  $I_f = k_f[A^*]$ . Thus we have

$$Q = \frac{I_f}{I_O} = \frac{k_f [A^*]}{I_a / \alpha l}$$
(1.25)

Substituting the equation (1.24) in the above expression and rearranging the terms, we get

$$\frac{1}{Q} = \alpha l \left[ 1 + \frac{k_q}{k_f} [A] + \frac{k_m}{k_f} [M] \right]$$
(1.26)

The terms  $k_q/k_f$  and  $k_m/k_f$  are the quenching constants for self quenching and quenching by a foreign molecule M respectively. The equation (1.11) can be written in terms of fluorescence intensity emitted by a excited state as

$$I_f(t) = I_0 e^{-\tau_{eff} t}$$
(1.27)

where  $\tau_{eff}$  is the effective observed fluorescence lifetime of the excited state. Using equation (1.15), the above equation modifies to

$$I_{f}(t) = I_{0}e^{-\{k_{f}+k_{q}[A]+k_{m}[M]\}t}$$
(1.28)

Hence from the observed intensity of fluorescence  $I_f(t)$  as a function of decay time after a pulsed excitation, the fluorescence rate constant and the quenching rate constants can be determined. If the concentration of the target molecule is large, the fluorescence emitted by the excited molecule  $A^*$  can be absorbed again by the molecule in the ground state A and this process gets repeated many times. The repeated process of emission and absorption is called radiation trapping. It lengthens the observed lifetime. In this case, where radiation trapping does occur, the observed fluorescence decay could be written as

$$I_f(t) = I_0 e^{-\{gk_f + k_q[A] + k_m[M]\}t}$$
(1.29)

where g is a factor dependent on the strength of radiation trapping, with (g < 1). Hence the fluorescence lifetime  $1/k_f$  gets modified to  $1/gk_f$ (Blickensdefer *et al* (1976)).

### **1.4 Electronic Transition in Molecule**

In a molecule, the electronic states are quantized states of energy describing the motion of the electrons and their coulombic interaction. The total energy of the molecule is then the sum of the kinetic energy of the electrons and nuclei plus the potential energy. The Schrödinger wave equation for a molecule is given by

$$\hat{H}\Psi(R,r) = E\Psi(R,r)$$
(1.30)

where  $\Psi$  is the total wave function of the molecule and the Hamiltonian is given as

$$\hat{H} = -\sum_{n} \frac{\hbar^{2}}{2M_{n}} \nabla_{n}^{2} + \sum_{e} \frac{\hbar^{2}}{2m_{e}} \nabla_{e}^{2} + V(R, r)$$
(1.31)

Here V(R, r) is the sum total of potential energy between electron-electron, nuclei-nuclei and electron-nuclei interaction. This represents a manybody problem coupled to the nuclear motion. It is extremely difficult to solve this equation taking into account the coupling of rotation, vibrational and electronic motions. If the frequencies of the three kinds of motions are widely apart, then the motions may be considered separately in a zero order approximation (condition of adiabaticity). Here one can write the zero-order solution for the rotation and vibration of an isolated molecule in terms of a rigid and harmonic oscillator respectively and apply the second order perturbation theory to describe the result of coupling the rotation and vibration of the molecule. The motions of electrons in the molecule are faster than the motion of the nuclei and hence one can freeze the nuclei at some inter-nuclear spacing and calculate the total electronic energy for this spacing. The calculation can be repeated for different spacing and the intra-molecular potential energy can be computed. The sum of the total electronic energy and the intra-molecular potential energy as a function of inter-nuclear distance gives the potential curve (or potential energy surface) which govern the vibrational motion of the nuclei. This approximation wherein the nuclei are regarded as stationary and the

energy of a particular electronic state is calculated for different relative positions of the nuclei is known by Born-Oppenheimer approximation (B-O approximation). Here the overlap between the electronic and nuclear wave function is neglected or the electronic states are considered to be adiabatic states. Thus the total wave function of the molecule is written as  $\Psi = \psi_e \psi_n$ where  $\psi_e$  and  $\psi_n$  are the electronic and nuclear wave functions and further  $\psi_n = \psi_v \psi_r$  (vibration and rotation motion). The total energy of the state is the sum of electronic, vibrational and rotational energy,  $ie \ E = E_e + E_v + E_r$ .

#### **1.4.1** Potential Energy Surface and Their Representation

In diatomic molecules, the potential energy curve (P.E. curve) of a particular electronic state is a two dimensional curve of potential energy  $U(R-R_e)$  versus the inter-nuclear distance  $(R - R_e)$ , where  $R_e$  is the point of equilibrium. In the case of triatomic (and polyatomic molecules), the representation of the potential energy of any electronic state becomes potential surfaces (or hypersurfaces) since they are represented in 3N-5 (3N-4 for linear molecules) dimensional space (where N is the number of nuclei in the molecule). In the case of diatomic molecules, depending on the nature of the P.E. curve, we have the bound state and the repulsive state represented by a Morse function. For a state to be bound, the P.E. curve should have a well defined minimum, where the force,  $F = -\nabla V = 0$ defines the point of equilibrium. But in the case of P.E. surface of polyatomic molecules, it is highly complicated to visualize this picture. Figure 1.2 shows a simple example of a triatomic potential energy surface for the He-CO van der Waals molecule.

The electronic states of diatomic molecules are denoted by the orbital angular momentum  $\Lambda$ , the total spin *S* and total angular momentum  $\Omega =$  $|\Lambda + S|$  and are spectroscopically written as  ${}^{2s+1}\Lambda_{\Omega}$  where 2s + 1 is the spin multiplicity and  $\Lambda = 0, \pm 1, \pm 2$ , the total angular momentum denoted as



Figure 1.2: The He-CO potential energy surface as a function of the radial distance R of the He atom from the center of mass of the CO molecule, and the angular position  $\theta$  of the He atom relative to the CO internuclear axis. The origin at 0° represents a colinear He-CO geometry

 $\Sigma, \Pi, \Delta$  respectively. In polyatomic molecules, the representation is done on the basis of the symmetry operators,  $C_p$  - the rotation about axis of symmetry,  $\sigma$  the reflection about a plane of symmetry, *i*, the inversion through a centre of symmetry with a rotation about an axis followed by reflection in plane perpendicular to it and *I* is the identity operator. The wave function when subjected to these symmetry operations can change the sign or remain unchanged which is defined by the point group the molecule belongs to. Each electronic state thus belongs to a certain point group with well defined symmetry property. An electronic eigenfunction can change sign on reflection at the symmetry plane or remain unchanged. For a  $\Sigma$  state, if the eigenfuction changes sign on reflection at the symmetry plane, it is denoted as  $\Sigma^-$  else denoted as  $\Sigma^+$  state. Diatomic molecules have an additional symmetry, called centre of symmetry. If the eigenfunction of the molecule does not change sign when the electronic coordinates x, y, z are replaced by -x, -y -z, the corresponding state is called even state and is denoted by a subscript g. If the eigenfunction of a state changes sign it is called odd state denoted by a subscript u. For example, the  $\Sigma$  state of a

molecule is denoted as  $\Sigma_g^+$  or  $\Sigma_u^-$ .

The NO<sub>2</sub> molecule ground state belong to  ${}^{2}A_{1}$  irreducible representation. The ground electronic state is denoted by  $\tilde{X}^{2}A_{1}$ . The NO<sub>2</sub> molecule belongs to the  $C_{2v}$  point group where it has got two-fold axis of symmetry about the z axis and two symmetry planes yz and xz through the symmetry axis as shown in Figure 1.3.



Figure 1.3: The ground state structure of NO<sub>2</sub> which belong to  $C_{2v}$  point group.

#### 1.4.2 Intensity of Vibrational and Rotational Transition

From the Born-Oppenheimer approximation, the total wave function can be written as

$$\Psi = \psi_e \psi_v \psi_r \tag{1.32}$$

For a transition between two electronic states, say m and n, the dipole moment operator  $\hat{M}(=\hat{e}.\vec{r})$  can be written as the sum of nuclei, electronic contribution.

$$M = M_e + M_n \tag{1.33}$$

where the total dipole transition moment  $R_{mn}$  is written as

$$R_{mn} = \int \psi_m^* M \psi_n d^3 r \tag{1.34}$$

Under the adiabatic approximation, the  $R_{mn}$  can be re-written as

$$R_{mn} = R_e^{mn} + R_v^{V_m V_n} + R_r^{J_m J_n}$$
(1.35)

where  $R_v^{V_m V_n}$  is called the Franck-Condon factor and  $R_r^{J_m J_n}$ , the line strength.

The intensity distribution for the transition in molecule between vibrational levels of two different electronic state is given by  $|R_v^{V_m V_n}|^2$ . The Franck-Condon factor which is the overlap integral of the vibration wave function is given as

$$R_{mn}^{V_m V_n} = \int \psi_{v_m}^* M \psi_{v_n} d^3 r_v$$
 (1.36)

According to Franck-Condon (Franck (1925) and Condon (1928)), during an electronic transition, the transition probability for any vibrational level in the ground electronic state to any of the vibrational levels in the excited electronic state is maximum for vibrational transition which involves very small or negligible change in the inter-nuclear distance. This is known as the Franck-Condon principle. This is again true for transition from an excited to ground state characterizing the intensity distribution of the fluorescence spectra of the molecule. The term  $|R_r^{J_m J_n}|^2$ , called line strength is also called the Hönl-London factor (Kovac (1962)) as it gives the probability for a transition from a rotational level  $J_m$  belonging to a vibrational level  $v_m$  of the excited state. These transition probabilities can be calculated from a set of formulae (Hönl-London) which depend on the symmetry of the rotational levels involved.

### 1.4.3 Selection Rules

The selection rules for electronic, vibrational and rotational transition in a molecule are derived from the properties of the transition moment  $R_e^{mn}$  given as

$$R_e^{mn} = \int \psi_m M \psi_n d^3 r \tag{1.37}$$

For an electronic transition, the transition moment  $R_e^{mn}$  should be different from zero for allowed transitions; otherwise it is known as forbidden transition. The nature of the transition is dependent on the symmetry properties of the wave function involved in the transition. This means that  $\psi_m$  and  $\psi_n$  must belong to the same symmetry group as M and should be symmetric for all symmetry operations allowed for the point group to which the molecule belongs. For example, NO<sub>2</sub> belongs to the point group  $C_{2v}$ , and the corresponding symmetry species are  $A_1$ ,  $B_1$  and  $B_2$ . Hence for allowed transition in the point group  $C_{2v}$ , the product of  $\psi_m$  and  $\psi_n$  must belong to  $A_1$ ,  $B_1$  or  $B_2$  states. If the ground state is  $A_1$ , transitions to  $B_1$ and  $B_2$  only are allowed. In some case, the symmetry forbidden transition becomes allowed (breakdown of B-O approximation) if there is vibronic interaction between different electronic state as there in formaldehyde,  $SO_2$ and  $NO_2$ . Under the B-O approximation, the transition between vibrational levels of different electronic states must follow the rule that  $\psi_n^m \psi_n^n$ must be symmetric with respect to all symmetry operations assuming that electronic transitions are allowed. However, the selection rule of spin multiplicity, as in diatomic molecule, is also valid for polyatomic molecules.

#### 1.4.4 Breakdown of Born-Oppenheimer Approximation

Under Born-Oppenheimer approximation, the exchange energy between electronic and nuclei motion is neglected or the electronic states are considered to be adiabatic states. But in molecules like  $SO_2$ ,  $NO_2$ ,  $C_6H_6$ , it is seen that there are transitions which occur due to the mixing of vibrational and electron motions which no longer can be explained under the above approximation. The different coupling schemes of vibrational and electron motions are discussed below.

#### **Herzberg-Teller Effect (Vibronic Coupling)**

Due to non-symmetric (asymmetric stretch) vibration, transitions occur in an electronic transition which are normally forbidden for electric dipole approximation. These transitions are in general very weak. For example, in  $C_6H_6$ , the  $\tilde{A} - \tilde{X}$  transition is a forbidden transition which becomes allowed by vibronic coupling and was first explained by Herzberg and Teller (Herzberg (1966) and Fischer (1984)). This effect is a case of breakdown of B-O approximation since the vibrational motion and the electronic degree of freedom get mixed and therefore, are no longer separable. For these transitions, the transition moment is given in terms of the vibronic symmetry. If the vibronic symmetry of the ground state, excited state and the transition moment are same, the transition moment integral is non zero. Provided that the vibrational and electronic degrees of freedom are mixed and cannot be factorized, these transitions are vibrationally allowed as in the case of  $C_6H_6$   $\tilde{A} - \tilde{X}$  transition. The intensity of a vibronic transition depends on the degree of mixing of vibrational and electronic motion.

#### **Jahn-Teller Effect**

This effect arises for non-symmetric vibration in an electronic transition of only bent molecules. Jahn and Teller (1937) proved that any nonlinear molecule in an orbitally degenerate electronic state will always distort in such a way as to lower the symmetry and remove the degeneracy. For non-singlet molecules, spin-orbit coupling competes with Jahn-Teller effect since spin-orbit splitting also lifts orbital degeneracies independently of Jahn-Teller effect. This is again the mixing up of vibrational and electronic motions as in vibronic coupling which is the breakdown of Born-Oppenheimer approximation. If the electronic wave functions are linearly independent, orbitally degenerate, then their degeneracy is lifted when the transition moment matrix element is non-zero. This effect is not seen in linear molecules for which undistorted, orbitally degenerate states are possible. For example, Jahn-Teller effect is seen in  $C_6F_6$  cation.

#### **Renner-Teller Effect**

Linear molecules are not subjected to Jahn-Teller effect, but they do experience vibronic coupling which is known as the Renner-Teller effect (Herzberg (1966), Fischer (1984)). The Renner-Teller effect is due to the interaction of the vibrational and electronic angular momenta in a linear molecule. The levels associated with bending modes are shifted in energy by an interaction that couples the vibrational and electronic motion for state for which  $\Lambda \neq 0$  (breakdown of Born-Oppenheimer approximation). This effect occurs because the double degeneracy of the linear molecule is lifted by the bending mode of vibrational motions which combines up with the electronic motions in the molecule mixing with the zeroth order vibrational and electronic wave functions. This effect is seen in SO<sub>2</sub> and NO<sub>2</sub>. In NO<sub>2</sub>, the <sup>2</sup>B<sub>1</sub> (linear state) couples with the <sup>2</sup>A<sub>1</sub> ground state through Renner-Teller effect which in fact influences the lifetime of the <sup>2</sup>B<sub>1</sub> excited state.

# 1.5 Radiative and Non-Radiative Transitions -Lifetime

A molecule in an excited electronic state can decay to the lower electronic state either by emission of a photon (radiative) or by other mechanism (non-radiative). If  $k_r$  and  $k_{nr}$  are the rate constants for radiative and non-radiative processes respectively, then the net rate constant for the excited

electronic state to decay is given by

$$k_{net} = k_r + k_{nr} \tag{1.38}$$

Then the net lifetime of the excited electronic state can then be written as

$$\tau_{net}^{-1} = \tau_r^{-1} + \tau_{nr}^{-1} \tag{1.39}$$

where  $\tau_r$  and  $\tau_{nr}$  are the decay time for the radiative and non-radiative processes respectively. These radiative and non-radiative processes are best illustrated in the form of state diagram commonly referred as Jablonski diagram (Figure 1.4). Here the ground state is singlet  $S_0$  and the excited singlet states are  $S_1$ ,  $S_2$ , ....with increasing energy.



Figure 1.4: Jablonski diagram showing various radiative and non-radiative processes in a large molecule.

In the electronic absorption transition in a molecule, the absorption occurs from various vibrational and rotational levels of the ground electronic state populated according to Boltzmann distribution. For many simple molecules it is assumed that only the zero-point level has significant population at room temperature which is not valid for polyatomic molecules with low-frequency vibrations. At high pressure, the molecule which is excited to one of the vibrational level of the upper excited state can undergo collisions before electronic relaxation can occur. In this process the excess vibrational energy is quickly lost and relaxes to the zero-point level of that excited state. This process is termed as vibrational relaxation. The emission from this zero-point level to the different vibrational level of the ground state is termed as normal fluorescence (referred as fluorescence ( $S_1 \rightarrow S_0$ ) in Figure 1.4). This process is seen in polyatomic molecules of large level density. If the emitted photon has the same energy as the absorbed photon then the process is termed as resonance fluorescence. This is seen in simple molecules at low pressure. The electronically excited molecules may not undergo collision in its excited state which is thus said to be isolated. Hence the emission occurs from the initially populated level when the time period of collision is larger than the decay time of the excited state.

An excited molecule can make a transition to a lower lying state of different multiplicity (singlet to triplet). This process is a non-radiative process occurring between electronic energy manifold of the different multiplicity and is known as intersystem crossing ( $S_1 \rightarrow T_1$ ). The emission from the triplet state  $T_1$  to the ground state coupled by the spin-orbit interaction is generally weak and is called the phosphorescence. Typically, phosphorescence has a lifetime of millisecond to seconds for large molecules.

An excited molecule can non-radiatively decay to high vibrational levels of the ground state. This non-radiative  $S_1 \rightarrow S_0$  process occurring between electronic energy manifold of the same multiplicity is known as internal conversion. The process of internal conversion in an isolated gas phase molecule can only occur because of high density of vibrational levels.

## **1.6 Photodissociation and Predissociation**

When a molecule is excited by a photon of energy greater than the bond energy of the molecule, the main process is either the complete dissociation (photodissociation) or the simultaneous occurrence of fluorescence and dissociation (predissociation). If the excited state of the molecule is a bound state, the molecule can undergo dissociation at the convergence limit of the upper state. If the upper state is a repulsive state, it can dissociate into product fragments.

In some molecules like SO<sub>2</sub>, NO<sub>2</sub>, etc., there is simultaneous occurrence of fluorescence and dissociation well below the dissociation limit and is referred as predissociation. Consider a molecule which is excited to a bound upper electronic state. If the molecule in this upper electronic state can undergo a transition to another electronic state whose potential curve is repulsive, the molecule will ultimately decay with a rate that depends on the coupling between these two electronic states. The final dissociation would take place in the repulsive electronic state rather than the one originally excited by the photon. This process is called electronic predissociation or Herzberg's type I predissociation (Herzberg (1966)). This process is illustrated in Figure 1.5 (a) where the excited molecule A undergoes a radiationless transition (rt) to the repulsive state R with subsequent decay.

If the upper electronic state *A* has an avoided crossing with a higher electronic state, the potential of *A* gets modified and has a well at close distance and a barrier that blocks the dissociation channel as illustrated in Figure 1.5 (b). In this case, the excited molecules which are inside the well are prevented from immediate dissociation by the potential barrier. They can decay either by tunneling (tu) the barrier or by internal vibrational energy re-distribution (IVR) between the various nuclear degrees of freedom if the molecule is polyatomic in nature. This process is referred as vibrational predissociation or Herzberg's type II predissociation



Figure 1.5: Schematic illustartion of (a) electronic and (b) vibrational predissociation.

(Herzberg (1966)).

In NO<sub>2</sub>, the electronic predissociation has been observed by Douglas and Huber (1965) near 397.9 nm. They recorded an onset of diffuseness of rotational band at 397.9 nm and the fluorescence of NO<sub>2</sub> gradually weakening below 420 nm and completely disappearing at 397.9 nm.

# 1.7 Anomalously Long Lifetime in Polyatomic Molecules

It is found that in molecules like  $CS_2$ ,  $SO_2$  and  $NO_2$ , the observed fluorescence lifetimes are much longer than those expected from the integrated absorption coefficient (section 1.3). In these molecules the rotational and vibration levels are generally perturbed exhibiting a complex absorption and fluorescence spectra in the UV and visible region. This discrepancy in lifetime of excited state is called lifetime anomaly and was first explained by Douglas (1966) on the basis of interelectronic level mixing. This process is illustrated in Figure 1.6.



Figure 1.6: Schematic illustration of the mechanism for inter-electronic mixing.

Consider a molecule for which the transition between the state  $\tilde{B}$  and  $\tilde{X}$  is fully allowed but there is little or none between  $\tilde{A}$  and  $\tilde{X}$  state. If there is an interaction between  $\tilde{A}$  and  $\tilde{B}$  state which may be vibronic, Coriolis or spin-orbit interaction, the B state may mix with A state depending on the density of vibrational levels associated with  $\tilde{A}$  and  $\tilde{B}$  state. This mixing does not alter the integrated absorption coefficient of the  $\hat{B}$  -  $\hat{X}$  system, but introduces a large number of extra levels which can be reached by excitation from the ground level. The interaction between the levels of A and  $\hat{B}$  state is a vibrational-electronic or a rotational-vibrational-electronic interaction which allows a particular level of *B* to interact with many levels of the A state. If the densities of levels in the A and B state are equal, the interaction may be equivalent to purely electronic interaction. If the level density of  $\tilde{A}$  state is much higher than that in  $\tilde{B}$ , then it is possible to dilute each of the levels of  $\hat{B}$  with many levels of  $\hat{A}$ . If the perturbing state has a high density of suitable vibrational levels and the interaction energy is large compared to the distance between these levels, the lifetime of the perturbed level is influenced. The degree of influence in lifetime depends upon the characteristics of  $\tilde{A}$  and  $\tilde{B}$  states and on the magnitude of the
interaction between them. If the interaction is less strong and varies with the rotational and vibrational quantum number of the excited state, the lifetimes of even closely spaced levels may differ. Under these conditions, the observed fluorescence decay obtained with a narrow band of radiation, will be non-exponential due to the mixing up of various lifetimes. Also if the different symmetry of  $\tilde{B}$  state is excited and its interaction with  $\tilde{A}$  is not similar, then a wide range of lifetime may be observed.

In NO<sub>2</sub> gas, the observed lifetime is two order more than that calculated from the integrated absorption coefficient. Therefore, it exhibits the lifetime anomaly. In NO<sub>2</sub>, the ground state is  ${}^{2}A_{1}$  and the excited states are  ${}^{2}B_{1}$  (linear) and  ${}^{2}B_{2}$  states in the visible region and there is considerable evidence that long lifetime is caused by inter electronic mixing of levels. The levels of  ${}^{2}B_{2}$  mixes up with the highly dense vibrational levels of the ground state through vibronic interaction and the resultant levels which are non B-O levels contains the characteristics of both  ${}^{2}B_{1}$  and  ${}^{2}A_{1}$  depending on the extent of interaction. Again the level  ${}^{2}B_{1}$  which is a linear state can undergo bending vibrations and this would result in coupling with the highly dense vibrational level of the ground state  ${}^{2}A_{1}$ , which is the case of the Renner-Teller interaction. The observed lifetime of these levels are long and the observed fluorescence decay is non-exponential due to the various lifetimes getting mixed up. These processes manifest itself in the form of an extremely complex absorption and fluorescence spectrum as seen in NO<sub>2</sub>. This process is also seen in molecules like SO<sub>2</sub>, CS<sub>2</sub> etc.

