Chapter 6

Conclusions And Scope For Future Work

6.1 Conclusions

The total fluorescence and lifetime of excited states of NO\textsubscript{2} 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 ±20.2\% for $\tau = 1$ $\mu$sec to ±3.3\% for $\tau = 120$ $\mu$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 NO₂ 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 (≥ 5 mTorr), the fluorescence decay is non-exponential, with lifetimes between 120 μsec to 1 μsec 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 \(^2B_2\) and \(^2B_1\) states are mainly responsible for fluorescence in this region above 465 nm and fluorescence emission from \(^2B_2\) is found to be stronger than that from the \(^2B_1\) state. The \(^2B_2\) undergoes vibronic coupling with the ground state \(^2A_1\) state and the \(^2B_1\) is coupled to the ground state \(^2A_1\) 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 \(^2B_1\). 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 NO₂. 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 present study that collisional quenching becomes much stronger than predissociation in non-radiatively depopulating the excited states of NO₂.

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 NO₂.

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 \( ^2B_1 \) and \( ^2B_2 \) states are found in the visible spectrum. The transitions \( ^2B_1 \rightarrow ^2A_1 \) and \( ^2B_2 \rightarrow ^2A_1 \) 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 $^2A_1$ ground state through vibronic coupling (for $^2B_2$ state) and Renner-Teller coupling (for $^2B_1$ state). These couplings also are responsible for the lengthened radiative lifetimes in NO$_2$. Also the transition from $^2B_2$ state is stronger than that from $^2B_1$. Here a possible interaction between $^2B_1$ and $^2B_2$ via $^2A_1$ cannot be ruled out. The interactions among these states are schematically shown in Figure 6.1

![Figure 6.1: Vibronic interaction schemes in NO$_2$ molecule](image)

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 ~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 NO₂ molecule to determine directly the lifetimes under collision free conditions. This can be achieved by expanding the NO₂ 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 collision-free 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 NO₂ and other molecules can be carried out in greater detail.

In the present setup, the dispersed fluorescence of NO₂ 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.