# **1.8 Need for Lifetime Measurement**

Lifetime measurement for excited states of different atoms and molecules are important for having a better insight in the understanding of mechanisms for radiative and nonradiative transitions. Also such measurements are of importance in a variety of applications such as study of emissions in the planetary atmospheres and interstellar clouds, and in the field of laser and plasma physics.

From the measured lifetime, the transition probability  $A_m$  for an excited state  $E_m$  to decay can be determined (section 1.2). Along with the relative intensities  $I_{mn}$  for a transition  $E_m \rightarrow E_n$  ( $A_m = \sum_n A_{mn}$ ), the absolute transition probability  $A_{mn}$  can be determined giving information on transition dipole matrix elements. These matrix elements computed theoretically are sensitive to approximation errors and depend on the nature of the upper and lower state. Thus lifetime measurements validate the quality of computed wave functions and can be used to optimize models of electron distribution in complex molecules in the determination of molecular structure.

The intensity of a spectral line depends not only on the population density of the molecule in the absorbing or emitting state but also on the transition probabilities of the corresponding molecular transition. Since absorption cross section is proportional to the transition probability (section 3.1), the lifetime measurement can be used to estimate the same. Also, measuring the absorption coefficient and lifetime, the number density of the absorber or the emitter can be determined. This problem is very important in the modelling of stellar atmospheres. Comparing the intensity of different lines of the same element further enables us to derive the temperature of the absorber or the emitter. The estimation of density, temperature and abundance of element in a source requires the knowledge of transition probability. In astrophysics, where spectral lines represent the main source of information from extraterrestrial world and in the study of Sun's atmosphere, the estimation of transition probability or the lifetime is essential. Lifetime measurements are also important in the study of collision dynamics. The determination of absolute cross section for quenching collision using the Stern-Volmer equation require an estimate of lifetime of the excited states involved.

# **1.9 Measurement of Lifetime Using Laser**

In the previous sections, we have discussed the need for the measurement of lifetime of excited states of atoms or molecule. There are different methods of measuring lifetime, namely, the optical excitation, electron impact excitation, level crossing and double resonance techniques. In this section, we will focus on the different techniques used in optical excitation. These are phase shift technique, delayed coincidence technique and pulsed excitation technique, which are discussed below.

### **1.9.1 Phase Shift Technique**

This technique uses modulated optical source to excite the molecule. Here the excitation light of intensity  $I_0$  is sinusoidally modulated at a frequency  $\Omega$ . The Intensity of excitation  $I_{ex}$  for such a modulation to excite a molecular level  $\mathbf{E}_i$  can be written as

$$I_{ex} = I_0 (1 + a \sin \Omega t) \cos \omega_{ik} t \tag{1.40}$$

The fluorescence emission from the level  $E_i$  can be written as

$$I_f = bI_0 \left[ 1 + \frac{a sin(\Omega t + \Phi)}{[1 + (\Omega \tau_{eff})^2]^{1/2}} \right] cos^2 \omega_{ik} t$$
(1.41)

where b is a proportionality constant. From the above equation, it is implied that the fluorescence intensity is modulated at the same frequency  $\Omega$ 

as the excitation source, but its phase is shifted by  $\Phi$  with respect to the modulation phase of  $I_{ex}$ . This is illustrated in the Figure 1.7. This phase shift depends on the modulation frequency  $\Omega$  and the effective lifetime  $\tau_{eff}$  and can be written as

$$tan\Phi = \Omega \tau_{eff} \tag{1.42}$$

If induced emission is neglected ( $\rho B_{ik} \ll A_{ik}$ ), then  $\tau_{eff}$  is the spontaneous lifetime of the level  $\mathbf{E}_i$ .



Figure 1.7: The observed delay in phase between the excitation source (laser) and the fluorescence intensity in Phase shift technique to measure lifetime.

In practice, the excitation light is sinusoidally excited since the time dependence of fluorescence is easy to evaluate. In a non-sinusoidal excitation, the time dependence of fluorescence is very complicated. The maximum sensitivity is achieved if the modulation frequency is chosen to give a phase difference of 45°. This technique is not well suited for measuring non-exponential decays since a single phase difference is measured. The influence of induced emission is a drawback in this technique when lasers are used for excitation.

### 1.9.2 Delayed Coincidence Method

This technique is widely used for measuring the lifetimes of excited states in weakly fluorescing molecules. Here the excitation pulse energy is kept very low such that the detection probability  $P_{det}$  of a fluorescence photon per laser excitation pulse is small ( $P_{det} \leq 0.1$ ) and the number of excitation cycle is kept very high ( $N \gg 1$ ). Then the probability of detecting a fluorescence photon in a time interval t to t + dt and the number of fluorescence photon detected in this time interval are given as

$$n_{fl}(t)dt = NP_{det}(t)dt$$
(1.43)

The basic principle of this technique is schematically shown in Figure 1.8.



**Figure 1.8:** Schematic diagram of the principle of lifetime measurement with the delayed coincidence technique.

Here when a single laser pulse is shot to excite the molecules, simultaneously an electronic start pulse is generated with respect to the excitation pulse. This start pulse triggers a time to amplitude converter (TAC). A photomultiplier (PMT) is used to detect the first fluorescence photon. On detection of this photon, a stop pulse is generated to stop the TAC. The TAC output is analysed by a multi channel analyzer (MCA) in pulse-height mode and the event is registered in the appropriate channel. Under the assumption that the detection probability of a fluorescence photon is very small in a given time, the probability of a stop pulse occurring at a specific time will be directly proportional to the probability of a photon being emitted by the sample at that time. If many laser pulses are fired, the MCA will register histograms having the shape of the sample decay curve representing the fluorescence decay. This method has many advantages. Since the probability of detecting a photon must be low, excitation intensity and optical efficiency are less important and the system response is not limited by the PMT output pulse width. The dynamic range and linearity are enormous and are free from the influence of induced emission. But this technique requires a few thousands of laser pulses to build a meaningful decay curve with good signal to noise ratio. Here, lasers with large repetition frequency are essential.

### **1.9.3 Pulsed Excitation Technique**

In this method, the molecules are excited by a short laser pulse. The falling edge of this pulse should be short compared with the decay time of the excited level, which is directly monitored after the end of the excitation pulse. The basic principle is illustrated in Figure 1.9. The observed time-dependent fluorescence is detected using a photomultiplier tube and viewed either with a fast sampling oscilloscope or may be recorded by a transient recorder or a box car averager. In this technique, when the excitation pulse width is very short as compared to the fluorescence decay time, the observed fluorescence curve represents the true decay curve. When the excitation pulse width is comparable with the decay time, the observed decay is not the true fluorescence decay, but is the convolution of the excitation pulse and the true fluorescence decay curve. Mathematical tools like deconvolution have to be applied on this data to recover the true lifetime. The direct observation of the decay curve on an oscilloscope has the advantage that non-exponential decays can be recognized immediately. Also, this method is free from the influence of induced emissions. For sufficiently intense fluorescing system, one needs only a single excitation pulse to record the decay curve although generally averaging over many excitation cycles improves the signal to noise ratio. This technique is well suited for laser system with low repetition rate. The detailed description of the experimental setup using this technique has been discussed in Chapter 2. The technique of pulse excitation has been used in the present work to measure the lifetimes of the excited states of NO<sub>2</sub>.



Figure 1.9: Schematic diagram of the principle of lifetime measurement with the pulsed excitation technique.

# **1.10 Review of Spectral and Theoretical Information of NO<sub>2</sub> Molecule**

The ground state of NO<sub>2</sub> is  $\tilde{X}^2 A_1$ , with bond angle 134.1°. The absorption spectrum of NO<sub>2</sub> in the near ultraviolet and visible is extremely complex and most of the regions have no apparent regularity in rotational and vibrational structure. The dissociation limit of NO<sub>2</sub> is 397.9 nm. When irradiated with light of wavelength above 397.9 nm, fluorescence of NO<sub>2</sub> has been observed. The fluorescence spectrum lies in the region starting from the exciting wavelength to above 800 nm.

Atherton *et al* (1964) carried out polarization studies of transition in NO<sub>2</sub> in the region 410-420 nm and reported  ${}^{2}B_{2} \leftarrow {}^{2}A_{1}$  transition and also suggested the possibility of a lower energy,  ${}^{2}B_{1} \leftarrow {}^{2}A_{1}$  transition to overlap with  ${}^{2}B_{2}$  state in this region. Douglas and Huber (1965) confirmed the presence of  ${}^{2}B_{1} \leftarrow {}^{2}A_{1}$  in the visible region 380-460 nm and located six band progressions. Using the technique of excited resonance fluorescence, Abe *et al* (1971, 1974) reported the transition from  ${}^{2}B_{2}$  at 496.5, 514.5 and 632.8 nm and  ${}^{2}B_{1}$  at 514.5 nm. They suggested that an excited state wave function containing contribution from  ${}^{2}B_{1}$  and  ${}^{2}B_{2}$  electronic states are involved. Later Steven *et al* (1973) had found the evidence for the existence of two excited states  ${}^{2}B_{2}$ ,  ${}^{2}B_{1}$  in the region 593.4 to 594 nm from the rotational analysis of the fluorescence spectra of NO<sub>2</sub>. They concluded that the  ${}^{2}B_{2}$  has lifetime of 30  $\pm$  5  $\mu$ sec and the  ${}^{2}B_{1}$  has a lifetime of 115  $\pm$  10

 $\mu$ sec. Sacket and Yardley (1971) observed several unperturbed levels with short lifetime from  ${}^{2}B_{1}$  state in the region 454.4-455 nm. Similar observation was made by Solarz and Levy (1974) at 488 nm. Paech *et al* (1975) measured collision free lifetime of NO<sub>2</sub> excited by a tunable laser near 488 and 514.5 nm. They observed three different lifetimes of fluorescence (3, 28 and 75  $\mu$ sec). They concluded that the initially found  ${}^{2}B_{1}$  state crosses rapidly to another state  ${}^{2}B_{2}$ , with high level density. The  ${}^{2}B_{2}$  state can have two different lifetimes (28 and 75  $\mu$ sec) depending on the extent of interaction with the ground state (vibronic coupling). The short component from  ${}^{2}B_{1}$  was primarily determined by the rate of internal conversion from  ${}^{2}B_{1}$ 

The fluorescence quantum yield as a function of incident wavelength was measured by Lee and Uselman (1972). The yield starts to increase from 0 at 394.9 nm to nearly 100% at 415 nm. The decrease of the yield below 415 nm is attributed to predissociation supplemented by the rotational energy of the molecule. Later, Uselman and Lee (1976) studied the absorption region 398-420 nm and found the fluorescence lifetime to be constant in this spectral region. They also found the evidence of another predissociating component with lifetime less than 0.1  $\mu$ sec. Recently Georges *et al* (1995) have observed a set of 300  ${}^{2}B_{2}$  vibronic levels of NO<sub>2</sub> in the visible region using laser induced fluorescence combined with supersonic jet experiments. In the same year, Delon *et al* (1995) studied the ro-vibronic interaction of NO<sub>2</sub> and concluded that  ${}^{2}B_{2}$  state is highly perturbed and confirmed that  ${}^{2}A_{1}$  and  ${}^{2}B_{2}$  vibronic interaction is due to the conical intersection of the potential energy surface of  ${}^{2}A_{1}$  and  ${}^{2}B_{2}$ .

Along with the experimental studies of NO<sub>2</sub>, theoretical studies were carried out to sort out the problem and model the structure of NO<sub>2</sub>. Mulliken (1942], Pearse and Gaydon (1950) and Walsh (1953) carried out calculation on the energy levels of NO<sub>2</sub> and concluded that  ${}^{2}B_{1}$  and  ${}^{2}B_{2}$  are the excited states above the ground state  ${}^{2}A_{1}$  and were responsible for the visible spectrum. They suggested that  ${}^{2}B_{2}$  is the state primarily responsible for fluorescence in visible spectrum which is stronger than  ${}^{2}B_{1} \leftarrow {}^{2}A_{1}$ transitions. Gangi and Burnelle (1971) did extensive configuration interaction calculation to compute the potential energy surface of NO<sub>2</sub> and placed  ${}^{2}B_{1} \leftarrow {}^{2}A_{1}$  and  ${}^{2}B_{2} \leftarrow {}^{2}A_{1}$  in the visible region and the forbidden  ${}^{2}A_{2}$ ,  ${}^{4}B_{2}$  and  ${}^{4}A_{2}$  states somewhat higher in energy. The computed potential energy curves for different bond angles are shown in Figure 1.10.





Figure 1.10: The potential energy curves of  $NO_2$  computed by Gangi and Burnelle (1971).

Herzberg (1966) pointed out that the vibronic levels of the  ${}^{2}\Pi_{4}$  state of the linear NO<sub>2</sub> molecule undergo a Renner-Teller splitting to form the  ${}^{2}A_{1}$ ground state and  ${}^{2}B_{1}$  excited state upon bending. All the wave functions contain contribution from both states and may be assumed to contain only small contribution from the  ${}^{2}B_{1}$  electronic state. While an integration of the absorption intensity should be capable of measuring essentially the

total oscillator strength of the  ${}^{2}B_{1} \leftarrow {}^{2}A_{1}$  transition, it will be distributed among the transitions between various vibronic levels more evenly and is smaller than expected in B-O approximation leading to a low estimated lifetime than those observed experimentally. This is known by the lifetime anomaly of excited states.

Gardner and Kasha (1969) pointed out that the  ${}^{2}B_{1}$  electronic state cannot interact with the  ${}^{2}B_{2}$  state directly except through a vibrational mode. Jackels and Davidson (1976) showed that  ${}^{2}A_{1}$  and  ${}^{2}B_{2}$  states are strongly coupled when asymmetric distortion was taken into account in their configuration interaction (CI) calculation. They studied the NO<sub>2</sub> in  $C_{2v}$  conformation and calculated the vertical excitation energies. They predicted the vibronic interaction between  ${}^{2}B_{2}$  and  ${}^{2}A_{1}$  state of NO<sub>2</sub>. Leonardi *et al* (1996) studied the  ${}^{2}A_{1}$  and  ${}^{2}B_{2}$  non-adiabatic interaction to compute the non-adiabatic ro-vibronic levels of  ${}^{2}A_{1} - {}^{2}B_{2}$  conical interaction.

The present work is addressed to the problem of anomalously long lifetime and the role of quenching collisions in  $NO_2$  molecular system. The measurement includes the study of pressure dependence of lifetime of excited state of  $NO_2$  in the excitation region 399 to 490 nm. The pulsed excitation technique was used to measure the excited state lifetime of  $NO_2$ . The detailed experimental setup and the technique is discussed in the next chapter.

# **Chapter 2**

# **Experimental Setup**

The importance of fluorescence and lifetime study of excited electronic states of molecules, and NO<sub>2</sub> in particular, has been discussed in the previous chapter. In this chapter, the experimental apparatus and its various components are discussed in detail.

The main considerations in designing experimental system for lifetime measurements are the volume to surface area ratio of the experimental chamber and choice of field of view depending upon the lifetimes of the excited state. The first aspect is in general important in any type of cell experiments involving chemically reactive gases. The chemical reactions at the surface will change the number density and introduce inhomogeneity in the gas sample. However, purity and homogeneity of the gas could be improved if dynamic equilibrium is maintained in the cell. This is achieved by constant introduction of the gas and throttled pumping of the chamber. This scheme was adopted in the present experiment, whereby building up of concentration of impurities due to surface chemical reactions was considerably reduced. Also the flow driven in the system mixes the gas, assuring homogeneity. The geometry and field of view for the collection optics is critical in the measurement of lifetime. This aspect has been discussed in chapter 4 in detail.

The experimental apparatus was designed and fabricated in the laboratory to measure the total fluorescence and lifetime (0.1-200 nsec) of the excited states of  $NO_2$  in the spectral range 399 to 490 nm at an instrumental resolution of 0.01 nm. These studies were carried out at room temperature (300 K). The setup consists of an excimer laser pumped tunable dye laser, beam expansion optics, beam splitter for monitoring the photon intensity and its variation, a cylindrical fluorescence chamber, light collection optics, photon detector and data acquisition system. The schematic diagram of the experimental system is shown in Figure 2.1. A detailed discussion on various components of the setup are presented in the following sections.





# 2.1 Sources of Excitation

For the measurement of lifetime of excited electronic states of molecules using the pulsed excitation technique, one requires a pulsed source of light to excite the molecule and the time resolved decay of the fluorescence after the excitation pulse. In the present work on NO<sub>2</sub>, the source required for the excitation of the molecule should be tunable in the visible region and the pulse width should be much less than 1  $\mu$ sec.

Laser is a source of light which excels in the overall scope of conventional sources, with the enhanced features like coherence, monochromaticity, power, collimation, polarization, temporal behaviour and tunability. Depending on the type of application, to-date there are hundreds of different lasers available which could mainly be classified as solid laser, semiconductor lasers, chemical lasers, free electron lasers, metal vapour lasers, gas lasers and liquid (dye) lasers.

Among the different types of lasers mentioned above, dye lasers are widely used as tunable laser in various configurations. The main features of dye lasers are:

- can be used both in CW and pulsed operation,
- wide range of wavelength tunability by changing dyes
- narrow line width
- broad homogeneous gain profile which under ideal condition gives larger power output when operated in single mode.

For experimental realization of dye lasers, either flash lamp, pulsed laser or CW laser is used as the pumping source. In the present experiment an excimer pumped tunable dye laser (LPX110e - LPD3001, Lambda Physik) was used as the excitation source. The dye laser could be wavelength tuned from 399 to 490 nm with an instrumental resolution of 0.01 nm using different dyes. The width of laser pulse is about 8 nsec with a nearly Gaussian intensity distribution. The beam diameter was 2 mm. The output energy of the laser could be tunable from few mJ to 10 mJ with 1 to 100 Hz pulse repetition rate.

#### 2.1.1 Excimer Laser

Certain molecules such as ArF, XeCl, KrF which are strongly bound only in excited states are known as excimers or exciplexes. The ground states of these exciplexes are characterized by repulsive potential. In the excimer laser, electrical discharge generates atoms and ions (in excited states) which combine to form excimer molecules. Since the ground state of such a molecule is essentially empty (because of rapid dissociation), a population inversion between the exciplex state and the ground state is easily obtained. Transition between these states occur instantaneously in the UV and vacuum UV region. These excimer lasers emit primarily at wavelength shorter than 350 nm. The high gain of excimer laser transition leads to highly efficient operation, and further, the short radiative lifetime of the excimer ( $\sim 10$  nsec) yields short pulse durations. The excimer laser could be operated at different UV lasing wavelengths using different combination of gases. However, during the present work only XeCl excimer was used to pump the dye laser. The lasing wavelength was 308 nm and its output energy could be varied from 80 to 200 mJ with a pulse width of 28 nsec. The pulse repetition rate is 1 to 100 Hz. The desired output energy of the excimer laser is achieved by applying suitable potential at the electrode used for pumping. In our LPX100e, at 18 KV potential the output energy was around 80 mJ and at 25 KV, the output was 200 mJ. The laser is normally operated at 10 Hz repetition rate. The excimer laser LPX100e is

used to pump the tunable dye laser LPD3001.

#### 2.1.2 Dye Laser

Dye lasers are tunable lasers whose active media are organic dye molecules dissolved in appropriate solvents. These dyes display strong broad band fluorescence spectra under excitation by visible or UV light. With different dyes the overall spectral range could be achieved using CW or pulsed laser operation. The reduction of the linewidth and wavelength tuning can be accomplished by pressure/angle tuned etalon, grating or interference filters. In a dye laser where the wavelength selection is performed with a grating, the dye laser beam is expanded so that the spectral resolution is better and the laser line width is smaller. These dye lasers employ either flash lamp or a pulsed laser.

In the present dye laser (LPD3001), the wavelength selection is performed with a grating (600 g/mm) in Littrow mount. The dye laser beam is expanded using a prime beam expander so that the spectral resolution is better and the laser line width is smaller. The dye laser is pumped using an excimer laser (LPX110e).

For the dye laser output in the desired spectral range (399-490 nm), three different dyes were used which were provided by Lambda Physik, Germany. The details of the dyes are given in Table 2.1. The desired output wavelength is selected by tuning the grating of the dye laser which is microprocessor controlled. The wavelength calibration of the dye laser was done at Lambda Physik, Germany. These calibrations were verified in the laboratory using a 0.5 meter monochromator ( $\lambda$ -Minuteman, USA) which was pre-calibrated using Hg 253.7 nm and other line sources. The output energy of the dye laser was varied by changing the excimer laser output used to pump the dye laser.

Name	Tuning wavelength	Conversion efficiency	Solvent
	(nm)	(%)	
Coumarin 102	460 - 490	14	Methanol
Coumarin 120	423 - 462	11	Methanol
DPS	399 - 416	7	DiOxane

Table 2.1: Laser dyes and their spectral characteristics

# 2.2 Beam Expansion and Folding Optics

The beam diameter of the dye laser was 2 mm. To avoid any nonlinear absorption of the laser photon by the target gas due to high energy density and to increase the interaction volume of the laser beam with target gas, the laser beam had to be expanded. For this purpose a 4X Galilean type beam expander (Spindler Hoyer) was used to expand the laser beam. The schematic diagram of laser beam expansion is shown in Figure 2.2.



Figure 2.2: Schematic diagram of a 4X beam expander

The beam expander consisted of a plano-concave and a plano-convex quartz lens mounted on a single casing. By adjusting the distance between the two lenses, a collimated and expanded beam is obtained. This expanded beam was further passed through a suitable aperture to obtain a laser beam of 6 mm diameter. With the help of two mirrors (front surface Al coated) the laser beam was folded and steered into the fluorescence chamber along its optic axis. This laser beam was allowed to pass through a beam splitter before entering the fluorescence chamber.

# 2.3 Beam Splitter

In the measurement of time-resolved fluorescence decay curve, it is essential to determine the time at which the fluorescence decay starts. This can be denoted as time-zero ( $t_o$ ) for each decay curve. The time  $t_o$  is important while averaging the decay profile so that there is no distortion in the shape of the decay curve. Also to account for the pulse to pulse variation in the dye laser output intensity in the study of excitation spectra and lifetime spectra, a portion of the incident beam has to be monitored. For this purpose a beam splitter was introduced in the experimental setup. The beam splitter essentially consists of a reflecting quartz surface held at  $45^o$ to the incident beam path. A small fraction of the incident radiation was reflected while the rest was transmitted along the incident beam direction. The intensity of the reflected beam was linearly proportional to the incident intensity and hence, any change in the incident intensity could be monitored.

In the present experiment, the beam splitter is a quartz plate of 25 mm diameter held at  $45^{\circ}$  to the incident laser beam path. About 5% of the total incident beam is reflected by the beam splitter and is detected using a photodiode. The transmitted beam from the beam splitter is allowed to enter the entrance port of the fluorescence chamber. The reflected beam is used as time marker (rise time ~ 1.2 nsec) for the measurement of decay curve in the range 0.1-200 msec. Also, this signal is used as a trigger to drive the data acquisition system.

# 2.4 Fluorescence Chamber

The transmitted laser beam from the beam splitter was made to pass through the entrance port of the fluorescence chamber into the interaction region where the laser photon interacts with the gas molecule under study. The portion of the beam after the interaction with the gas molecules was passed through the exit port and trapped inside a light dump.

The fluorescence chamber was designed and fabricated in the laboratory. It is a cylindrical chamber, 25 cm long and 15 cm in diameter. It is made of nonmagnetic stainless steel 304. A pumping port of 6 cm diameter was used to evacuate the chamber which is positioned perpendicularly downward with respect to the chamber axis. There are two ports of 2.5 cm diameter and 30 cm long which are mutually perpendicular to the fluorescence chamber axis and the pumping port. There are the entrance and the exit port for the laser beams. The exit port is coupled to a light dump. There are two more ports for gas inlet and gas pressure measurement.

The entrance port of the fluorescence chamber contains 5 circular aperture of 6 mm diameter each stacked with suitable spacers and a quartz window at the entrance side to seal the chamber, but to allow the laser beam inside. A set of apertures were used to reduce the scattering of light from the quartz window into the chamber and to collimate the laser beam. It also defines the cross section area for the interaction volume. To avoid any backscattering of light at the exit port, the laser beam is again passed through a series of circular apertures in the exit port and is finally trapped into a horn-shaped light dump made of glass and coated from inside with aquadag (carbon black). The fluorescence port is positioned perpendicular to the entrance port which is coupled to the light collection optics.

# 2.5 The Vacuum System

The experimental chamber has to be evacuated to remove the residual gas present inside the chamber. Using a combination of oil diffusion pump (1000 l/sec, Model 0-1000, Hind High Vacuum Co. Ltd., India), Roots pump (300 1/sec, RSV300, Alcatel) and a mechanical rotary pump (800 l/sec, Vacuum Tech., India), the chamber was evacuated to  $10^{-6}$  Torr. The reference side of the MKS differential capacitance manometer was evacuated to pressure < $10^{-6}$  Torr using a oil diffusion pump (300 l/sec, Model OD-2, Hind High Vacuum Co. Ltd., India) and a mini-rotary pump (50 l/sec., Model VT 2012, Vacuum Tech, India). The vacuum in the fluorescence chamber and reference side of the manometer were measured using Penning ionization gauge. The pressure in all the backing lines of the vacuum system were monitored using thermocouple gauges.

## 2.6 Pressure Measurement System

In the study of pressure dependence of lifetime and the estimation of the self-quenching rate constants, the measurement of absolute number density of the target gas is essential. This can be calculated from ideal gas law if the absolute pressure and the temperature of the target gas are known. MKS Baratron (differential capacitance manometer) measures very low pressure at very high accuracy and precision.

The manometer consists of two metal chambers separated with a thin metal membrane. One side of the chamber called pressure sensing side is connected to the system while the other chamber, called reference side is connected to a reference vacuum system. If the reference side is maintained a pressure  $P_{ref}$  and the pressure  $P_{sys}$  be applied to the pressure sensing side, the differential pressure ( $P_{sys} - P_{ref}$ ) between these two sides

produce a deflection in the membrane which in turn changes the capacitance between the membrane and the chamber. This change in capacitance is calibrated against the applied differential pressure. Thus the manometer measures the differential pressure given by  $P_{brt} = P_{sys} - P_{ref}$ . An absolute pressure measurement can be made by pumping down the reference side to pressures at least three orders of magnitude lower than the applied pressure ( $P_{ref} \ll P_{sys}$ ). In such a case  $P_{ref}$  can be neglected and the pressure in the system is given by  $P_{sys} = P_{brt}$ .

In the present work, an MKS differential capacitance manometer was used to measure the pressure in the interaction region of the fluorescence chamber. The gauge head used was Head 310 BH-1 (1 Torr head). This head was factory calibrated. The reference side of the baratron was maintained at a pressure less than  $10^{-6}$  Torr to measure the absolute pressure (1-200 mTorr) in the chamber. The material used in the construction of the capacitance manometer is sensitive to ambient temperature. So the manometer head was maintained at a constant elevated temperature (318 K). The Figure 2.3 shows the arrangement of MKS capacitance manometer. The reference side of the manometer was directly connected to the reference vacuum pump through a 6 mm diameter copper tubing. The pressure sensing side was also connected to the system using similar tubing and Kontes valve V1. Also the reference and pressure sensing sides were connected to each other by a Kontes valve V2.

To measure the pressure in the system, the valve V1 was kept closed and valve V2 open. In this configuration, the manometer was allowed itself to go through zero adjustment ('balancing the gauge') as both the chambers are maintained at the same pressure ( $<10^{-6}$  Torr). When the pressure measurement is to be done, the valve V2 is closed and V1 is let open. The pressure readout from the manometer is taken as the absolute pressure of the target gas inside the fluorescence chamber.



**Figure 2.3:** Schematic diagram of the MKS capacitance manometer for measuring the absolute pressure.

# 2.7 Gas Handling System

The NO<sub>2</sub> gas used in the present experiment was procured from L'Air Liquide, France and was used directly without any further purification. The purity of the gas as mentioned by the company is 99.9%. The gas from the cylinder is connected to the gas inlet port of the fluorescence chamber through a leak valve (Model No.203, Granville Philips). Using the fine control of the leak value and the flow control of the cylinder, a constant target gas pressure from 1 to 200 mTorr could be maintained in the chamber.

## 2.8 Light Collection Optics

To enhance the light gathering factor at the detector end, a collection optics was designed in the laboratory which is coupled to the fluorescence port of the chamber as shown in Figure 1b. It consists of two sets of circular aperture and a lens of f/3 optics. Figure 1(b) shows the arrangement for the collection optics. The size of the apertures S1 and S2 was optimized such that the field of view is around 12 cm. Here the care was taken so that the geometrical effects (discussed in chapter 4, section 4.1) are minimum in the measurement of lifetime and also the fluorescence signal is effectively and efficiently collected at the detection plane avoiding any light scattered from the walls of the chamber from entering into the detection system.

## 2.9 Photon Detection System

Two types of detectors were used in the present experiment. To monitor the incident laser beam from the beam splitter, a photodiode was used and to detect the fluorescence signal, a fast photomultiplier tube was used.

### 2.9.1 Photodiode

Photodiodes are doped semiconductors which can be used as a photovoltaic or photo-conductor devices. When the P-N junction of a diode is irradiated, the photo-voltage is generated at the open output of the diode. For their use as radiation detection, the spectral response of the diode is of fundamental importance. The photo-current generates a signal voltage across the load resistor which is proportional to the absorbed radiation power. In a PIN diode, an undoped zone I of an intrinsic semiconductor separates the P and N junctions. Since no space charges exist in this zone, the bias voltage applied to the diode will cause a constant electric field which accelerates the carriers. The width of the intrinsic zone determines the capacitance of the P-N junction and for a large width, the capacitance is very low and provides a basis for a very fast and sensitive detection. Silicon PIN diodes have fast response and high sensitivity making it suitable for the present purpose.

In the present setup, a high speed (rise time <1 nsec) silicon PIN diode dielectric DET-Si (Thorn Labs Inc.) is used to monitor the incident laser beam from the beam splitter. The spectral response of the diode in the region 185-110 nm is shown in Figure 2.4.



Figure 2.4: Spectral response of DET-Si photodiode.

### 2.9.2 Photomultiplier Tube

For the detection of the low light levels, photomultiplier tubes (PMT) are best suited due to the internal amplification of the photocurrent using the secondary electron emission from the internal dynodes to multiply the number of photoelectrons. It consists of a photocathode, electron multiplier (a set of dynodes) and an anode. The incident light is detected by the photocathode which emits electron by the photoelectric effect. These photoelectrons are electrostatically accelerated and focussed into the first dynode of the electron multiplier. On impact with the dynode, each electron liberates a number of secondary electrons which are in turn accelerated and focussed on to the next dynode. This process is repeated at each subsequent dynodes and the secondary electrons from the last dynode are collected at the anode. The ratio of the secondary to primary electrons emitted at each dynode depends on the energy of the incident electrons and is controlled by the inter-electrode potential. By using a variable high voltage power supply and a voltage divider network to provide the interelectrode voltage, the amplitude of the PMT output can be varied over a wide dynamic range and for better signal to noise ratio.

For experiments demanding high time resolution, the response of the photomultiplier tube should be fast. This property of the photomultiplier tube is characterized by the rise time, FWHM and transit time of the output pulse. These parameters depend on the geometry and the form of the dynode structure of the PMT.

For low level light detection, the noise factor is of fundamental importance. The main source of noise in the PMT is the dark current. When the PMT is operated in complete darkness, electrons are still emitted from the photocathode. This dark current is mainly due to the thermionic emission and partly caused by cosmic rays or by radioactive decay of spurious radioactive isotopes in the photomultiplier material. In order to decrease this dark current, the temperature of the photocathode is reduced. The optimum temperature depends on the type of cathode and its work function.

In the present experimental setup, the time response and the spectral response of the PMT are of great importance. Since the PMT is operated in current mode to measure the instantaneous current or voltage which should faithfully reproduce the decay of the fluorescence signal. For this purpose, the PMT 9079B (Thorn EMI Electron Tubes) was used. The spectral response was S20 type as shown in Figure 2.5. The gain of the PMT is

around 2.5 x  $10^5$ . The effective size of the cathode is 1.5 cm and the rise time of the PMT is 1.8 nsec.



Figure 2.5: Spectral response of a S-20 type photocathode photomultiplier

A series of voltages are applied to the different elements of the PMT derived from a single high voltage supply (Model HV1008E, Electronics Corporation of India Ltd.) using a resistance divider network. The cathode was biased to a negative voltage with respect to the anode. The anode was kept floating. The dynodes were linearly biased with decreasing negative voltage with respect to the cathode. Since the PMT is used for pulsed signal detection, the last few stages of dynodes were biased more to overcome the space charge effect and capacitance were connected in parallel at these stages to store energy and supply to the charge pulses. The high voltage power supply used was a variable voltage (0-3000 V) with very low ripple factor and good voltage stability.

To reduce the dark current, the photocathode was cooled to  $-25^{\circ}$ C. Cooling below this temperature has little or no effect in the reduction of dark current of the PMT with S-20 response. A commercially available, thermoelectrically cooled PMT housing (FACT Mk.III, Thorn EMI, UK) was used to cool the PMT to  $-25^{\circ}$ C. The optimization of signal to noise ratio was carried out for the PMT by looking at the ratio of the intensity from a standard Hg lamp and the dark current as a function of the applied voltage to the PMT. The optimum voltage was found to be 1000 Volts.

## 2.10 Data Acquisition System

The signal output from the PMT anode is directly coupled to a fast preamplifier (Philips 7177) having a rise time of about 1 nsec and an input impedance of 50  $\Omega$ . The band width of the preamplifier is 200 MHz which ensures that the preamplifier does not distort the nature of the decay curve. The preamplified signal is then fed to a digital storage oscilloscope and later to a personal computer for off line analysis.

A four channel digital storage oscilloscope (DSO) (Tektronix TDS 540B) with a band width of 500 MHz was used to acquire and store the signal. The fluorescence decay curve was sampled at 100 to 200 nsec interval and digitized as 8 bit data by the DSO. The DSO accquires both the pre-trigger data as well as post-trigger data thereby giving exact estimation of baseline for time resolved data. To minimize the digitization error, the vertical scale of the DSO was tuned in such a way that the fluorescence signal covers the full digitization limit. Depending on the signal strength, the fluorescence decay curves were averaged for 200 to 1000 laser shots as shown in Table 2.2. The DSO was externally triggered to acquire the signal. This trigger was supplied from the photodiode which monitored the incident dye laser intensity. The photodiode signal was also acquired by the DSO.

**Table 2.2:** The relevant experimental parameters used in the present experiment.  $\tau_1$ ,  $\tau_2$  and  $\tau_3$  are the lifetimes in 1–3, 20–40 and 70–120  $\mu$ sec groups respectively identified in the present work.

Pressure	Identified	Mean free	Collision	S/N Ratio	No. of laser
(mTorr)	lifetimes	path (cm)	frequency		shots
			(MHz)		
1	$ au_2$	6.53	0.0065	25	1,000
3	$ au_2$	2.18	0.019	35	800
5	$ au_1,  au_2,  au_3$	1.31	0.032	60	400
15	$ au_1$ , $ au_2$	0.44	0.097	100	100
51	$ au_1,  au_2,  au_3$	0.13	0.333	180	20
81	$ au_1$ , $ au_2$	0.08	0.52	180	20
110	$ au_1$ , $ au_2$	0.06	0.71	180	20

# **Chapter 3**

# **Method and Analysis**

The measurement of total fluorescence and time resolved decay curve for NO<sub>2</sub> molecule were carried out with the experimental set up described in chapter 2. These measurements were made at room temperature (300 K) at target gas pressure varying from 1 to 110 mTorr in the excitation wavelength region 399 to 490 nm. The pulsed excitation technique used for these measurements has already been discussed in chapter 1. In this chapter we will discuss the experimental procedures and different mathematical tools used in the analysis and estimation of lifetime and self quenching rate constant.

# **3.1 Fluorescence Excitation Spectra (FEX)**

A high resolution FEX spectrum (total undispersed fluorescence intensity versus excitation wavelength), in principle could reveal evidence for the existence of two or more nearby upper electronic states with differing radiative properties, if the radiationless transition connecting the upper electronic states were slow compared to the radiative processes. The pressure dependence study of these FEX spectra could reveal the evidence for the collisional depopulation and repopulation of these upper electronic states. Considering these implications, the FEX spectra were measured for  $NO_2$  in the excitation wavelength 399 to 490 nm in the interval of 0.2 to 0.5 nm (instrumental resolution 0.01 nm). These measurements were carried out at room temperature (300 K) at different pressures ranging from 1 to 110 mTorr.

To measure the total fluorescence intensity, the fluorescence signal detected by the photomultiplier tube is integrated in time (fixed duration) after the excitation laser pulse at a given exciting wavelength. Depending on the signal to noise ratio, the integrated signals were averaged. Here the integrations were delayed by 2 to 4  $\mu$ sec after the exciting laser pulse to eliminate the scattered signal due to reflections from the walls of the fluorescence chamber. The measurements were repeated at different exciting wavelengths to build up the fluorescence excitation spectrum by tuning the dye laser to the adjacent wavelength. Here the FEX spectrum were corrected for the variation in the incident laser intensity but uncorrected for spectral response of the detector. Such FEX spectrum were obtained at different target gas pressures.

In all these studies, the fluorescence chamber is evacuated to a pressure of 10<sup>-6</sup> Torr and the target gas is introduced into the fluorescence chamber to the required pressure. The pressure of the target gas is monitored using the MKS capacitance manometer.

# 3.2 Fluorescence Lifetime Measurement

For a two level system, the fluorescence decay intensity as a function of time after the exciting pulse (in pulsed excitation technique) at a given incident photon wavelength is given by

$$I(t) = \int_0^\infty R(T) exp\left(\frac{-[t-T]}{\tau}\right) dT$$
(3.1)

where R(T) is the instrumental response function which is a convolution of the fluorescence excitation pulse and the detector response.  $\tau$  is the average lifetime of the upper state.

When the decay time of the fluorescence signal is long compared to the decay time of the excitation pulse, the measured decay curve is a direct measure of the true fluorescence decay and the decay of intensity can be written as

$$I(t) = I(0)e^{\left(\frac{-t}{\tau}\right)}$$
(3.2)

where I(0) is the amplitude factor. However when the lifetime is short or comparable to that of the excitation pulse, the experimental data are distorted significantly by the finite decay time of the excitation pulse, resolving time of the detector and associated electronics. Hence the measured fluorescence decay will be a convolution of the actual fluorescence decay and the instrumental response function as given by equation 3.1. And hence it is necessary to analyze the data by deconvolution in order to extract the true lifetime.

When there are more than one upper level contributing to the observed fluorescence satisfying the condition that each of fluorescence decay times is longer than the duration of the excitation pulse, the fluorescence is given as  $N_{M} = \langle x_{1} \rangle$ 

$$I(t) = \sum_{i=1}^{N} a_i e^{\left(\frac{-t}{\tau_i}\right)}$$
(3.3)

where  $a_i$  and  $\tau_i$  are the amplitudes and average fluorescence lifetime of the  $i^{th}$  component contributing to the observed fluorescence.

In the above discussion, it is assumed that the excited states decay to ground state only through radiative emission in a collision free environment (mean free path for the gas is much larger than the dimension of the cell). But when collision among the gas molecules are appreciable, one has to account for it. And hence the equation 3.2 gets modified as

$$I(t) = I(0)e^{-(k_f + k_q[M])t}$$
(3.4)

for a single exponential decay. Here  $k_f = 1/\tau$  is the fluorescence decay constant,  $k_q$  and [M] are the self quenching rate constant and number density of gas molecules respectively.

Measuring the decay of fluorescence intensity as a function of time, the lifetime can be estimated under collision free condition using equations 3.2 and 3.3 depending on the number of excited levels involved in the fluorescence process. When collisions are not negligible, knowing the self quenching rate constant and the number of density of molecules, the fluorescence lifetime can be estimated using equation 3.4.

In our present experimental setup the excitation pulse width is around 8 nsec (FWHM) while the fluorescence decay time are  $\sim$ 100 nsec. Since the fluorescence signal is long compared to the decay time of the excitation pulse, the measured decay curve is a direct measure of the true fluorescence decay, and hence the problem of de-convolution of the fluorescence decay curve is not essential. Using equations 3.2, 3.3, 3.4, the true fluorescence lifetime can be directly estimated.

In the study of FEX spectra, the fluorescence signal was integrated in time to collect the total fluorescence signal at a given exciting wavelength. In the lifetime measurement, the fluorescence signal is measured as a function of time, i.e., the time resolved fluorescence decay curve. Using the PMT and a DSO (described in Chapter 2, sections 2.9.2, 2.10), the fluorescence decay curves were recorded. Depending on the signal-to-noise ratio, these time resolved curves were averaged over many laser shots.

In the measurement of lifetime, the laser light scattered from the walls of the chamber manifests itself as a sharp peak in the decay curve in spite of the fact that lot of care has been taken to minimize this (discussed in Chapter 2, section 2.4). Therefore, first few blocks of the decay curve had to be omitted before analyzing the signal. The choice of data blocks for omission from the decay curve was done taking into account the decay time for the scattered signal and was optimized for proper convergence of lifetime value. This optimum value was used for the data sets obtained in the same experimental conditions. This test was carried out for all data sets taking into account the change in experimental condition.

To estimate the lifetime from the fluorescence decay curve, a proper knowledge of the baseline is required. Few data blocks were stored before the start of the each exciting pulse to determine the exact baseline for the decay curve. The main contribution for this baseline shift was from the dark current of the PMT which was found to be constant in all experimental runs. To achieve the required signal levels, the fluorescence decay curves were averaged over many laser shots. Proper averaging of the decay curve without any distortion in the shape of the decay curve was achieved by using the photodiode signal as a time marker, thereby avoiding any shift in time over the averaging cycle. The experiment was carried out at different target gas pressures and at different exciting wavelengths. The relevant experimental parameters used in this work are given in Table 2.2.

In the present lifetime measurement, an initial 25  $\mu$ sec data were collected before the exciting laser pulse to determine the baseline for the decay curve along with the decay data. Then the measured decay curve is corrected for the scattering of incident laser light by removing around 2 to 3  $\mu$ sec data block from the initial part of the decay curve. The amount of data block removed is optimum for the present experimental set up which has been obtained from the convergence of the estimated lifetime from the fitting of decay curve. The corrected data sets are fitted and validated for the estimated parameter using the mathematical tools described in section 3.4. The estimated lifetime from the fitting techniques is plotted against excitation wavelength (lifetime spectra). These experiments were carried out at different pressures in the exciting wavelength region 399 to 490 nm in three different sets (instrumental resolution 0.01 nm) to study the pressure dependence of these lifetimes.

# 3.3 Self Quenching Rate Constant

Fluorescence from the excited molecules is collisionally quenched by the ground state molecules as well as by foreign gas molecules. When the gas pressure inside the fluorescence chamber is increased, the fluorescence also increases. After certain critical pressure, the NO<sub>2</sub> fluorescence signal is found to decrease with further increase in pressure as shown in Figure 3.1. At this pressure, the rate of self-quenching of the gas overtakes the fluorescence emission rate. The fundamental processes that occur are given below:

$$\begin{array}{cccc} A & \xrightarrow{h\nu} & A^* \\ A^* & \xrightarrow{k_f} & A + h\nu' \\ A^* + A & \xrightarrow{k_q} & A + A \end{array}$$

where  $k_q$  and  $k_f$  are the self-quenching rate constant and the fluorescence decay rate.

Let  $I_0$  be the intensity of incident light and  $I_f$  is the fluorescence intensity, then the quenching Q is defined by  $Q = I_f / I_0$ . The amount of light absorbed by the gas molecules is given by the following equation

$$I_a = k_f [A^*] + k_q [A^*] [A]$$
(3.5)

The fluorescence decay rate  $(k_f)$  and the self-quenching rate  $(k_q)$  can be estimated from the measurement of intensity of fluorescence as a function

of decay time after the excitation pulse as given by

$$I_f(t) = I_f(0)e^{-[k_f + k_q[M]]}$$
(3.6)

where the observed lifetime is given by

$$\frac{1}{\tau_{obs}} = k_f + k_q[M] \tag{3.7}$$

or

$$\frac{1}{\tau_{obs}} = \frac{1}{\tau_f} + k_q[M] \tag{3.8}$$

From the slope of the plot,  $\tau_{obs}$  versus [M], the electronic self-quenching rate constant can be estimated. The y-intercept gives the extrapolated zero-pressure lifetime of the electronic state involved in the fluorescence process. This plot is known as Stern-Volmer plot (S-V plots) (Stern and Volmer (1919)). The nature of the plot gives an evidence for the kind of collisional process involved.



Figure 3.1: Variation of NO $_2$  fluorescence with pressure at excitation wavelength 473.8nm

When the S-V plot is linear, the collisional process is a single step process. In some cases, it is seen that there is an upward curvature at the lower pressure end of the S-V plot. This would suggest that the collisional process is complicated and involves a multistep process (Keyser *et al* (1971), Donnelly *et al* (1979)). To obtain the plots, the estimates of observed lifetime at different target pressure are obtained from the fitting procedure. In the study of S-V plots, the knowledge of the absolute number density of the gas molecules are essential. The number density of the gas molecules in the fluorescence chamber is given by

$$n = n_0 \times \frac{P}{760} \times \frac{273}{T} \tag{3.9}$$

where  $n_o$  is the Loschmidt number ( =  $2.69 \times 10^{19}$  molecule/cc), P is the absolute pressure measured by the MKS capacitance manometer (described in Chapter 2, section 2.4) in Torr and T is the absolute temperature of the target gas. The temperature of the gas is assumed to be the same as that of the walls of the fluorescence chamber, *ie* the ambient room temperature 300 K.

# 3.4 Mathematical Tools

In the study of fluorescence decay curve, different numerical methods like the exponential sum fitting, linear least square fitting, residual autocorrection techniques were used to estimate the average lifetimes and the self-quenching rates. These techniques are briefly discussed below.

### 3.4.1 Exponential Sum Fitting Method

A fast numerical method for exponential sum fitting was used to analyze the fluorescence decay curve. This numerical technique was given by Wiscombe and Evan (1977). The salient features of this technique are:

<sup>1.</sup> It is well conditioned and guaranteed convergence to the best fit.

- 2. Automatically selects the optimal number of exponential terms as determined by data quality, round off error and use specified parameters.
- 3. It is constrained to the amplitude factor  $a_i > 0$ , the rate constant  $k_i \ge 0$  and  $\sum a_i = 1$  for the decay function of the type

$$y(t) = \sum_{i} a_{i} e^{-k_{i}t}$$
(3.10)

The overview of this method is shown in the flow chart (Figure 3.2).



Figure 3.2: Logical flow of exponential-sum fitting algorithm

The function used for fitting is

$$E(U) = \sum_{i=1}^{m} a_i e^{-k_i u_n}$$
(3.11)
Here  $u_n = n\Delta_u$  (n = 0, ..., N). Then the least square residual is given by

$$R_0 = \sum_{m=0}^{n} W_n \left[ T(u_n) - E(u_n) \right]^2$$
(3.12)

where  $E(u_n) = \sum_{i=1}^m a_i \theta_i^n$  and  $T(u_n)$  is the observed decay function. Here it is clearly seen that  $\theta_i \in [0,1]$  when  $k_i \ge 0$ 

The best fit is defined as the one which minimizes  $R_0$  over all allowable values of m,  $a_i$  and  $k_i$ . Here the standard linear least square normal equations for  $a_i$  ......  $a_m$  are

$$\frac{\partial R_0}{\partial a_i} \sim P(\theta_i) = 0 \quad [i = 1, 2, \dots m]$$
(3.13)

where

$$P(\theta) = 2\sum_{n=0}^{N} P_n \theta^n$$
(3.14)

and

$$P_n = W_n \left[ E(u_n) - T(u_n) \right]$$

The set of  $a_i$  which satisfy equation 3.13 clearly minimize  $R_0$  for fixed  $\theta$ . Here the  $P(\theta)$  is called the residual polynomial because its coefficient  $P_n$  are the (weighted) point by point difference between the fit and the data. For a best fit to the data (with  $a_i > 0$  and  $k_i \ge 0$ )

$$P(\theta_i) = 0, \text{ for } i = 1, ...m;$$
 (3.15)

$$P(\theta) \ge 0 \quad for \ \theta \in [0, 1] \tag{3.16}$$

In this method, E(u) is initialized to zero and a new  $\theta$  factor is added to minimize  $P(\theta)$  as shown in the flow chart (Figure 3.2). Then using the divided difference factorization and modifed Gram-Schmidt method (Wiscombe and Evan (1977)), the residual polynomial coefficients  $P_n$  and the residual  $R_0$  are obtained. Then the  $a_i$  and  $k_i$  are calculated. Here the dropping of negative  $a_i$  terms are carried out and the interaction is carried with addition of another  $\theta$  factor. If at any stage of this major iteration, all  $a_i$  are positive and the convergence criteria (equations 3.15, 3.16) are satisfied, then the process of coalescing is carried out to remove any closed pair of  $\theta_i$ . The condition for coalescence is supplied in the programme (user defined) depending on the resolution to which the data is acquired and the type of function one expects. This coalescing procedure also overcomes the numerical problem of double solution which in turn ill conditions the equation 3.13. The maximum absolute error and the sum error in the estimated fit E(u) is given by

$$e_{max} = max(0 \le n \le N) \mid T(u_n) - E(u_n) \mid$$
 (3.17)

$$e_{rms} = \left(\frac{1}{N+1}\right) \left\{ \sum_{n=0}^{N} \left[ T(u_n) - E(u_n) \right]^2 \right\}^{\frac{1}{2}}$$
(3.18)

Using this technique, a Fortran programme given by Wiscombe and Evan (1977) was used in a RISC 6000 machine to fit the experimentally obtained fluorescence decay curves in the present study. Since this method is initialized by an identically zero exponential sum E(U) = 0, the initialization difficulties are overcome. A typical fit of an observed fluorescence decay curve is shown in Figure 3.3(a).

#### 3.4.2 Residual Autocorrelation Study

The interpretation of multi-exponential fluorescence decay data often requires the knowledge of the model function being used to fit the data, as well as the numerical values of the pertinent parameters, which characterize the decay process. Different model functions can often be proposed which describe the data equally well within the experimental uncertainty. For example, a model function of two or three exponential components can be fitted to the same decay data with the RMS values of error being low. Also if the model function is well known, it may be difficult to evaluate satisfactorily the numerical values of the parameter which appear in the model function and differ from each other by small RMS values. This intrinsic difficulty in the analysis of decay curve sets a limit to the amount of information that can be extracted from the decay curve data alone. Hence the study of autocorrelation function of residuals set the criterion for the quality of the curve fitting.

For a good and realistic fit of the decay curve, the experimentally determined points should be scattered about the model function in a random fashion. The sum of the squares of the residual (R) will be then at a minimum and its magnitude is determined by the intrinsic noise of the measurement as shown in Figure 3.3(b). If a wrong model function is chosen for the decay data, the experimentally determined points would be scattered about the function in a non-random way. A suitable diagnostic tool for the randomness of scattering of the experimental points about a function suggested to describe the data is the autocorrelation function of the residuals (Grinvald and Steinberg (1974)). The auto correlation function C(t) of the weighted residuals is defined as

$$C(t_j) = \frac{\frac{1}{m} \sum_{i=1}^{m} (\omega_i)^{\frac{1}{2}} \Delta_i (\omega_{i+j})^{\frac{1}{2}} \Delta_{i+j}}{\frac{1}{n} \sum_{i=1}^{n} \omega_i \Delta_i^2}$$
(3.19)

where  $\Delta_i = F_c(t_i) - F_o(t_i)$ , *n* is the number of the time interval for which experimental data are available and *m* is the number of terms in the numerator and  $\omega_i$  is the weighting factor. The variable *j* can assume the value 1, 2, ....(n-m). It has been our practice to evaluate  $C(t_j)$  for *j* values ranging from 0 to n/2, so that it is always greater than n/2 (small values for *m* are undesirable since improper averaging for  $C(t_i)$  may result).

From equation 3.19, it is obvious that C(0) = 1. If the experimentally determined points scatter randomly about the model function and if m tends to infinity,  $C(t_j)$  will assume the values of zero for J = 0. But in practice due to the finite values of m,  $C(t_j)$  shows high frequency fluctuation for low amplitude about the zero-line, when plotted as a function of  $t_j$  as shown in Figure 3.3(c). If the scatter of the experimental points about a proposed decay function is not random,  $C(t_j)$  will exhibit pronouncedly

low frequency oscillations around the zero line. Such behaviour is a symptom of a poor choice of the proposed decay function. The shape of  $C(t_j)$  is more sensitive to such non-random deviation than the shape of  $\Delta_j$  and the sensitivity of  $C(t_j)$  with non-random fluctuations are high when the noise level is low.



**Figure 3.3:** The fluorescence decay curve showing details of exponential fitting. (a) The observed and the bi-exponential fitting with  $\tau_1 = 70.3 \ \mu \text{sec}$ ,  $\tau_2 = 27.4 \ \mu \text{sec}$  at excitation wavelength 474.0 nm. (b) The residual plot of the fitted data. (c) The autocorrelation plot of the residues.

This study of residuals were carried out for all decay curves fitted with the above mentioned exponential sum fitting technique to validate the fitted parameters.

#### 3.4.3 Least Square Fitting

According to the method of least square, the optimum values of the parameters  $a_i$  of a function  $y(n, a_i)$  are obtained by minimizing the Chi-square ( $\chi^2$ ) with respect to each other parameter simultaneously as given by.

$$\frac{\partial}{\partial a_j}\chi^2 = \frac{\partial}{\partial a_j}\sum_i \left[\frac{1}{\sigma_i^2}[y_i - y(x_i)]^2\right] = 0$$
(3.20)

#### **Linear Function**

For a linear function such as  $y(x) = a_0 + b_0 x$ , the probability  $P_i$  for making the observed measurement  $y_i$  assuming a Gaussian distribution with a standard deviation  $\sigma_i$  is given by

$$P_i = \frac{1}{\sigma_i \sqrt{2\pi}} exp\left\{-\frac{1}{2} \left[\frac{y_i - y(x_i)}{\sigma_i^2}\right]^2\right\}$$
(3.21)

The probability for making the observed set of measurement of N values of  $y_i$  is the product of these probability. Here the coefficients  $a_0$  and  $b_0$  for the given function are

$$P(a_0, b_0) = \pi \frac{1}{\sigma_i \sqrt{2\pi}} exp\left[-\frac{1}{2} \sum_i \left(\frac{\Delta y_i}{\sigma_i}\right)^2\right]$$
(3.22)

The best estimate for  $a_0$  and  $b_0$  are therefore those values which maximize the probability  $P(a_0, b_0)$ . This is the method of maximum likelihood with the assumption that the observed set of measurement is more likely to have come from the actual parent distribution.

In this method, the optimum fit to the data will be to minimize the weighted sum of squares of deviation  $\chi^2$  and hence to find the fit that produces the smallest sum of square or the least square fit. In our present

work the numerical routine written in Fortran language (Bevington (1969)) was used to fit a set of points to a straight line.

#### **Nonlinear Function**

In case of fitting a nonlinear function, it is not convenient to derive an analytical expression for calculating the parameter. Instead  $\chi^2$  is considered a continuous function of the n-parameter  $a_i$  describing a hypersurface in n-dimensional space and this space is searched for the appropriate minimum value of  $\chi^2$ . Here an algorithm which combines the technique of the gradient search with the method of linearizing the fitting function is used (Gradient - Expansion algorithm, Bevington (1969)). This algorithm is also called Marquardt Method (Marquardt and Donald (1963)). The algorithm of Marquardt method is as follows:

- 1. Compute  $\chi^2(a)$
- **2**. Start initially with  $\lambda = 0.001$
- **3.** Compute  $\delta(a)$  and  $\chi^2(a + \delta a)$  with this choice of  $\lambda$
- **4.** If  $\chi^2(a + \delta a) > \chi^2(a)$  increase  $\lambda$  by a factor of 10 and repeat the step(3)
- **5.** If  $\chi^2(a + \delta a) > \chi^2(a)$  decrease  $\lambda$  by a factor of 10
- 6. Consider  $a' = a + \delta a$  to be the new starting point and return to step(3) substituting a' for a.

This algorithm is shown in the flow chart (Figure 3.4).



Figure 3.4: Logical flow of non-linear least square fitting algorithm

Here in each iteration, the parameter increment  $\delta a_j$  are recomputed to optimize  $\lambda$ . As the solution approaches the minimum, the value of  $\lambda$  will decrease and the solution will locate the minimum with few iterations. A programme CURFIT (Bevington (1969)) was used to fit exponential (single) function in the present work. This least square fitting procedure was used to deconvolve single exponential decay curve which is combined with the instrumental response function. This process is known as deconvolution by iterative recombination method. Here the discrete convolution function for the observed decay function F(t) which is the convolution of the instrumental function R(t) with the fluorescence decay f(t) is given by

$$F(t) = \sum_{0}^{\infty} R(T)f(t-T)dT$$
(3.23)

where  $f(t) = a e^{-\frac{t}{\tau}}$ 

Using this equation of discrete convolution and the method of least square fitting procedure for nonlinear function (i.e. nonlinear least square fitting), the parameter  $\tau$  is estimated for the true decay function with the prior knowledge of the instrumental response function R(t). A Fortran routine was written for evaluating the parameter in the present work.

# **Chapter 4**

# **Error Analysis**

The systematic errors which were taken care and the lifetime estimates were corrected in the time resolved measurements of fluorescence decay curve are being discussed in detail in this chapter. Also, the most probable errors in the measurement of lifetime and self-quenching rate constants have been estimated in the present experiment.

## 4.1 Observation Geometry

In the time resolved measurements of fluorescence, it is important that the detector treats fluorescence from all excited molecules equally. In other words, the collection efficiency should be same for all the excited molecules emitting fluorescence. Thus the experimental setup must not allow detection of a larger percentage of radiation from long lived molecules, which move closer to the detector than from short lived molecules. Care must be taken to ensure that there is no net flow of excited molecules out of the region of observation. It is quite likely to make large errors in the measurement of decay constants in a collision free (*ié* at low target gas pressures) if the region is restricted to the dimension of the same order of magnitude as  $\tau v_p$  where  $\tau$  is the radiative lifetime and  $v_p = (2kT/m)^{1/2}$ , the most probable velocity of the target molecules. For the present experiment with NO<sub>2</sub>, at room temperature (300 K), with  $\tau = 75 \ \mu$ sec, this unit of length is

$$\tau v_p = (75 \times 10^{-6} sec)(3.3 \times 10^4 cm/sec) = 2.5 cm$$
(4.1)

It is obvious that fluorescence cell with observation region similar to  $\tau v_p$  (for NO<sub>2</sub>,  $\tau v_p = 2.5$  cm) in dimensions is simply inappropriate for time resolved fluorescence measurement under collision free condition. In the present experiment, the observation region was around 12 cm to minimize this effect. Sackett (1972) has discussed this problem in detail and has developed equations for the migration of longer lived molecules to the boundaries of a cylindrical observation region. Here, one can assume that all excited molecules move with a Maxwell-Boltzmann radial velocity distribution given by the equation

$$f(\nu) = \left(\frac{2v}{v_p^2}\right) exp\left(-\frac{v^2}{v_p^2}\right)$$
(4.2)

In a collision free environment emitting fluorescence which is exponential in decay, the fluorescence intensity originating between the line of interaction of the laser beam to the cell radius *P* is given by

$$I(t,p) = \frac{N_0}{\tau} exp\left(\frac{-t}{\tau}\right) \left[1 - exp\left(\frac{-p^2}{t^2 v_p^2}\right)\right]$$
(4.3)

If again all excited molecules which strike the walls are quenched, the above equation 4.3 is transformed to

$$I(T, R_0) = \frac{N_0}{\tau} exp(-T) \left[ 1 - exp\left(\frac{-R_0^2}{T^2}\right) \right]$$
(4.4)

where  $T = t/\tau$ ,  $R_0 = p/\tau v_p$  and  $R = \rho/\tau v_p$  and  $\rho$  is the variable distance of the emitting layer from the center. From equation 4.4, it is obvious that as

 $R_0 \rightarrow \infty$ , the decay becomes purely exponential and in this limit, integration over all time gives an integrated intensity of N<sub>0</sub>. The time dependent apparent lifetime may be calculated to be

$$\tau_{app}(T, R_0) = \tau \left\{ 1 + \frac{2R_0^2}{T^3 \left[ exp\left(\frac{R_0^2}{T^2}\right) - 1 \right]} \right\}^{-1}$$
(4.5)

This equation is valid only at pressures low enough so that the mean free path exceeds the cell radius. At higher pressure, collisions will interrupt the movement of the molecules away from the excitation axis. These collisions can also produce vibrational and electronic relaxations. This means that extreme care must be taken when making Stern-Volmer extrapolation to zero pressure.

In the present experimental setup, the fluorescence measurements were carried out at pressure ranging from 1 to 110 mTorr. The fluorescence chamber used in the present experiment is 15 cm in diameter and 25 cm in length. The field of view of the collection optics could view a flourescing column of 12 cm inside the chamber. This value is optimized so as to minimize the geometrical effect and to collect more fluorescence signal with reduced scattered laser light from the walls of the chamber.

## 4.2 Bandwidth of Detection Electronics

Both high and low frequency electronic roll-off can affect the observed fluorescence decay signal. In the present experiment, the bandwidths of the electronics used were from DC to 200 MHz. Hence the bandwidth has no effect at time scales greater than few nanoseconds. Thus the bandwidth of detection electronics play insignificant role in distorting the decay signal.

## 4.3 Digitization Error

The analog signal from the detector (photomultiplier tube) is sampled and digitized using a fast digital storage oscilloscope. Errors can be introduced because of digitization. This error, called digitization error, is severe at very low signal-to-noise ratio. In the present work, an 8-bit digitization of the analog signal was carried out by the oscilloscope. Also the signal levels encountered here after preamplification were quite high as shown in Table 2.2. Therefore the digitization error is insignificant in the present work.

## 4.4 **Baseline Estimation**

In the measurement of fluorescence decay intensity as a function of time I(t), it is important to know the precise level of the output signal in the absence of any signal on it. The main sources which contribute to the error in baseline estimate are baseline offset and noise (Dowell and Gillies (1991)). For example, a baseline error of  $\pm$  0.1% would give an error of  $\pm$  0.25  $\mu$ sec in the estimation lifetime of 70  $\mu$ sec. In the present work, the baseline for the decay curve is measured before the laser pulse excitation, thereby accurately determining the baseline for each set of data acquisition. Also any offset of the baseline was corrected in the acquisition system before the measurement of the fluorescence signal. Any residual baseline offset was further taken care in the fitting procedure, where the residual baseline is also estimated.

#### 4.5 Time Base

The Tektronix TDS540 digital storage oscilloscope was used for sampling and digitization of the fluorescence signal. The time base for this system is determined by the crystal oscillator which has an uncertainty much less than 1:10. This oscilloscope was factory calibrated for time base.

# **4.6** $NO_2 \rightleftharpoons N_2O_4$ Equilibrium Constant

In the estimation of self-quenching rate constant and the zero-pressure intercept, the knowledge of the number density of molecule inside the fluo-rescence chamber is essential. The main sources of systematic error in the estimation of number density are from  $NO_2 \Rightarrow N_2O_4$  dimer formation and, the thermal transpiration effect while using an MKS capacitance manometer to measure the absolute pressure.

It is known that  $NO_2$  forms its dimer  $N_2O_4$  as given by the reaction

$$NO_2 + NO_2 \rightleftharpoons N_2O_4$$
 (4.6)

The reaction rate for the dimer formation is sensitive to temperature and pressure (Amoruso *et al* (1993)) and hence complicates the measurement of NO<sub>2</sub> partial pressure. The amount of NO<sub>2</sub> present in the fluorescence chamber is determined by the self-reaction (equation 4.6) whose equilibrium conditions are controlled by the reaction constant  $k_p$  given as

$$k_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}}$$
(4.7)

where  $P_{NO_2}$  and  $P_{N_2O_4}$  are the partial pressures of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub>. Here the estimation of the reaction constant  $k_p$  is critical for the determination of the partial pressure of NO<sub>2</sub> in a mixture of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub>. In the literature,

the value of  $k_p$  has been estimated by chemical, theoretical and spectroscopic methods. Verhoek and Daniels (1931) chemically estimated the value of  $k_p$ . Novick *et al* (1972) used thermodynamic constant obtained from the molecular geometry and the vibrational frequencies to estimate  $k_p$ . The estimation of  $k_p$  was obtained spectroscopically by measuring the partial pressure of NO<sub>2</sub> with the assumption that the absorption feature of the two gases do not overlap in the wavelength region considered (Jacob (1959), Dunn *et al* (1962), Harris and Churney (1967), Chao *et al* (1974)). Amoruso *et al* (1993) estimated  $k_p$  and its temperature dependence using spectroscopic method. They calculated the variation of  $k_p$  with T after measuring the total pressure of the gas mixture at different temperature ranging from 220 to 300 K and best fitting the parameter  $k_{p,298.16}$ and  $\Delta H$  (which are the equilibrium constant at temperature T = 298.12 K and standard enthalpy change respectively) involved in the Vant-Hoff law where

$$k_{p,T} = k_{p,298.16} \ exp\left(\frac{\Delta HT}{R} - \frac{298.16}{298.16T}\right)$$
(4.8)

where *R* is the gas constant. They obtained the values for  $k_p$  and  $\Delta H$  in their experiment as  $k_{p,298,16} = 0.1362$  atm and  $\Delta H = 13668.5$  cal/mol

The value of  $k_{p,300}$  was estimated from equation 4.8 using the values of  $k_{p,298.16}$  and  $\Delta H$ . Using this value of  $k_{p,300}$  in equation 4.7, the partial pressure of NO<sub>2</sub> in the fluorescence chamber was determined. The plots in Figure 4.1 and Figure 4.2 show the variation of  $k_p$  with temperature and the required correction factor for partial pressure of NO<sub>2</sub>. Its is seen that with increase in temperature, the equilibrium constant  $k_p$  also increases.

The maximum error involved in the estimation of NO<sub>2</sub> partial pressure in NO<sub>2</sub>  $\Rightarrow$  N<sub>2</sub>O<sub>4</sub> mixture at room temperature was around 0.2% in the pressure range 1 to 110 mTorr.



Figure 4.1: Variation of equilibrium constant K<sub>P</sub> with temperature



Figure 4.2:  $NO_2 \rightleftharpoons N_2O_4$  equilibrium correction for  $NO_2$  at 300 K

## 4.7 Thermal Transpiration Correction

In the present work, the absolute measurement of target was carried out using an MKS Baratron capacitance manometer. The detailed functioning of the Baratron capacitance manometer has been discussed in detail in Chapter 2, section 2.6.

In order to stabilize the diaphragm of the Baratron head against the thermal expansion due to temperature variations, the Baratron head was always maintained at a steady elevated temperature (usually at 318 K). Due to the difference in temperature between the Baratron head and the fluorescence chamber, there exists thermal transpiration effect which leads to overestimates of the target pressure in the fluorescence chamber. Hence the pressure measured by Baratron capacitance manometer need to be corrected for this effect.

#### 4.7.1 Thermal Transpiration Effect

When two vessels containing a gas at pressures  $P_1$  and  $P_2$  are held two different temperature  $T_1$  and  $T_2$  respectively and are connected by a tubing of diameter d, it is shown from kinetic theory that  $P_1 = P_2$  when the mean free path of the gas molecules are very small compared to the diameter of the tube (MFP  $\lambda \ll d$ ). But when the mean free path is greater than the diameter of the tube, then there exists a thermo-molecular flow of gas from the colder vessel to the hotter vessel. This effect is known as thermal transpiration effect. From the kinetic theory, it may be shown that  $P_1 \neq P_2$ when  $\lambda \gg d$ , but is given by

$$P_1 = P_2 \sqrt{\frac{T_1}{T_2}}$$
 (4.9)

Also at intermediate pressures, the ratio of  $P_1$  and  $P_2$  will be between unity and the value given by equation 4.9.

The effect of thermal transpiration has been well studied by Dushman (1962) and Knudsen (1910). They showed that the effect can be explained by two opposing flows of gas, an axial flow from hotter to colder region and a surface flow along the walls in the reverse direction. Due to these flows, there exists a forward momentum transfer towards the hotter side. This effect becomes significant when the temperature difference is large and the pressure involved are small.

In recent years, extensive theoretical studies have been undertaken on thermal transpiration which has enabled the magnitude of the effect to be calculated for a wide range of temperatures, pressures and gases. (Annis (1972), Loyalka (1971, 1975) and Storvick et al (1978)). These methods involve numerical solutions of complex integral equation and therefore not much suited for routine use in laboratory. Hence empirical equations were developed by various workers to calculate the magnitude of the thermal transpiration effect and are thus useful for laboratory work. One of the widely used empirical relation is Liang's equation (Liang (1953)) and Takaishi-Sensui equation (Takaishi and Sensui (1963)). Baldmin and Gaerttner (1973) conducted an extensive study on this effect with capacitance manometer and found that their experimental result did not follow the Liang's equation. Poulter et al (1983) conducted similar experiments and found that the results from the empirical equation given by Takaishi and Sensui (1963) fitted their data well. According to Poulter et al (1983), this equation could satisfactorily represent thermal transpiration effect of gas in MKS Baratron capacitance manometer.

Takakaishi-Sensui equation is given by

$$\frac{P_2}{P_1} = \frac{A X^2 + B X + C\sqrt{X} + \sqrt{T_2/T_1}}{A X^2 + B X + C\sqrt{X} + 1}$$
(4.10)

where

$$A = A^{*}(T^{*})^{-2}$$
$$B = B^{*}(T^{*})^{-1}$$
$$C = C^{*}(T^{*})^{-0.5}$$
$$T^{*} = 0.5(T_{1} + T_{2})$$

$$X = 0.133 P_2 d$$

Here  $P_1$  and  $P_2$  are the pressures in Pascal, d is the diameter of the tube

in meter,  $A^*$ ,  $B^*$  and  $C^*$  are the reduced constants given by

$$\begin{aligned} A^* &= 1.4 \times 10^4 \, \exp(1.17 \times D \times 10^{10}) \\ B^* &= 5.6 \times \, \exp(1.4 \times D \times 10^{10}) \\ C^* &= (1.10 \times 10^{-8}/D) \, - \, 14 \end{aligned}$$

where D is the molecular diameter in meter. D is calculated using kinetic theory expression for viscosity of gas as

$$\eta = \frac{5}{16 D^2} \left(\frac{m \, k \, T}{\pi}\right)^{\frac{1}{2}} \tag{4.11}$$

where m is the molecular weight (in kilogram),  $\eta$  the viscosity (in poise) and k is the Boltzmann constant

In our present work, to estimate the thermal transpiration effect, the Takaishi-Sensui equations were used. The MKS Baratron capacitance manometer was connected to the fluorescence chamber by a copper tube of 6 mm diameter. The thermal transpiration correction for NO<sub>2</sub> was calculated at room temperature (300 K) in the pressure range of 1-110 mTorr. This correction factor versus the pressure is shown in Figure 4.3. It is found that at room temperature, the thermal transpiration effect for NO<sub>2</sub> at 1 mTorr pressure is 2.84% and is about 2.78% at 15 mTorr. The molecular diameter of NO<sub>2</sub> was determined by the equation 4.11 using the viscosity data available from *CRC Handbook of chemistry and physics* (1984). The plot in Figure 4.3 shows the % of thermal transpiration correction  $(1 - P_{cmr}/P_{brt}) \times 100$  versus the measured pressure  $P_{brt}$  for NO<sub>2</sub>. P<sub>cmr</sub> is the actual pressure in the chamber. Since the thermal transpiration correction is most significant at low pressures, only the region 0-15 mTorr is shown in Figure 4.3.



Figure 4.3: Thermal transpiration correction for NO<sub>2</sub>

### 4.8 Error in Lifetime Measurement

Error contribution from different sources are tabulated in Table 4.1 The coherent sum of all these errors gives an estimate of the upper limit of the actual error. Here in the life time measurement, the estimated lifetime are classified on the range as (i) 1-3  $\mu$ sec (ii) 20-40  $\mu$ sec and (iii) 70-120  $\mu$ sec. The coherent sum all error are  $\pm 23.0\%$ ,  $\pm 5.6\%$  and  $\pm 5.0\%$  for the above ranges respectively. The root mean square (RMS) errors are  $\pm 20.2\%$ ,  $\pm 3.9\%$  and  $\pm 3.3\%$  respectively.

# 4.9 Error in Self Quenching Rate Constants and Zero-Pressure intercept

The main sources of error in the estimation of self quenching rate constants and zero-pressure intercepts were from (i) the NO<sub>2</sub> number density (statistical error in of the pressure measurement using MKS capacitance manometer), (ii) the error in the estimation of lifetime and (iii) the statistical error in fitting (scatter of S-V plots). The most probable or RMS

	Life Times		
Error	$1-3\mu$ sec	$20-40\mu sec$	$70-120\mu sec$
Sampling	$\pm 3\%$	$\pm 3\%$	$\pm 3\%$
Statistics			
Curve	$\pm 20\%$	$\pm 2.6\%$	$\pm 2\%$
Fitting			
Coherent	$\pm 23\%$	$\pm 5.6\%$	$\pm 5\%$
Sum			
Incoherent	$\pm 20.2\%$	$\pm 3.9\%$	$\pm 3.3\%$
Sum			

**Table 4.1:** The most probable error in the measurement of life times in thepresent experiment.

error in the estimation of self quenching rate constants and zero-pressure intercept were found to be  $\pm 7\%$  and  $\pm 5\%$  respectively.

# **Chapter 5**

# **Results and Discussion**

Nitrogen dioxide was taken up for the present study. The importance of this study has been discussed in detail in Chapter 1. In the present study, the total fluorescence measurement and lifetime studies were carried out at different target gas pressures (1 mTorr - 110 mTorr) at room temperature (300 K) in the excitation regions (i) 399 to 416 nm (at 0.2 nm interval), (ii) 423 to 462 nm (at 0.5 nm interval), (iii) 465 to 590 nm (0.2 nm interval). In all these studies, the instrumental resolution was of 0.01 nm.

# 5.1 Fluorescence and Lifetime Study

#### 5.1.1 Excitation Region 465-490 nm.

The measurement of total fluorescence and study of time resolved decay curves were carried out in the region 465 to 490 nm at an interval of 0.2 nm at gas pressures 1, 3, 5, 10, 15, 51, 81 and 110 mTorr. The fluorescence lifetimes were computed using the multi-exponential fit routine

as discussed in Chapter 3, section 3.5. Around 1008 fluorescence decay curves were analyzed in this region. The fluorescence excitation spectrum, which is a plot of total fluorescence intensity versus excitation energy is shown in Figure 5.1 at different pressures. Excitation spectra were constructed by measuring the area under each of the decay curves at different wavelength for each of the pressures used in the experiment. These spectra, though measured at low resolution, could help in explaining the lifetime spectra wherever possible. From these, spectra it was evident that the overall shape of the spectrum is same for 1 and 3 mTorr pressure. But at 5 mTorr pressure, the shape of the spectrum changed at the lower wavelength side. As the pressure is further increased beyond 5 mTorr, the overall shape remained nearly the same. But on careful examination of the relative intensities of the banded structure with pressure, it is seen that few of the structures were quenched, *ie* there was a decrease in fluorescence intensity with increasing pressure as one expects while the fluorescence intensity of few other bands increase with pressure. This effect is pronounced at pressures greater than 3 mTorr. This clearly suggests that collisional depopulation of levels and repopulation of intermediate levels occur with increasing pressure which contribute to the total fluorescence. The observed fluorescence excitation spectra is in agreement with those obtained by Douglas and Huber (1965) at 3 mTorr pressure.

From the analysis of the fluorescence decay curve in this region, it was seen that at 1 and 3 mTorr pressure, the fluorescence decay is purely exponential. The values of this fluorescing component varies between 26 to 40  $\mu$ sec. This component is termed as the "static component". The static component was also seen at higher pressures. As the pressure is further increased, the component gets quenched to lower values towards a collisionally stabilized limit. The variation of the static component with increasing excitation energy is shown in Figure 5.2 (a) and (b) for different pressures. The estimated values of lifetimes (static component) are tabulated in Table 5.1. It is seen that the magnitude of variation is more at lower pressure than at high pressure where they were nearly constant.



Figure 5.1: Fluorescence excitation spectra of  $NO_2$  at different gas pressures in the excitation region 465 to 490 nm.

The lifetime components at 1 and 3 mTorr does not show any systematic variation with increasing wavelength. At few wavelengths, the magnitude of variation was more than 50% of the average value.

At 5 mTorr pressure, a long lifetime component in the range of 70 to 120  $\mu$ sec was seen at three different excitation wavelengths (466.8, 473.8 and 474 nm). The strength of these components varied from 3.7 to 12.4% of the total in terms of amplitude. Paech *et al* (1975) studied this region at collision-free condition using free jet expansion and found that at 488 nm, there are two components responsible for fluorescence with lifetime 28 and 76  $\mu$ sec. Our present observation is in agreement with those of Paech *et al* (1975) at pressure greater than 3 mTorr. We also find these two components at a few excitation wavelengths. But at low pressures (3 mTorr and below), we do not find the long lived components in these regions. This might be due to the finite pulse width of around 8 nsec being used in the present experiment which is very small as compared to the fluorescence lifetime. Paech *et al* (1975) used around 0.1  $\mu$ sec pulse width



Figure 5.2: The fluorescence lifetime spectra of the static component in  $NO_2$  at different gas pressures in the excitation region 465 to 490 nm.

to excite the molecules and also studied the lifetime as a function of excitation pulse width. The present observation is in agreement with Donnelly and Kaufman (1978) who observed that the fluorescence decay is multiexponential at pressure around 5 mTorr and reported that these long lived components varied from 88 to 120  $\mu$ sec as the excitation wavelength was increased from 473 to 562 nm.

From the excitation spectra, it is seen that there is a rapid change in fluorescence intensity with excitation wavelength and pressure. And from the lifetime analysis, the fluorescence decay is found to be multi-exponential at 5 mTorr pressure. It could be safely concluded that even though the electronic state rearrangements are initiated through collision resulting in the redistribution of energy of the excited state, its effects on quenching of the states are pronounced at pressures larger than 5 mTorr but are weak at lower pressures. This observation is in agreement with the observation of Donnelly and Kaufman (1978). They observed long lived components at few excitation wavelengths. The static component which is seen in the entire excitation region and at all pressures is attributed to the emission from  ${}^{2}B_{2}$  state which is highly perturbed due to inter-electronic mixing. The  ${}^{2}B_{2}$  state which is a bent excited state mixes with the highly dense vibrational levels of the ground state  ${}^{2}A_{1}$  due to which the electronic spectra gets complicated (break-down of B-O approximation). The radiative lifetime of these perturbed  ${}^{2}B_{2}$  state are lengthened and are very much different from the levels of unperturbed state (Paech *et al* (1975), Douglas (1966) and Gangi and Brunelle (1971)).

At pressures greater than 5 mTorr, we find the occurrence of shorter components at different excitation wavelengths whose lifetime vary between 1 to 4  $\mu$ sec and their frequency of appearance increases with pressure. The lifetime of these components at different pressures are tabulated in Table 5.2. The values of these components were seen to be quenched with pressure. At pressures 81 and 110 mTorr, the value of lifetime decreases to 0.1  $\mu$ sec. However, their frequency of appearance at different excitation wavelength up to 81 mTorr was found to increase as the pressure was increased. At 110 mTorr, collision frequency becomes so large that the collision time is comparable or of the same order as the fluorescence lifetime and therefore the frequency of occurrence of these short components are seen to decrease at 110 mTorr pressure. It was also seen that at higher pressures, the total fluorescence emission at different wavelengths changes with pressure. Hence one can safely suggest that these components are from the collisionally repopulated intermediate state. These components were studied by Sackett and Yardley (1971), Solarz and Levy (1974) and Paech et al (1975) under different experimental conditions and at few excitation wavelengths only but the pressure dependence of these short components were not carried out by any group. These short lived components are attributed to the  ${}^{2}B_{1}$  state which is perturbed due to Renner-Teller coupling. The  ${}^{2}B_{1}$  state is a linear excited state which when undergoing bending vibration gets coupled to the highly dense vibrational levels of the ground state  ${}^{2}A_{1}$  manifesting itself as a complicated irregular vibrational structure of the electronic spectra (clear break-down of B-O approximation) as suggested by Douglas (1966), Paech et al (1975) and Gangi and Burnelle (1971).

#### 5.1.2 Excitation Region 423-462 nm

The measurement of total fluorescence and time resolved decay curves of NO<sub>2</sub> in the excitation region 423 to 462 nm at an interval of 0.5 nm were carried out at gas pressures 1, 3, 5, 7, 10 and 15 mTorr. Around 468 fluorescence decay curves were obtained and analyzed. All the experiments were carried out at room temperature (300 K). The fluorescence excitation spectra are shown in Figure 5.3 for different gas pressures. From these fluorescence excitation spectra drawn at different pressures, it is evident that the general shape of the spectra is insensitive to the pressure. It is nearly similar to the absorption spectra which is irregular and shows distinct structures superimposed on a broad continuum. The complexity of this spectrum clearly suggests that the excited states involved in this region are highly perturbed. The spectra obtained in the present study are much similar to those obtained by Douglas and Huber (1965) at 3 mTorr pressure of NO<sub>2</sub>. Lee and Uselman (1972) reported that the fluorescence efficiency of the electronically excited NO<sub>2</sub> is found to be independent of the excitation wavelength in the region 415 to 520 nm and observed no evidence of any time structure which in turn indicates that short lived fluorescing components do not contribute to the total fluorescence or they are absent in this region. They suggested that  ${}^{2}B_{1}$  state is responsible for the total fluorescence in this region. In the present study of NO<sub>2</sub> lifetimes at different gas pressure, we find that at low pressure (1, 3 mTorr), the contribution is mainly from a single excited level. But at pressure greater than 3 mTorr (5, 7, 10, 15 mTorr), we do find the presence of short lived components whose frequency of occurrence increases with pressure. This clearly suggests that these components are collisional in origin.

The lifetime spectra of the static component which is present in the



Figure 5.3: Fluorescence excitation spectra of  $NO_2$  at different gas pressures in the excitation region 423 to 462 nm.

entire region are shown in Figure 5.4 against excitation energy at different pressure. These components are seen at all wavelengths and are found to be quenched with increasing pressure. The fluorescence lifetime of these components vary between 39 to 46  $\mu$ sec at 1 mTorr (nearly collision free pressure). As the pressure is increased, the variation in the lifetime was seen to be large and it decreased in value due to collisional quenching. The estimated values of the lifetime (static component) are tabulated in Table 5.3. Using phase shift technique, Abe (1973) and Abe et al (1971, 1974) measured the fluorescence lifetime of NO<sub>2</sub> in this region. Our lifetime data is in agreement with them. Sackett and Yardley (1972) found that there were some components seen in this region whose values were between 60 to 70  $\mu$ sec. Again Sackett and Yardley (1970) found that the value of radiative lifetime increases with excitation energy. These workers used phase-shift technique to measure lifetime. In the present work, where the pulsed excitation technique (direct observation of decay) is employed, the obtained lifetimes were lower in value than those obtained by others. This is attributed to the short pulse width ( $\sim$  8 nsec) used to measure lifetime in  $\mu$ sec time scale. Here we do not attribute this discrepancy to the geometric

effect as sufficient care has been taken (discussed in Chapter 2) in this direction. Also we do not find any trend in the lifetime spectra. These static components are attributed to the fluorescence from the severely perturbed  ${}^{2}B_{1}$  state to the ground state  ${}^{2}A_{1}$  (Schwartz and senum (1975)). Since  ${}^{2}B_{2}$ state also overlap with  ${}^{2}B_{1}$  state, the contibution from  ${}^{2}B_{2}$  state cannot be neglected in this region (Sackett and Yardley (1972)). Douglas and Huber (1965) studied the absorption spectra of  $NO_2$  in the region 370 to 460 nm. According to Douglas and Huber (1965),  ${}^{2}B_{1}$  is a linear excited state above the bent ground state  ${}^{2}A_{1}$ . This  ${}^{2}B_{1}$  state can undergo bending vibration and can mix up with the highly dense vibrational levels of the ground state to form  ${}^{2}\Pi_{u}$  state of the molecule in linear configuration (Renner-Teller effect). Due to this mixing up, the radiative lifetime of these perturbed  ${}^{2}B_{1}$ state are lengthened and are very much different for the levels of these state. This explains the anomalous long lifetime in NO<sub>2</sub>. The Renner-Teller effect which is a break down of the adiabatic B-O approximation is the consequence of the coupling between electronic and bending motion in linear triatomic molecule. Here, the coupling is between  ${}^{2}B_{1}$  which is linear excited state getting coupled to the highly dense vibrational level of the  ${}^{2}A_{1}$  ground state manifesting itself as a complicated irregular vibrational structure of the electronic spectra.

Alongwith the static component in this region, we do find short lifetime components superimposed on static component of lifetime. These components are absent at 1, 3 mTorr pressure. At 5 mTorr pressure, these components start appearing and then frequency of occurrence increases with pressure. The lifetime of these short components vary between 1 to 4  $\mu$ sec. The estimated value and their occurrence at different pressures are given in Table 5.4. The values of the observed short lived components are in agreement with those obtained by Sackett and Yardley (1971) in the excitation region 425 to 460 nm. These components are attributed to the fluorescence from the unperturbed  ${}^{2}B_{1}$  state. Similar reports were published by Smalley *et al* (1975). Earlier Sakurai and Capelli (1970) and Keyser *et al* (1971) concluded from the fluorescence studies of NO<sub>2</sub> that



Figure 5.4: The fluorescence life time spectra of the static component in  $NO_2$  at different gas pressures in the excitation region 423 to 462 nm.

no NO<sub>2</sub> excited state in the visible radiation can have lifetime in the order of 1  $\mu$ sec. The present work and the work of Sackett and Yardley (1971) disproves their conclusion and confirms the presence of unperturbed  ${}^{2}B_{1}$ state in this region. The discrepancy for this observation may be due to the wide bandwidth of excitation employed, which excites a proportionally large member of the mixed longlived states. From the present work with narrow band excitation, it is clear that  ${}^{2}B_{1}$  state is highly perturbed and also we find unperturbed  ${}^{2}B_{1}$  levels at few excitation wavelength.

As pressure is increased, it was seen that the frequency of occurrence of these components also increased. This suggests that there are collision induced transitions. Jortner and Berry (1968) suggested that this could be due to intra-molecular processes. The dense manifold of states which are not optically connected to the ground state are collisionally populated at finite pressure and later undergo transition to the ground state. But this is not again evident from the fluorescence excitation spectra in the present work which are nearly insensitive to pressure, preserving their general shape. But the lifetime spectra in this region at different pressure clearly indicate the role of collision as these components start appearing more frequently with increasing pressure at the longer wavelength side. Hence one can safely state that these components are from those levels which are collisionally populated at finite pressure. In this region of study, we find that  ${}^{2}B_{1}$  is the state mainly responsible for fluorescence and this state is severely perturbed since its levels mix with the highly dense vibrational levels of the ground state  ${}^{2}A_{1}$  (break down of B-O approximation: Renner Teller effect). This mixing of levels manifests itself in the anomalous density and complexity of the absorption spectrum and hence in lengthening of lifetime for the mixed state. The unmixed state would have simple absorption spectrum and the radiative lifetime would be of shorter value than those from the mixed state as we observe in the present region of excitation 423 to 462 nm.

Alongwith the static and short components, we do find still shorter components at higher pressures which show similar trend as that for the short components discussed above. The lifetime of these components were of the order of  $10^{-7}$  sec. The value and occurrence of these components are tabulated in Table 5.5. Creel and Ross (1969) studied the photodissociation of NO<sub>2</sub> the region 457.9 to 630 nm by measuring the O<sub>2</sub> pressure produced during the photolysis of NO<sub>2</sub> and showed that their observation is consistent with the collision of excited state molecule with the ground state at high pressure as given by

$$NO_2^* + NO_2 \rightarrow 2NO + O_2$$

In the present work, the detailed origin of these components could not be studied. But it is evident that they appear at high pressures. Hence we attribute these components to arise from the collisionally populated intermediate states.

#### 5.1.3 Predissociation Region 399-416 nm

The measurement of total fluorescence and time resolved decay curves of NO<sub>2</sub> was carried out in the first predissociation region 399 to 416 nm at 0.5 nm interval. The measurements were made at different gas pressures 1, 3, 5, 7, 10 and 15 mTorr. Around 516 fluorescence decay curves were obtained and analyzed. The fluorescence excitation spectra taken at different gas pressures are shown in Figure 5.5. It is known that NO<sub>2</sub> photodissociates at wavelength less than 398 nm. From the fluorescence excitation spectra, it is clearly seen that at 399 nm, the total fluorescence intensity is nearly zero and increases steeply above 399 nm. This is because the fluorescence quantum efficiency  $\phi_f$  starts diminishing below 416 nm and falls steeply as we approach the photodissociation limit at 397.9 nm. This is very much in agreement with Douglas and Huber (1966). From these fluorescence excitation spectra at different pressures, it is evident that the overall shape of the spectrum is nearly constant. But on examination of the relative intensities of the banded structure at different pressures, it is seen that few of the structures are quenched, *ie* a decrease is observed in the fluorescence intensity with increasing pressure but the fluorescence intensity of some of the banded structure increases. This effect is pronounced at gas pressures greater than 5 mTorr. It is known that  $NO_2$ undergoes predissociation near 399 nm. As pressure is increased, collision starts depopulating the excited states. But at low pressure the predissociation process overcomes the collisional depopulation process. With increase in pressure, the two processes compete with each other in the depopulation of excited states. At high pressures, collisional depopulation is stronger than the predissociation process. Due to the presence of these processes, the fluorescence quantum yield is nearly zero at 399 nm and increases to 100% at 415 nm. Uselmann and Lee (1976) reported that the fluorescence quantum yield decreases with increasing pressure due to self quenching but the shape of the excitation spectra is insensitive to pressure variation. But present work disproves that the shape of the excitation spectra are insensitive to pressure variation where the relative intensities of the bands change with increasing pressure. This suggests that at high pressure collision plays an important role. This is further evident from the lifetime study as discussed below.



Figure 5.5: Fluorescence excitation spectra of  $NO_2$  at different gas pressures in the predissociation region 399 to 416 nm.

The lifetime spectra of the static component which is present in the entire region are shown in Figure 5.6 against excitation energy at different pressures. These components seen at all wavelengths are found to be quenched with increasing pressure. The observed lifetime is found to increase with increase in excitation wavelength till 405 nm and thereafter lifetime gets stabilized as seen in Figure 5.6. The estimated values of the lifetime (static) components are given in Table 5.6. Here it should be noted that as the pressure is increased, the variation in the lifetime also increases. The fluorescence quantum efficiency  $\phi_f$  is nearly zero at 399 nm and increases to 100% at 415 nm (Uselmann and Lee (1976)). At gas pressure of 1 mTorr, the fluorescence decay curves were purely exponential with lifetime varying from 35 to 42  $\mu$ sec. At 3 mTorr pressure, the fluorescence decay is again a simple exponential but the quenching of lifetime near the photodissociation limit is found to increase. At pressures above 3

mTorr, the fluorescence decay is found to be non-exponential at few wavelengths. The present observations are in agreement with those of Donnelly et al (1979). They attributed this variation in lifetime to emissions from the perturbed  ${}^{2}B_{2}$  state to the lower state  ${}^{2}A_{1}$  and argued that the lengthening of lifetime is due to the mixing of  ${}^{2}B_{2}$  with highly excited vibrational levels of the  ${}^{2}A_{1}$  state. In the present work, these long lived components varying between 80-120  $\mu$ sec are seen at different excitation wavelengths which is due to the inter-electronic mixing of  ${}^{2}B_{2}$  state with  ${}^{2}A_{1}$  ground state. The observed static component in the present experiment is attributed to the emission from perturbed  ${}^{2}B_{1}$  state which is coupled to the  ${}^{2}A_{1}$  ground state through mixing of vibrational levels (Renner-Teller effect). This is in agreement with the work of Douglas and Huber (1965) who confirmed that  ${}^{2}B_{1}$  state is mainly responsible for the total fluorescence in this region and above it accounts much for the complex structure in this region. Uselmann and Lee (1976) used phase shift technique to study this predissociation region and found that the lifetime is independent of the excitation wavelength and is shorter at higher pressure. This observation is true only at low pressure (1 mTorr) in the present work. But at pressures greater than 1 mTorr, we find that the lifetime is reduced to a lower value but increased with excitation energy. The variation in lifetime is pronounced at wavelengths below 405 nm and is found to stabilize at wavelengths above 405 nm. At low pressures, the predissociation processes are responsible for shortening of observed lifetime. As the pressure is increased, the collisional depopulation also occurs alongwith the predissociation process, and the magnitude of collisional depopulation increases with pressure and is much stronger than the predissociation processes at higher pressures. This leads to the decrease in observed lifetime with larger and pronounced variation near 399 nm. As pressure is increased, the variation of lifetime below 405 nm also increases. This is in agreement with the findings of Schwartz and Johnston (1969). This implies that the probability for collisional quenching was not the same for every state since the lifetime would tend towards a strict collision limited value as seen in region 465 to 490 nm. Here one should account for the predissociating species in this region

or for any pressure dependent cascade process which populated some of the intermediate levels.



Figure 5.6: The fluorescence life time spectra of the static component in  $NO_2$  at different gas pressures in the predissociation region 399 to 416 nm.

Along with the static component and the few long lived components, we find very short fluorescing components whose lifetime are  $10^{-7}$  sec. This has been attributed to the predissociation of NO<sub>2</sub> in this region which may happen through any of the following channels :

$$NO_2^* \rightarrow NO + O$$
$$NO_2^* + NO_2 \rightarrow 2NO + O_2$$
$$NO_2^* + NO_2 \rightarrow NO_2 + NO_2$$

These very short fluorescing components did not show any pressure dependence or any special trend of occurrence. Uselmann and Lee (1976) reported from their studies using phase shift techniques that there is a very short lifetime component which does not show collisional fluorescence stabilization and confirmed that these short-lived components are from the predissociating species. Hence we attribute our observation of these short lived components to predissociation of  $NO_2$  in this region. Uselmann and Lee (1976) studied the molecular predissociation of  $NO_2$  using fluorescence excitation spectroscopy and reported that predissociation dominates over the emission processes below 410 nm. This photodissociation behaviour is ascribed to case II photodissociation by vibration (Herzberg (1966)). In this case, the dissociation continuum belongs to the same electronic state but joins on to a lower dissociation limit than that to which the series of discrete levels converge. This happens through the change in the vibrational motion of the molecule.

# 5.2 Quenching Studies in the Region 399-490 nm

The electronic self-quenching studies of  $NO_2$  were carried out from the measured lifetime data at different pressures of the target gas at room temperature. These studies were carried out in the excitation regions 465-490 nm, 423-462 nm and 399-416 nm.

The Stern-Volmer model of fluorescence quenching considers only one excited level which is produced by photon absorption, and which may radiate or be collisionally quenched to the ground state. Under this assumption of single excited state, the zero-pressure intercept of the Stern-Volmer plot (inverse of radiative lifetime versus pressure) corresponds to the fluorescence rate constant  $(k_f)$ . If an observed state is excited both directly and by a pressure dependent cascade process, the zero-pressure intercept should not be the true fluorescence rate constant. Also if there is a significant amount of variation in the zero-pressure intercept, it is evident that molecular states of considerable different lifetimes are directly populated

by the excitation photons. The shape of the Stern-Volmer plot further gives an indication about the nature of the quenching process involved with the excited state. If the Stern-Volmer plot is linear, it clearly indicates that only one excited state is involved in the fluorescence emission process. When the Stern-Volmer plot deviates from linearity, then one has to account the emission from states which are collisionally populated or through a pressure dependent cascade processes.

In the present study, the estimation of all self quenching rate constants for NO<sub>2</sub> were carried out from the lifetime data measured by direct observation of fluorescence decay in the excitation regions (i) 465-490 nm, (ii) 423-462 nm and (iii) 399-416 nm at an interval of 0.2, 0.5 and 0.5 nm respectively at room temperature. The estimated rate constants for the quenching of total fluorescence (*ie* they represent an electronic state change) is mainly contributed by the static components in these regions. These rate constants should be distinguished from vibrational and rotational transfer constants. The Stern-Volmer plots were drawn for the static components using the lifetime data and fitted using a linear least square routine to estimate the self-quenching rate constant  $k_q$  (slope of the S-V plot) and the zero-pressure intercept ( $\tau_{zero}$ ).

In the excitation region 465 to 490 nm, it is seen that the Stern-Volmer plots were linear above 5 mTorr gas pressure while an upward curvature is seen below this pressure. Figure 5.7 shows one such Stern-Volmer plot at the excitation wavelength 466.2 nm. The plot was fitted to a straight line to obtain the values of the self quenching rate and zero-pressure intercept as  $k_q = 3.6 \times 10^{-11}$  cm<sup>3</sup>/molecule/sec and  $\tau_{zero} = 44.9 \,\mu$ sec. Similar plots were drawn in this region at an interval of 0.2 nm and were found to be nearly linear but with a small upward curvature at low pressures. The Figures 5.8 and 5.9 show the plots of self quenching rate constant (SQRC) and the zero-pressure intercept versus increasing excitation wavelength. It is clearly seen from these plots that the zero-pressure intercept varies between 36 to 47  $\mu$ sec indicating that more than one electronic states


**Figure 5.7:** Stern-volmer plot of NO<sub>2</sub> static lifetime component at wavelength 466.2 nm. The estimated values of  $k_q = 3.6 \times 10^{-11} \text{ cm}^3/\text{molecule/sec}$  and  $\tau_{zero} = 44.9 \,\mu\text{sec}$ .

are involved in the emission processes with different lifetime where as the self quenching rate constant is found to gradually increase from 3.55 to  $4.25 \times 10^{-11}$  cm<sup>3</sup>/molecule/sec with decreasing energy. This is in good agreement with the present lifetime studies. Table 5.7 gives the estimated self quenching rate constants and the zero-pressure intercepts. Similar results have been obtained by Keyser et al (1971) using steady state excitation in the estimation of quenching constants. It was suggested by them that due to the stepwise vibrational deexcitation in the excited electronic state of NO<sub>2</sub> which is concurrent to the electronic and radiative deexcitation, there is a deviation from linearity of the Stern-Volmer plots. Donnelly et al (1979) measured  $NO_2$  fluorescence as a function of time, pressure and fluorescence wavelength and came to a conclusion that the banded to continuum intensity in the dispersed fluorescence spectra decreases with increasing pressure indicating that continuum is partially of collisional origin at high pressure. They also observed a red shift of fluorescence at high pressure, indicative of vibrational relaxation of the emitting state  ${}^{2}B_{2}$ in this region. They identified that the quenching of banded feature has

a fast component  $k_B$  and a weaker, long lived component with underlying continuum. The slow process has been identified with stepwise vibrational quenching while the fast process is best interpreted as collision induced change in the rotational quantum state of the initially excited state. They concluded that the two states responsible for fluorescence in this region are  ${}^2B_1$  and  ${}^2B_2$  and the contribution from  ${}^2B_2$  is stronger than from  ${}^2B_1$ .



**Figure 5.8:** Plot of quenching rate constant of NO<sub>2</sub> in the excitation region 465 to 490 nm.

From the present work on the analysis of Stern-Volmer plots and from the evidence obtained from the fluorescence excitation spectra and the lifetime spectra, it is evident that the quenching mechanism in this region is not a single step process but is a multistep process which is highly complicated due to the interaction of  ${}^{2}B_{1}$  and  ${}^{2}B_{2}$  states with the highly excited vibrational levels of the ground state  ${}^{2}A_{1}$ . Our estimated values of self quenching rate constant and zero-pressure intercept are on the lower side than those obtained by other workers. This discrepancy is attributed to the pulse excitation technique used to observe the decay of fluorescence with an excitation pulse width of around 8 nsec due to which the observed long lived components tend to shorten. Here one should emphasize that



Figure 5.9: Plot of zero-pressure y-intercept of  $NO_2$  in the excitation region 465 to 490 nm.

the upward curvature seen in the Stern-Volmer plots is not due to the geometric effect, but it reflects about nature of the quenching process which is mainly due to collisions.

In the excitation region 423 to 462 nm, it is seen that the Stern-Volmer plots are deviating from linearity at pressures below 5 mTorr with an upward curvature seen at near the lower end of the pressure. Figure 5.10 shows one such plot drawn at the excitation wavelength 427.5 nm. The estimated self quenching rate constant and the zero-pressure intercept using a linear least square fit are  $k_q = 1.49 \times 10^{-11}$  cm<sup>3</sup>/molecule/sec and  $\tau_{zero} = 41.8 \ \mu$ sec. Similar plots of  $\tau^{-1}$  versus pressure were drawn in this excitation region at an interval of 0.5 nm. These plots were nearly linear with an upward curvature at low pressures. The Figures 5.11 and 5.12 show the variation of self quenching rate constant and zero-pressure intercept with increasing excitation wavelength. It is very much seen that the value of zero-pressure intercept varies between 37 to 45.9  $\mu$ sec and the self quenching rate constant ranging between 0.36 to 2.09  $\times 10^{-11}$  cm<sup>3</sup>/molecule/sec. This clearly indicates that the quenching mechanism



**Figure 5.10:** Stern-volmer plot of NO<sub>2</sub> static lifetime component at wavelength 427.5 nm. The estimated values of  $k_q = 1.49 \times 10^{-11}$  cm<sup>3</sup>/molecule/sec and  $\tau_{zero} = 41.8 \,\mu$ sec.

is not a single step process and there are pressure dependent cascade processes involved. The fluorescence excitation spectra do not show any variation with pressure but the lifetime spectra show an increasing variation in lifetime with increasing pressure. Table 5.8 gives the estimated self quenching constants and the zero-pressure intercepts.

In this excitation region, the perturbed  ${}^{2}B_{1}$  excited state is responsible for fluorescence which mixes with the highly dense excited vibrational levels of the ground state  ${}^{2}A_{1}$ , with the  ${}^{2}B_{1}$  perturbed level exhibiting a large variation in their decay rates. Schwartz and Johnston (1969) carried out the pressure dependence of lifetime and fluorescence intensity, and found that the lifetimes were different at different incident photon wavelengths. These plots of  $\tau^{-1}$  versus pressure were not in general linear and they concluded that short lived components if contributing to the total fluorescence would lead to Stern-Volmer plots whose slope (positive) decreased with pressure. In the present experiment, the S-V plots were drawn for the static lifetime components which contributed mainly to the



**Figure 5.11:** Plot of quenching rate constant of NO<sub>2</sub> in the excitation region 423 to 462 nm.

total fluorescence. Similar studies were carried out by Keyser *et al* (1971) at few wavelengths in this region using steady state excitation technique. They also observed that the quenching curves deviate from linearity at low pressures (below 10 mTorr). They came out with the explanation that the upward curvature is due to the steep rise in vibrational deexcitation of the excited electronic state  ${}^{2}B_{1}$  of NO<sub>2</sub>. The present estimates of self quenching rate constants and zero-pressure intercepts are lower than those estimated by other workers. This discrepancy is again attributed to the pulse excitation pulse width around 8 nsec which is very much smaller than the observed lifetimes. This in turn shortens the lifetime of the observed longlived components and hence the Stern-Volmer estimates which use these lifetime data.

In the predissociation region 399 to 416 nm of  $NO_2$ , it is generally seen that the Stern-Volmer plots deviate from linearity and this deviation increases as we approach the photodissociation limit. Figures 5.13 and 5.14. show S-V plots at two different excitation wavelengths 404 and 410.8 nm



**Figure 5.12:** Plot of zero-pressure y-intercept of NO<sub>2</sub> in the excitation region 423 to 462 nm.

respectively. It is seen that the deviation from linearity is more at the excitation wavelength 404 nm than at 410.8 nm with zero-pressure intercept varying from 34.5  $\mu$ sec at 404 nm to 40.7  $\mu$ sec at 410.8 nm. Similar plots of  $\tau^{-1}$  versus pressure were drawn in this excitation region at an interval of 0.5 nm. The Figures 5.15 and 5.16 show the variation of self quenching rate constant and zero-pressure intercept with increasing excitation wavelength. It is evident from these plots that as we approach the photodissociation limit, the variation in self quenching rate constant and the zero-pressure intercept increase with their estimated values varying between 0.06 to  $11 \times 10^{-11}$  cm<sup>3</sup>/molecule/sec and 19.9 to 42.8  $\mu$ sec respectively. This is a clear indication of collision induced processes coupling with the predissociation of NO<sub>2</sub>. The estimated self quenching rate constants and the zero-pressure intercepts are tabulated in Table 5.9. Our estimation of  $k_q$  and  $\tau_{zero}$  are lower than those reported by other workers. This may be due to the finite and short pulse width of laser light used in the experiments. The lifetime study in this region suggests that only one excited state is responsible for the fluorescence which is highly perturbed



**Figure 5.13:** Stern-Volmer plot of NO<sub>2</sub> static lifetime component at wavelength 404 nm. The estimated values of  $k_q = 9.2 \times 10^{-12}$  cm<sup>3</sup>/molecule/sec and  $\tau_{zero} = 34.5 \,\mu$ sec.

by the vibrational mixing with a lower state. From the fluorescence excitation spectra, it is seen that the relative intensities of the band change with increasing pressure, suggesting that collisional depopulation and repopulation of intermediate level occur. The lifetime spectra shows a large variation in lifetime at shorter wavelength which increases with pressure. This suggests that there should be short fluorescing components with very small lifetime. The lifetime study shows that at high pressures, there are short lifetime components whose frequency of occurrence increases with pressure. This large variation in lifetime with excitation wavelength may be due to the combined effect of predissociation and collisional quenching in this region. Uselmann and Lee (1976) studied in great detail the quenching of NO<sub>2</sub> in the predissociation region using phase-shift technique. They found that the fluorescence quantum yield decreases with increasing pressure due to self quenching and the shape of fluorescence curve is insensitive to pressure. They reported the pressure of a predissociating fluorescing species with a very short lifetime ( $< 10^{-7}$  sec). The quenching effects were seen more at larger pressures and confirmed that



**Figure 5.14:** Stern-volmer plot of NO<sub>2</sub> static lifetime component at wavelength 410.8 nm. The estimated values of  $k_q = 9.6 \times 10^{-12}$  cm<sup>3</sup>/molecule/sec and  $\tau_{zero} = 40.8 \,\mu$ sec.

the self quenching rate and zero-pressure intercept were invariant with excitation energy. But our present work shows variation in  $k_q$  and  $\tau_{zero}$  in the region 399 to 409 nm and stabilizes at wavelengths greater than 409 nm. This large variation in the estimated  $k_q$  and  $\tau_{zero}$  are attributed to the observed variation in lifetime due to the pressure induced collisional transfers and the occurrence of the predissociated species in this region. Also in this region the fluorescence quantum yield which is nearly zero at 399 nm increases gradually to 100% at 415 nm.



Figure 5.15: Plot of quenching rate constant of  $NO_2$  in the predissociation region 399 to 416 nm.



Figure 5.16: Plot of zero-pressure y-intercept of  $NO_2$  in the predissociation region 399 to 416 nm.

Excitation	Life ti	mes (µ	sec.) fo	or vario	us pres	sures	(mTorr)
Wavelength (nm)	1	3	5	15	51	81	110
465.0	34.7	35.0	35.6	28.2	12.1	8.5	6.4
465.2	35.0	35.5	36.5	<b>28.5</b>	12.2	8.6	6.6
465.4	35.2	36.4	36.8	28.6	12.3	8.6	6.7
465.6	34.1	36.2	36.4	28.2	12.1	8.5	6.4
465.8	34.0	36.3	35.9	28.3	12.4	8.6	6.5
466.0	36.3	37.8	36.9	28.5	12.4	8.7	6.7
466.2	35.7	38.3	35.4	<b>28.5</b>	12.3	8.7	6.5
466.4	35.6	39.9	35.3	28.7	12.2	8.8	6.6
466.6	36.4	36.0	35.4	<b>28.4</b>	12.5	8.8	6.6
466.8	32.1	32.9	31.4	27.4	12.2	8.7	6.5
467.0	37.5	37.5	34.0	27.9	12.2	8.8	6.6
467.2	37.5	37.5	35.2	28.1	12.4	8.8	6.6
467.4	37.7	38.8	35.9	28.0	12.3	8.7	6.5
467.6	36.7	38.2	35.7	28.0	12.1	8.7	6.6
467.8	37.3	39.7	35.9	28.6	12.3	8.8	6.7
468.0	37.9	38.7	35.6	27.5	12.3	8.7	6.5
468.2	37.4	39.0	35.9	28.3	12.3	8.7	6.5
468.4	38.1	38.5	35.8	<b>28.4</b>	12.3	8.8	6.6
468.6	35.5	37.4	35.4	27.4	12.2	8.6	6.5
468.8	38.1	38.9	36.6	28.1	12.3	8.7	6.6
469.0	38.6	39.4	35.3	27.9	12.3	8.7	6.6
469.2	38.1	39.2	35.5	28.5	12.3	8.7	6.5
469.4	38.4	39.2	36.5	28.8	12.3	8.7	6.6
469.6	38.3	39.4	37.1	<b>28.5</b>	12.2	8.7	6.5
469.8	38.6	39.8	36.3	28.7	12.4	8.6	6.5
470.0	38.9	40.7	36.6	<b>28.4</b>	12.3	8.6	6.5
470.2	39.0	40.0	36.6	<b>28.4</b>	12.2	8.6	6.5
470.4	40.1	41.2	35.9	28.3	12.3	8.6	6.6
470.6	38.7	39.7	35.7	28.3	12.2	8.5	6.6
470.8	40.4	40.5	36.2	27.7	12.2	8.5	6.6
471.0	41.0	40.6	35.4	27.7	12.2	8.6	6.4
471.2	39.6	<b>39.6</b>	36.3	27.9	12.3	8.6	6.4
471.4	40.8	40.3	36.9	28.3	12.2	8.6	6.5
471.6	34.9	41.7	35.5	27.6	12.2	8.5	6.4
471.8	35.5	35.4	36.4	28.1	12.1	8.6	6.4
472.0	34.0	33.5	33.8	27.5	12.1	8.6	6.4
472.2	34.2	33.9	31.8	27.0	12.1	8.4	6.4
472.4	34.5	34.8	34.8	27.8	12.2	8.5	6.4
472.6	34.4	34.2	35.8	28.2	12.1	8.5	6.4
472.8	35.2	35.7	35.6	27.8	12.1	8.4	6.4
473.0	35.0	35.5	35.9	28.4	12.0	8.4	6.4
473.2	37.1	37.0	37.1	28.4	12.0	8.4	6.5
473.4	36.2	37.1	36.6	28.1	12.2	8.5	6.3
473.6	36.7	37.4	33.8	27.6	12.0	8.5	6.3

Table 5.1: The fluoresecence lifetime (static component) of excited state of  $NO_2$  at different pressures in the excitation region 465 - 490 nm.

#### Table 5.1: Contd.

Excitation	Life ti	mes (µ	sec.) fo	r vario	us pres	ssures	s (mTorr)
Wavelength (nm)	1	3	5	15	51	81	110
473.6	36.7	37.4	33.8	27.6	12.0	8.5	6.3
473.8	30.0	29.8	32.1	27.5	12.3	8.6	6.5
474.0	30.9	29.7	27.5	27.2	12.0	8.4	6.4
474.2	32.2	31.7	35.6	27.9	12.1	8.5	6.5
474.4	38.0	37.7	35.5	28.0	12.1	8.4	6.4
474.6	39.6	39.3	32.7	28.1	12.3	8.6	6.5
474.8	38.2	37.6	36.0	28.1	12.3	8.5	6.4
475.0	38.2	37.5	34.8	28.2	12.3	8.4	6.4
475.2	39.2	38.0	36.0	27.9	11.9	8.4	6.4
475.4	38.2	37.5	36.4	28.8	12.1	8.4	6.4
475.6	37.3	37.2	36.5	<b>28.5</b>	12.1	8.4	6.4
475.8	37.3	37.2	36.8	<b>28.4</b>	12.0	8.4	6.3
476.0	36.4	36.6	35.9	27.7	11.9	8.4	6.3
476.2	37.0	37.2	35.8	27.4	12.1	8.3	6.4
476.4	36.5	36.5	35.8	27.9	12.1	8.4	6.3
476.6	37.6	37.2	36.5	28.2	12.2	8.5	6.4
476.8	37.7	37.0	35.2	28.1	12.1	8.4	6.3
477.0	36.0	35.7	35.4	27.9	11.9	8.4	6.2
477.2	36.7	36.7	36.7	27.6	12.0	8.3	6.2
477.4	36.8	36.7	35.9	27.5	12.2	8.3	6.2
477.6	36.5	36.7	34.8	27.8	12.1	8.3	6.2
477.8	37.3	37.0	36.7	28.3	12.1	8.4	6.3
478.0	37.1	36.8	37.2	28.8	12.1	8.5	6.3
478.2	37.5	37.1	37.8	28.3	12.1	8.4	6.3
478.4	36.6	36.5	37.5	28.1	11.9	8.3	6.3
478.6	37.6	37.1	38.5	28.2	12.0	8.4	6.3
478.8	37.7	37.4	38.3	28.3	12.0	8.3	6.2
479.0	37.2	36.8	37.7	28.3	11.8	8.3	6.2
479.2	37.6	37.2	36.8	28.2	11.7	8.3	6.2
479.4	38.5	37.4	35.2	27.7	11.8	8.3	6.2
479.6	38.7	37.6	35.6	27.4	11.7	8.3	6.2
479.8	37.2	35.6	35.0	27.5	11.7	8.3	6.2
480.0	37.6	36.7	36.0	27.5	11.8	8.1	6.2
480.2	37.5	36.3	37.0	27.8	12.0	8.1	6.2
480.4	36.1	35.8	34.5	26.5	11.9	8.1	6.1
480.6	35.5	34.0	33.9	27.3	12.0	8.1	6.1
480.8	36.5	36.1	34.9	27.3	11.7	8.1	6.2
481.0	36.4	35.5	35.7	27.3	12.0	8.1	6.2
481.2	36.9	35.8	34.4	27.3	11.7	8.2	6.1
481.4	35.6	34.5	35.2	27.2	11.7	8.2	6.1
481.6	35.8	35.5	34.0	27.1	11.8	8.1	6.1
481.8	36.6	35.5	35.2	27.1	11.6	8.1	6.1

Table 5.1: Contd.

Excitation	Life ti	mes ( $\mu$	sec.) fo	r vario	us pres	ssures	s (mTorr)
Wavelength (nm)	1	3	5	15	51	81	110
482.0	35.9	35.4	36.0	27.2	11.6	8.1	6.1
482.2	35.8	40.7	37.1	27.4	11.6	8.1	6.1
482.4	36.1	41.6	34.6	27.2	12.1	8.1	6.1
482.6	35.2	40.7	34.7	27.4	11.7	8.1	6.0
482.8	<b>39.4</b>	39.3	33.5	27.5	11.7	8.1	6.1
483.0	38.5	38.7	34.0	27.9	11.7	8.1	6.0
483.2	38.9	39.4	36.0	27.9	11.7	8.1	6.0
483.4	37.7	38.4	37.8	<b>28.4</b>	11.7	8.1	6.0
483.6	38.2	38.4	36.5	28.1	11.7	8.1	6.0
483.8	37.5	38.3	33.4	27.4	11.7	8.0	6.0
484.0	38.3	38.6	33.9	27.5	11.9	8.0	6.0
484.2	38.3	39.1	32.4	27.3	11.5	8.0	6.0
484.4	38.6	39.1	35.4	27.1	11.6	8.0	6.0
484.6	38.4	38.0	34.5	26.9	11.5	8.0	5.9
484.8	38.4	39.2	36.0	26.9	11.4	7.9	6.0
485.0	38.0	39.3	36.3	27.9	11.5	7.9	6.0
485.2	38.1	39.1	34.7	27.1	11.5	7.9	6.0
485.4	38.1	38.8	35.1	27.9	11.7	8.0	5.9
485.6	38.2	38.9	35.1	27.4	11.6	7.9	5.9
485.8	38.1	<b>39.5</b>	35.9	26.9	11.4	7.9	5.8
486.0	38.9	39.9	34.1	27.3	11.5	7.9	5.9
486.2	38.1	39.3	35.9	27.6	11.5	8.1	6.0
486.4	36.6	43.2	34.2	26.7	11.7	8.1	6.0
486.6	37.1	43.6	34.6	27.1	11.6	8.0	6.0
486.8	36.1	44.1	32.9	26.7	11.8	7.9	5.9
487.0	37.8	43.6	35.6	27.8	11.7	8.0	6.0
487.2	37.2	43.3	35.4	26.8	11.3	7.9	6.0
487.4	37.6	43.0	33.8	27.2	11.4	8.0	5.9
487.6	37.2	41.8	35.8	26.5	11.3	7.9	5.9
487.8	36.8	42.9	31.0	26.6	11.4	7.8	5.8
488.0	36.8	43.9	34.2	27.2	11.3	7.9	5.8
488.2	38.1	46.5	33.4	26.7	11.2	7.8	5.8
488.4	38.7	38.6	31.1	26.4	11.1	7.8	5.8
488.6	37.8	38.7	32.1	25.8	11.4	7.7	5.7
488.8	39.3	27.3	31.7	25.6	11.5	7.7	5.7
489.0	36.9	37.8	31.3	27.1	11.1	7.7	5.7
489.2	36.3	36.6	31.1	26.0	11.2	7.7	5.8
489.4	36.9	37.4	31.1	26.8	11.0	7.7	5.8
489.6	36.8	37.0	33.5	26.7	11.3	7.8	5.9
489.8	36.4	37.1	33.1	26.8	11.1	7.8	5.8
490.0	36.4	37.1	32.9	28.0	11.0	7.8	5.8

Excitation	Life	times	(µsec	.) for v	arious pressures (mTorr).
Wavelength (nm)	5	15	51	81	110
466.8	-	-	-	0.24	-
467.0	-	1.4	-	-	-
472.0	-	-	-	0.25	-
472.2	1.1	-	-	0.31	-
472.4	_	-	-	0.21	-
473.8	2.6	-	-	0.20	-
474.0	_	1.8	-	0.36	0.18
474.6	_	_	_	0.18	-
475.2	-	-	-	0.16	-
476.8	-	-	1.0	0.17	-
477.6	-	-	_	0.12	-
479.6	_	-	_	0.24	-
479.8	-	-	-	0.42	-
480.0	_	_	_	0.29	-
480.4	_	_	_	0.38	-
480.6	_	1.1	_	0.21	-
480.8	_	-	_	0.29	0.12
481.0	_	_	15	0.15	0.12
481.2	_	_	-	0.10	0.12
481.4	_	_	_	0.16	-
481.6	_	_	_	0.29	-
481.8	_	_	_	0.23	-
482.6	_	_	_	0.20	-
482.8	_	_	_	0.22	_
484 2	_	_	_	0.10	-
101.2 484 4	_	_	_	0.10	_
484.6	_	_	_	0.00	-
101.0	_	_	_	0.20 0.14	_
485.6	_	10	_	-	0.11
405.0	_	-	_	0 72	-
486.0	_	_	_	0.72	_
486.6	_	_	17	0.00	0.20
486.8	_	_	1.7	0.58	0.13
400.0	_	_	_	0.30	0.15
187 G	-	-	-	0.40	-
407.U 187 R	-	-	-	0.33	-
407.0	-	_	_	0.40	-
400.0	1 1	-	-	0.37	- 0.20
400.2	1.1	1 5	-	0.43	0.20
400.4 188 g	-	1.J 2 A	17	0.00	0.13
400.U 188 8	-	2.U 2.G	1./	0.00	$0.3\mathcal{L}$
400.0 100.0	-	۵.0 ۱۵	- 19	0.30	0.41
407.U 100 9	-	1.9	1.2	0.30	0.33
409.2 100 1	-	-	-	0.33	- 0.24
409.4	-	-	-	0.04	0.34
489.0	- 1 0	-	- 10	0.29	-
489.8	1.2	1./	1.2	0.44	0.29
490.0	-	-	1.2	0.43	0.20

Table 5.2: Life times 1 - 4  $\mu$ sec. present in the fluorescence excitation region 465 - 490 nm of NO<sub>2</sub> at different pressures.

Excitation	Life ti	mes (µ	sec.) fo	r vario	us pres	sures (mTorr)
Wavelength (nm)	1	3	5	7	10	15
423.0	40.2	38.5	35.6	34.1	32.0	31.4
423.5	40.9	38.7	37.0	37.2	38.8	30.1
424.0	40.9	38.9	37.1	37.8	37.7	30.5
424.5	39.2	38.8	39.8	34.4	33.4	30.4
425.0	40.0	39.5	38.8	35.2	34.1	32.8
425.5	40.8	41.2	40.2	36.8	35.2	30.5
426.0	40.3	40.7	39.7	36.5	34.7	30.7
426.5	40.4	41.1	40.6	36.9	35.2	31.3
427.0	39.7	39.2	37.9	38.5	38.4	31.5
427.5	40.0	40.0	38.5	37.1	34.8	32.0
428.0	39.7	39.3	39.4	36.7	34.8	32.8
428.5	40.3	40.4	40.6	37.7	35.4	33.9
429.0	40.1	40.2	39.8	37.6	35.3	33.5
429.5	41.0	41.2	39.4	37.8	35.4	32.5
430.0	40.9	40.9	40.4	38.2	36.2	33.8
430.5	40.6	42.1	39.3	38.8	37.6	34.2
431.0	40.5	42.5	39.2	39.8	38.1	35.1
431.5	40.7	41.9	39.3	39.6	37.4	34.8
432.0	41.1	41.9	39.6	39.6	37.6	34.4
432.5	41.2	42.0	39.5	39.2	36.9	34.0
433.0	41.6	42.9	40.3	40.2	38.9	34.9
433.5	41.0	43.2	40.0	40.2	38.3	35.4
434.0	40.8	41.1	40.2	40.2	38.5	36.9
434.5	41.2	41.3	39.9	40.4	38.0	36.4
435.0	40.7	40.9	40.0	40.9	39.9	38.1
435.5	40.7	41.2	40.2	40.2	38.1	36.4
436.0	40.3	44.3	39.6	39.7	37.7	36.3
436.5	40.7	43.6	40.0	40.1	37.7	35.7
437.0	41.3	42.6	40.1	40.1	37.8	35.4
437.5	41.7	42.4	40.2	<b>39.4</b>	36.8	33.9
438.0	42.1	42.5	40.1	39.6	37.0	34.2
438.5	41.4	42.5	40.3	39.9	37.7	34.7
439.0	41.4	42.2	40.5	43.1	39.5	37.8
439.5	41.3	42.3	40.9	40.9	39.0	37.6
440.0	40.8	41.5	39.5	40.2	37.7	35.8
440.5	41.7	41.8	39.8	38.8	36.9	33.6
441.0	41.3	42.0	39.6	39.3	36.8	34.1
441.5	41.5	41.7	39.5	38.6	36.0	33.4
442.0	42.0	42.2	40.1	38.9	36.0	33.0
442.5	40.8	40.6	40.3	38.5	36.0	33.2

Table 5.3: The fluoresecence lifetime (static component) of excited state of NO $_2$  at different pressures in the excitation region 423 - 462 nm.

Table	5.3:	Contd

Excitation	Life ti	mes (µ	sec.) fo	r vario	us pres	ssures (mTorr)
Wavelength (nm)	1	3	5	7	10	15
443.0	39.8	39.5	41.2	37.7	36.0	32.8
443.5	41.9	42.3	42.5	39.4	36.9	33.8
444.0	43.0	43.7	42.4	39.9	37.5	33.9
444.5	41.8	42.2	40.7	39.7	38.3	34.4
445.0	41.6	44.3	40.0	40.5	37.7	34.2
445.5	40.8	40.0	38.8	38.6	36.6	33.3
446.0	41.7	41.9	39.7	38.8	36.4	33.2
446.5	41.1	40.9	40.1	38.2	35.7	32.7
447.0	41.8	41.7	40.4	38.9	35.8	33.4
447.5	41.7	40.9	41.7	38.7	35.7	33.2
448.0	39.6	39.0	36.1	37.6	36.4	33.9
448.5	40.5	39.9	41.5	37.5	35.6	32.6
449.0	41.8	40.9	39.4	40.1	35.2	32.1
449.5	41.9	41.0	39.1	38.1	34.7	31.4
450.0	42.9	41.7	39.4	37.9	35.6	31.1
450.5	41.0	40.3	38.5	36.4	36.0	30.8
451.0	42.4	40.7	41.5	36.6	35.5	30.6
451.5	41.6	40.2	39.1	35.8	33.7	31.9
452.0	40.2	38.6	38.3	34.3	31.5	31.1
452.5	35.6	32.5	34.5	48.3	31.1	30.9
453.0	40.8	40.1	37.5	35.9	32.9	36.1
453.5	41.4	39.1	35.7	33.9	33.7	29.5
454.0	42.8	41.9	40.7	39.7	38.1	34.3
454.5	42.9	41.6	40.6	40.0	38.3	34.7
455.0	42.7	43.5	41.7	41.6	39.6	36.1
455.5	42.5	41.7	40.6	39.8	38.0	34.2
456.0	43.0	42.4	41.6	40.5	38.9	34.7
456.5	43.9	43.1	41.7	40.4	37.4	33.9
457.0	42.9	41.8	41.1	39.1	36.8	33.3
457.5	40.8	40.5	37.7	38.9	38.9	34.0
458.0	41.3	40.2	38.9	38.4	36.8	33.5
458.5	42.0	40.5	38.4	37.5	36.2	33.1
459.0	42.8	41.1	39.9	38.0	35.8	31.6
459.5	41.7	39.4	39.2	36.5	35.7	31.8
460.0	40.6	37.2	37.9	34.9	34.6	31.2
460.5	43.0	40.8	39.8	40.4	35.6	31.1
461.0	42.2	40.9	38.9	38.0	37.9	30.7
461.5	43.8	41.3	39.7	37.4	36.0	30.7
462.0	43.7	41.5	38.6	36.9	35.0	31.9

Excitation	Lif	fe ti	mes (µ	usec.)	for va	rious pressures (mTorr).
Wavelength (nm)	1	3	5	7	10	15
424.5	-	-	-	-	-	2.5
425.5	-	-	-	-	-	2.2
426.0	-	-	-	-	-	1.2
448.0	-	-	5.7	4.9	2.6	2.6
450.5	-	-	-	-	-	1.6
452.0	-	-	-	1.3	2.1	2.1
452.5	-	-	-	5.1	4.3	4.3
453.0	-	-	-	-	-	3.3
453.5	-	-	-	-	-	3.7
457.5	-	-	1.0	1.8	1.8	1.8
458.5	-	-	-	1.5	1.5	1.5
460.0	-	-	-	2.6	1.5	1.5

**Table 5.4:** Lifetimes1 - 6  $\mu$ sec.present in the fluorescence excitationregion 423 - 462 nm of NO2 at different pressures.

Table 5.5: Lifetimes  $~\sim 10^{-7} sec$  present in the fluorescence excitation region 423 - 462 nm of NO\_2 at different pressures.

Excitation	Li	fe ti	mes	s ( ×10	$0^{-7}$ sec.)	for various pressures (mTorr).
Wavelength (nm)	1	3	5	7	10	15
424.5	-	-	-	<b>3.6</b>	3.6	3.6
426.0	-	-	-	-	-	2.2
427.0	-	-	-	-	-	3.3
428.0	-	-	-	-	2.4	2.4
443.0	-	-	-	1.1	7.4	5.8
445.0	-	-	-	-	4.1	4.1
445.5	-	-	-	-	-	3.4
446.5	-	-	-	-	-	1.9
448.0	-	-	-	-	-	8.5
448.5	-	-	-	8.5	8.5	5.6
449.0	-	-	-	-	9.2	5.7
449.5	-	-	-	-	-	1.4
451.0	-	-	-	-	-	3.5
452.5	-	-	-	-	9.5	9.5
457.0	-	-	-	1.2	1.2	.12
457.5	-	-	-	1.3	1.3	5.6
458.5	-	-	-	-	7.7	2.5
459.5	-	-	-	<b>3.3</b>	1.1	1.1
461.0	-	-	-	-	-	9.0
461.5	-	-	-	-	-	7.8
462.0	-	-	-	1.1	1.1	1.1

Excitation	Life times (µsec.) for various pressures (mTorr)						
Wavelength (nm)	1	3	5	7	10	15	
399.0	37.0	27.6	20.9	28.6	16.7	25.8	
399.2	36.4	28.3	20.6	30.0	25.4	26.0	
399.4	36.2	24.5	14.9	11.4	26.3	28.1	
399.6	37.9	25.2	15.7	11.4	26.3	30.1	
399.8	36.9	<b>24.6</b>	13.3	13.4	17.0	14.0	
400.0	37.0	27.0	20.7	19.5	26.1	30.1	
400.2	36.4	28.2	19.1	13.6	32.9	33.5	
400.4	36.3	24.6	26.5	14.8	37.7	10.9	
400.6	36.6	24.8	23.7	20.6	18.5	22.0	
400.8	37.6	30.3	<b>24.6</b>	18.9	17.0	19.3	
401.0	36.4	30.1	29.5	18.9	25.4	29.8	
401.2	37.3	30.3	19.4	22.8	25.3	32.3	
401.4	37.5	31.2	27.0	20.7	25.1	30.2	
401.6	38.2	32.0	22.3	26.6	25.1	32.9	
401.8	37.8	31.8	27.1	16.8	33.6	32.3	
402.0	38.1	32.8	25.7	16.7	34.3	35.2	
402.2	38.3	33.6	27.4	26.8	33.8	30.0	
402.4	38.4	34.0	27.5	19.4	25.2	31.8	
402.6	38.8	33.9	27.5	20.0	33.5	30.1	
402.8	38.3	34.3	27.5	18.8	25.0	31.9	
403.0	38.3	35.2	<b>29.4</b>	22.2	42.6	31.8	
403.2	37.7	35.6	<b>29.4</b>	20.1	24.5	31.5	
403.4	37.8	35.6	30.9	21.2	24.5	32.3	
403.6	38.6	35.7	32.4	21.0	24.8	32.5	
403.8	38.5	39.3	30.5	25.9	37.9	36.9	
404.0	37.9	34.3	31.2	27.6	32.4	31.5	
404.2	38.7	34.8	30.7	26.8	33.7	31.9	
404.4	38.5	35.3	31.8	27.7	24.6	31.3	
404.6	38.8	35.9	32.5	30.8	24.6	31.5	
404.8	38.7	36.0	32.8	31.1	24.6	30.9	
405.0	39.0	35.9	33.3	31.3	24.7	32.3	
405.2	36.9	35.3	33.0	32.1	32.5	32.2	
405.4	38.5	36.0	33.3	32.3	32.7	32.2	
405.6	39.0	36.4	34.5	33.0	32.6	32.4	
405.8	39.2	37.2	34.4	33.0	24.6	31.8	
406.0	38.8	36.7	34.2	32.2	24.7	31.9	
406.2	39.0	37.1	35.2	32.9	32.5	31.9	
406.4	38.9	37.1	34.7	33.2	32.6	32.1	
406.6	39.3	37.6	34.4	32.9	32.7	31.7	
406.8	38.9	37.5	35.1	33.1	32.6	31.9	

**Table 5.6:** The fluoresecence lifetime (static component) of excited stateof  $NO_2$  at different pressures in the predissociation region 399 - 416 nm.

Table 5.6: Contd.

Excitation	Life ti	mes (µ	sec.) fo	r vario	us pres	sures (mTorr)
Wavelength (nm)	1	3	5	7	10	15
407.0	39.1	37.7	35.3	33.5	33.3	32.1
407.2	39.6	37.7	35.8	33.3	32.4	32.0
407.4	39.3	37.6	35.1	33.3	33.0	32.0
407.6	39.5	38.1	36.2	34.3	33.7	32.0
407.8	39.8	39.0	36.7	35.9	34.8	32.5
408.0	39.5	41.0	37.5	36.9	36.5	33.7
408.2	39.0	40.4	37.0	36.7	36.1	33.6
408.4	39.2	38.6	37.6	36.9	37.0	33.8
408.6	39.2	40.4	37.5	36.8	36.7	35.2
408.8	39.9	40.4	37.7	37.3	36.6	34.2
409.0	39.5	40.4	37.5	38.0	36.9	34.3
409.2	40.0	40.1	37.4	36.6	35.3	33.5
409.4	39.7	40.9	37.3	36.9	35.6	34.1
409.6	40.1	40.3	37.7	36.8	35.7	33.9
409.8	40.3	40.5	37.9	37.0	35.5	33.8
410.0	39.9	40.1	37.6	36.9	36.3	33.5
410.2	40.3	40.4	37.9	36.9	36.8	34.3
410.4	40.0	40 7	37.9	37.3	37.1	34 7
410.6	40.3	40.7	38.1	37.3	37.4	34 7
410.8	39.8	40 1	37 7	37 2	37.0	34.0
<i>1</i> 10.0	<i>4</i> 0 1	10.1	376	373	367	33 /
411.0 A11.2	10.1	10.1	378	36.9	35 7	33.6
411. <i>ω</i> Λ11 Λ	10.0	40.0 30 /	37 1	36.3	35 /	33.2
411.4 A11.6	40.0	<i>4</i> 0 0	386	36.4	35.4 35.8	30.≈ 32.1
411.0	40.0	20.0	38.8	30.4	35.5	32.1
411.0	20.4	30.5 30.6	378	36.1	33.5	32.0
412.0	<i>40 4</i>	30.5	37.0	36.1	25 1	32.2
412.2	40.4	39.5	37.3	30.4	37.0	31.9
412.4	40.2	19 G	270	25.0	24.3	22.0
412.0	40.1	42.0	37.0	35.3	34.2	32.2
412.0	40.4 20.5	43.0 29 G	200	25 6	24.5	22.2
413.0	39.5	20.0 20.6	30.9 27 Q	25 5	34.3 24 1	33.2 22 A
413.2	20.1	276	270	21 1	24.1	22.4
413.4	20.0	37.0 20 E	37.0 27 5	04.4 91 5	04.1 22 G	36.4 91 9
413.0	39.9	30.3	37.3	34.3	32.0	31.3
413.8	39.2	39.7	37.3	33.4	33.4 24 E	30.9
414.0	39.7	39.0	30.3 20.3	34.0	34.5	30.1
414.2	39.9	39.3	30.2	34.8 99.1	33.2 20.4	31.2
414.4	39.5	37.5	36.9	33.1	32.4	30.4
414.6	39.7	37.9	35.6	35.3	31.9	27.1
414.8	38.8	38.0	34.4	35.7	32.1	27.6
415.0	40.3	37.9	34.4	34.0	32.5	27.5
415.2	40.6	38.5	35.2	32.7	32.4	27.5
415.4	39.7	37.4	35.0	32.3	32.4	27.4
415.6	39.0	38.9	35.7	33.8	32.3	27.4
415.8	39.4	38.6	34.4	33.4	31.0	27.4
416.0	39.4	38.0	34.4	33.1	32.4	31.7

Wanalasath	1	
wavelength	$\kappa_q$	$\tau_{zero}$
(nm)	(×10 <sup>-1</sup> cm <sup>3</sup> /molecule/sec)	$(\mu sec)$
405.0	3.7	43.3
405.2	3.0	43.5
405.4	3.0	43.0
465.6	3.7	44.1
465.8	3.6	43.7
466.0	3.6	44.9
466.2	3.6	44.9
466.4	3.6	45.0
466.6	3.6	43.9
466.8	3.6	39.3
467.0	3.6	43.8
467.2	3.6	44.8
467.4	3.7	45.8
467.6	3.6	44.7
467.8	3.6	45.7
468.0	3.7	45.4
468.2	3.7	45.8
468.4	3.6	45.6
468.6	3.6	43.8
468.8	3.6	46.0
469.0	3.6	45.5
469.2	3.7	46.4
469.4	3.7	46.8
469.6	3.7	46.8
469.8	3.7	47.4
470.0	3.7	47.6
470.2	3.7	47.1
470.4	3.7	47.2
470.6	3.7	46.2
470.8	3.7	46.7
471.0	3.8	47.6
471.2	3.8	47.3
471.4	3.7	48.2
471.6	3.7	45.4
471.8	3.7	44.2
472.0	3.7	41.5
472.2	3.7	40.8
472.4	3.7	43.0
472.6	3.7	43.0
472.8	3.8	43.8
473.0	3.8	44.0
473.2	3.7	45.4
473.4	3.8	45.7
473.6	3.8	44.4

**Table 5.7:** The estimated values self quenching rate constant  $(k_q)$  and zeropressuure intercept  $(\tau_{zero})$  of NO<sub>2</sub> in the exctation region 465 - 490 nm.

	Tab	ole	5.	7:	Contd
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Wavelength	$k_{a}$	$\tau_{zero}$
(nm)	$(\times 10^{-11} \text{ cm}^3/\text{molecule/sec})$	(µsec)
473.8	3.5	37.8
474.0	3.6	36.1
474.2	3.6	40.5
474.4	3.7	45.5
474.6	3.7	45.6
474.8	3.8	46.2
475.0	3.8	45.9
475.2	3.8	46.1
475.4	3.8	46.4
475.6	3.8	46.0
475.8	3.8	46.0
476.0	3.8	44.6
476.2	3.8	44.9
476.4	3.8	45.0
476.6	3.8	46.0
476.8	3.8	45.6
477.0	3.8	44.5
477.2	3.9	45.9
477.4	3.9	45.6
477.6	3.9	45.2
477.8	3.8	46.5
478.0	3.8	46.7
478.2	3.8	47.0
478.4	3.9	46.0
478.6	3.9	47.2
478.8	3.9	47.4
479.0	3.9	46.6
479.2	3.9	46.4
479.4	3.9	45.8
479.6	3.9	45.9
479.8	3.9	44.4
480.0	3.9	45.8
480.2	3.9	40.5
480.4	3.9	43.9
480.0	3.9	43.4
48U.8	3.Y 2.0	44.4
401.U 101 0	<b>১.</b> ৬ ৫.০	44.9 11 7
401.2 101 1	<b>১.</b> ৬ ২.০	44./ 19 0
401.4 101.6	3.9 4 0	43.ð 44.0
401.0 101 0	4.0	44.U 11 G
401.0	4.0	44.0

	Tab	ole	5.	7:	Contd
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Wavelength	$k_{q}$	$\tau_{zero}$
(nm)	$(\times 10^{-11} \text{ cm}^3/\text{molecule/sec})$	(µ <b>sec</b> )
482.0	4.0	44.6
482.2	4.0	47.1
482.4	4.0	47.0
482.6	4.0	46.1
482.8	4.0	46.7
483.0	4.0	46.9
483.2	4.0	48.1
483.4	4.1	48.6
483.6	4.1	48.1
483.8	4.0	46.1
484.0	4.0	46.9
484.2	4.0	45.4
484.4	4.1	47.3
484.6	4.1	46.4
484.8	4.1	47.1
485.0	4.1	47.9
485.2	4.1	46.4
485.4	4.1	48.1
485.6	4.2	47.9
485.8	4.2	48.1
486.0	4.1	47.7
486.2	4.1	47.9
486.4	4.1	47.4
<b>486.6</b>	4.1	48.0
486.8	4.1	47.3
487.0	4.1	49.4
487.2	4.1	47.7
487.4	4.1	47.8
487.6	4.2	47.7
487.8	4.2	46.3
488.0	4.2	48.2
488.2	4.3	48.9
488.4	4.2	45.2
488.6	4.2	45.6
488.8	4.1	40.8
489.0	4.2	44.9
489.2	4.2	43.5
489.4	4.2	44.1
489.6	4.2	44.9
489.8	4.2	44.7
490.0	4.2	45.1

Wavelength	$k_{a}$	$\tau_{zero}$
(nm) ັ	$(\times 10^{-11} \text{ cm}^3/\text{molecule/sec})$	(µ <b>sec</b> )
423.0	1.6	40.1
423.5	1.6	42.2
424.0	1.6	42.3
424.5	1.8	41.5
425.0	1.4	41.0
425.5	2.0	44.0
426.0	1.9	43.2
426.5	1.8	43.5
427.0	1.3	41.7
427.5	1.5	41.8
428.0	1.3	41.2
428.5	1.2	42.1
429.0	1.2	41.8
429.5	1.5	43.0
430.0	1.3	42.7
430.5	1.1	42.6
431.0	0.9	42.5
431.5	1.0	42.5
432.0	1.1	42.9
432.5	1.2	43.1
433.0	1.1	43.7
433.5	1.0	43.2
434.0	0.6	41.8
434.5	0.8	42.2
435.0	0.4	41.4
435.5	0.7	42.0
436.0	0.9	42.7
436.5	1.0	43.1
437.0	1.0	43.2
437.5	1.3	43.8
438.0	1.3	43.9
438.5	1.1	43.5
439.0	0.6	42.8
439.5	0.6	42.6
440.0	0.8	42.1
440.5	1.3	43.5
441.0	1.2	43.1
441.5	1.4	43.3
442.0	1.6	44.2
442.5	1.3	42.8

**Table 5.8:** The estimated values self quenching rate constant  $(k_q)$  and zeropressuure intercept  $(\tau_{zero})$  of NO<sub>2</sub> in the excitation region 423 - 463 nm.

Table	5.8:	Contd
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Wavelength	$k_{q}$	$\tau_{zero}$
(nm)	$(\times 10^{-11} \text{ cm}^3/\text{molecule/sec})$	(µsec)
443.0	1.3	42.1
443.5	1.4	44.6
444.0	1.5	45.8
444.5	1.2	43.8
445.0	1.3	44.5
445.5	1.2	42.0
446.0	1.5	43.7
446.5	1.5	43.2
447.0	1.5	43.8
447.5	1.5	43.9
448.0	0.9	39.8
448.5	1.4	42.7
449.0	1.7	44.0
449.5	1.8	43.9
450.0	2.0	45.0
450.5	1.8	42.9
451.0	2.1	45.0
451.5	1.8	42.7
452.0	1.8	41.1
452.5	0.9	37.1
453.0	1.0	40.2
453.5	2.1	41.8
454.0	1.3	44.3
454.5	1.2	44.0
455.0	1.0	44.7
455.5	1.3	44.0
456.0	1.2	44.8
456.5	1.6	45.9
457.0	1.5	44.7
457.5	1.0	41.7
458.0	1.2	42.3
458.5	1.4	42.6
459.0	1.8	<b>44.6</b>
459.5	1.6	42.7
460.0	1.5	40.7
460.5	1.9	45.3
461.0	1.8	44.4
461.5	2.1	45.5
462.0	1.9	44.4

Wavelength		$\tau_{zero}$
(nm)	$(\times 10^{-11} \text{ cm}^3/\text{molecule/sec})$	(µ <b>sec</b> )
399.0	3.1	29.4
399.2	1.5	29.5
399.4	-	19.9
399.6	-	20.4
399.8	8.0	24.7
400.0	0.3	25.9
400.2	-	22.9
400.4	11.1	41.1
400.6	3.8	<b>28.9</b>
400.8	6.4	33.3
401.0	1.4	29.7
401.2	0.2	26.9
401.4	1.4	30.2
401.6	0.6	29.7
401.8	0.4	<b>28.5</b>
402.0	-	27.9
402.2	0.9	33.3
402.4	1.4	30.7
402.6	1.1	31.5
402.8	1.5	30.5
403.0	0.4	32.7
403.2	1.7	31.9
403.4	1.7	32.6
403.6	1.7	33.2
403.8	0.1	34.2
404.0	0.9	34.4
404.2	0.9	34.4
404.4	1.9	35.4
404.6	1.9	36.6
404.8	2.1	37.0
405.0	1.8	36.9
405.2	0.8	35.8
405.4	1.0	36.8
405.6	1.1	37.7
405.8	2.1	38.3
406.0	2.0	37.7
406.2	1.3	38.3
406.4	1.2	38.1
406.6	1.3	38.5
406.8	1.3	38.5

**Table 5.9:** The estimated values self quenching rate constant  $(k_q)$  and zeropressuure intercept  $(\tau_{zero})$  of NO<sub>2</sub> in the predissociation region 399 to 415 nm.

Table 5.9: Contd.

Wavelength	k <sub>a</sub>	$\tau_{zero}$
(nm)	$(\times 10^{-11} \text{ cm}^3/\text{molecule/sec})$	(µ <b>sec</b> )
407.0	1.3	38.7
407.2	1.4	39.1
407.4	1.3	38.7
407.6	1.3	39.6
407.8	1.3	40.3
408.0	1.1	40.9
408.2	1.0	40.3
408.4	0.8	39.8
408.6	0.7	40.0
408.8	1.0	40.9
409.0	0.9	40.7
409.2	1.2	40.9
409.4	1.1	40.7
409.6	1.1	40.9
409.8	1.2	41.2
410.0	1.1	40.9
410.2	1.0	41.0
410.4	0.9	40.9
410.6	0.9	41.1
410.8	1.0	40.8
411.0	1.1	41.1
411.2	1.1	41.1
411.4	1.2	40.6
411.6	1.5	42.0
411.8	1.4	41.8
412.0	1.4	41.1
412.2	1.5	41.6
412.4	1.4	41.3
412.6	1.6	42.4
412.8	1.8	42.8
413.0	1.2	40.3
413.2	1.3	40.3
413.4	1.2	39.5
413.6	1.7	40.6
413.8	1.7	41.2
414.0	1.8	41.0
414.2	1 7	41.3
414.4	1.7	40.0
414.6	2.6	42.1
414.8	2.3	41.0
415.0	24	41 4
415.2	$\tilde{2}5$	41.8
415.4	2.4	40 7
415.6	$\tilde{2}5$	41.6
415.8	2.5	41 1
416.0	1.4	38.7

# **Chapter 6**

# **Conclusions And Scope For Future Work**

## 6.1 Conclusions

The total fluorescence and lifetime of excited states of NO<sub>2</sub> has been studied at different gas pressures at room temperature. These measurements were carried out from the dissociation limit near 399 nm to 490 nm in three regions as discussed in Chapter 5 using pulsed excitation technique. All these measurements were done at an instrumental resolution of 0.01 nm. Depending on the lifetime ( $\tau$ ) being measured, the most probable error involved was estimated to be  $\pm 20.2\%$  for  $\tau = 1 \ \mu \text{sec}$  to  $\pm 3.3\%$  for  $\tau = 120 \ \mu \text{sec}$ .

From the studies of total fluorescence (excitation spectra), it is clear that the overall structure of the spectrum is not sensitive to pressure. But at the same time, it is noted that the relative intensity distribution of the banded structure changes with pressure. This clearly implies that collisional depopulation of initially populated levels and repopulation of intermediate levels occurs at increasing pressure. Near the dissociation limit 399 nm, the total fluorescence intensity is nearly zero and sharply increases above 399 nm. The decrease in total fluorescence intensity near the dissociation limit is attributed to the electronic predissociation of  $NO_2$ in this region. Due to this, the fluorescence quantum efficiency starts diminishing below 416 nm.

The fluorescence studies carried out at different pressures clearly show that, at low pressures ( < 5 mTorr), the fluorescence decay is exponential which implies that only a single excited state is responsible for the fluorescence. This static component gets quenched with increase in pressure. At higher pressures (  $\geq$  5 mTorr), the fluorescence decay is non-exponential, with lifetimes between 120  $\mu$ sec to 1  $\mu$ sec at several excitation wavelength along with the static component. This implies that there are more than one excited state responsible for the total fluorescence. The frequency of occurrence of the short components has been found to increase with pressure and the excited state gets quenched with pressure. It could be safely concluded that, even though the electronic state rearrangements are initiated through collisions resulting in the redistribution of energy of the excited state, its effect on the quenching of the excited states is pronounced at pressures larger than 5 mTorr. The perturbed  ${}^{2}B_{2}$  and  ${}^{2}B_{1}$ states are mainly responsible for fluorescence in this region above 465 nm and fluorescence emission from  ${}^{2}B_{2}$  is found to be stronger than that from the  ${}^{2}B_{1}$  state. The  ${}^{2}B_{2}$  undergoes vibronic coupling with the ground state  ${}^{2}A_{1}$  state and the  ${}^{2}B_{1}$  is coupled to the ground state  ${}^{2}A_{1}$  state by Renner-Teller coupling. Hence the lifetimes of these perturbed states are lengthened. In the region below 462 nm to the dissociation limit, the fluorescence emission is mainly from perturbed  ${}^{2}B_{1}$ . At a few wavelengths, the emission from unperturbed levels also have been observed. Along with these lifetime components mentioned above, a very short fluorescing component ( $< 10^{-7}$ sec) has been observed which is attributed to the products of the predissociation of  $NO_2$ . Near the predissociation region, the lifetime

of the static component starts decreasing as the dissociation limit is approached. This is because fluorescence quantum efficiency decreases due to the increase in predissociation. As the pressure is increased, the fluctuations in the lifetime becomes much more pronounced in this region. In the predissociation region, both predissociation and collisional quenching are responsible for the decrease in the fluorescence intensity as a function of pressure. However, at higher pressures, it has been found from the predissociation in non-radiatively depopulating the excited states of NO<sub>2</sub>.

The Stern-Volmer study of the static component carried out at all excitation wavelengths confirms that the quenching process is a multi-step process. The Stern-Volmer plots were generally found to be non-linear having an upward curvature at the lower pressure side due to step wise vibrational deexcitation. The studies of Stern-Volmer plots for the estimation of zero-pressure lifetime in the entire region suggested that more than one electronic states are, in general, involved in the emission process. As the wavelength of excitation approaches the predissociation limit, the variation (scatter in the values deduced) in self-quenching rate constant and zero-pressure intercept were found to increase. This gives a clear indication that collision induced processes couple with the predissociation of  $NO_2$ .

In the present study, the estimated values of lifetime were found to be lower than those reported in literature for the static component. This discrepancy is attributed to the short excitation pulse used to excite the molecule whose lifetimes are much longer than the excitation pulse. Hence the long lifetime components are apparently shortened due the small finite excitation pulse.

To conclude, it is clear that transitions involving both  ${}^{2}B_{1}$  and  ${}^{2}B_{2}$  states are found in the visible spectrum. The transitions  ${}^{2}B_{1} \rightarrow {}^{2}A_{1}$  and  ${}^{2}B_{2} \rightarrow {}^{2}A_{1}$ have been observed at several wavelengths in the entire excitation region suggesting that these two states overlap in the entire visible spectrum. These states are perturbed by high lying dense vibrational levels of the  ${}^{2}A_{1}$  ground state through vibronic coupling (for  ${}^{2}B_{2}$  state) and Renner-Teller coupling (for  ${}^{2}B_{1}$  state). These couplings also are responsible for the lengthened radiative lifetimes in NO<sub>2</sub>. Also the transition from  ${}^{2}B_{2}$  state is stronger than that from  ${}^{2}B_{1}$ . Here a possible interaction between  ${}^{2}B_{1}$  and  ${}^{2}B_{2}$  via  ${}^{2}A_{1}$  cannot be ruled out. The interactions among these states are schematically shown in Figure 6.1



Figure 6.1: Vibronic interaction schemes in NO<sub>2</sub> molecule

For detailed information about the different states involved in the total fluorescence, lifetime measurements at wavelengths corresponding to single fluorescence lines are necessary which can unambiguously be correlated with the corresponding upper levels.

#### 6.2 Scope for Future Work

In the fluorescence and lifetime studies of excited states of  $NO_2$ , the main problems that have prevented the complete analysis of  $NO_2$  visible spectrum are

1. The spectrum extends from the excitation wavelength to  $\sim$ 800 nm with too many lines.

- 2. The spectrum shows no obvious regularity or periodicity and in general, it is difficult to identify a set of lines in a vibronic band.
- 3. The excitation spectrum recorded at room temperature is of poor resolution because of the setting in of intra-vibrational relaxation (IVR) processes. Further broadening is due to the ro-vibrational distribution of the ground state at the equilibrium room temperature.

These problems can be overcome with a better technique which can state selectively excite a single hyperfine structure of NO<sub>2</sub> molecule to determine directly the lifetimes under collision free conditions. This can be achieved by expanding the NO<sub>2</sub> gas using a supersonic nozzle into vacuum. Due to Joule cooling, temperatures as low as less than 10 K could be easily achieved in supersonic beam, which sets almost all molecules to their zero-point energy. As a result, the excitation and emission spectra become well resolved, rendering interpretation of the data easy. The unambiguous lifetime measurement at wavelength corresponding to single fluorescence lines can be achieved by using an excitation source of highly narrow bandwidth along with the use of supersonic jet expansion of the molecule, resulting in a much less complicated fluorescence spectrum. Under such collision-free environment, the probability for collisionfree transitions from one level to another excited or ground state level by a radiative transition or by internal conversion can be studied and hence the different vibronic coupling mechanisms can be studied in detail. With upgradation of the present experimental setup with a supersonic jet assembly, the study of  $NO_2$  and other molecules can be carried out in greater detail.

In the present setup, the dispersed fluorescence of  $NO_2$  can be studied by dispersing the total fluorescence using a monochromator (or a spectrograph). This kind of study would help in understanding the pressure dependence of fluorescence and the quenching mechanism in a better way. With the upgradation of the dye laser tuning range towards the ultra violet region, the fluorescence and lifetime studies of molecule like  $SO_2$ , CO etc can be studied which are important in the study of atmospheric chemistry. Such experiments are currently being planned in our laboratory.

# **List of Publications**

- The study of NO<sub>2</sub> lifetimes in the excitation wavelength 465–490 nm.
   V. Sivakumaran, K.P. Subramanian and Vijay Kumar
   J. Quant. Spectro. Rad. Trans., (accepted for publication).
- 2. The study of NO<sub>2</sub> lifetimes in the excitation wavelength 423–462 nm.
  V. Sivakumaran, K.P. Subramanian and Vijay Kumar (Under preparation)
- 3. Fluorescence and life time studies of NO<sub>2</sub> in the predissociation region (399 416 nm).
  V. Sivakumaran, K.P. Subramanian and Vijay Kumar (Under preparation)
- 4. Fluorescence quenching studies of NO<sub>2</sub> in the excitation region 399–490 nm.
  V. Sivakumaran, K.P.Subramanian and Vijay Kumar *(Under preparation)*
- Flourescence life time measurement of sodium salicylate at 308 nm.
   V. Sivakumaran, K.P. Subramanian and Vijay Kumar (Under preparation)

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