CHAPTER VI

PHOTOACOUSTIC STUDIES IN NITROGEN DIOXIDE

ABSTRACT

Chapter VI deals with the results of the pulsed and cw PAS studies in gas phase nitrogen dioxide. The role of NO$_2$ in atmospheric pollution and the importance of its detection are tioned. An attempt has been made to obtain the PA signature spectra of NO$_2$ in the visible region using both pulsed and cw dye lasers in the 560–570 and 570–600nm respectively. The absorption characteristics and the variation of the PA signal using the high low concentration NO$_x$ samples with the gas pressure and laser power are given. The noise level and the minimum detectable signal are also calculated. Due to the extreme complexity of the ble spectrum of NO$_2$, a complete analysis of the same has been and to be very difficult.
CHAPTER VI

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6.1. Introduction

Structurally speaking, NO₂ is a very simple, non-linear triatomic molecule. However, from a spectroscopic point of view, it has a wide and varied physical and chemical properties and it yields a very complex absorption spectrum stretching from the UV into the IR regions due to its coloured nature. Pure NO₂ is highly reactive and toxic and it combines with ambient oxygen to form a mixture of various oxides of nitrogen (its dimerization to nitrogen tetroxide, N₂O₄, is a classic example of chemical equilibrium), is deeply coloured making it highly absorbing in the visible region, and is apparently a chief chemical agent in the atmospheric pollution process. Its affinity to water is the main cause for formation of acid rain. The chief source of atmospheric oxides of nitrogen are from high temperature combustion sources. It has been proved that the oxidation process in the oxides of nitrogen-hydrocarbon-sunlight system is the main cause of photochemical air pollution and it is found to be a major component of smog formation [1]. NO and NO₂ are present in pollution free atmospheres at nominal concentrations of 0.2ppb and 0.5 to 4ppb respectively. It is seen that their residence times in the atmosphere is about 4 and 3 days respectively [5]. Effects like colouration of the atmosphere,
photochemical reactions, hazards to vegetation and animals and other health effects are the pronounced results of NO₂ pollution. The effect of atmospheric pollutants on plants and animals has been studied by many workers in the past [6]. Exposure of plants to concentration levels of ~ 10 ppm of NO₂ has been found to reduce their growth by over 35% [7]. For humans, it was seen that the airway resistance of the lungs increases with moderate exposures to NO x. Higher levels of concentrations can also be fatal. It was also reported that the illness rates were higher in environments having NO₂ concentrations exceeding 0.06 ppm [8]. The acute symptoms from these high concentrations that prevail in urban atmospheres are similar for SO₂ exposure also.

The inter-relationships between the various oxides of nitrogen viz, NO, N₂O, NO₂, NO₃, N₂O₄ etc. symbolized by NO x are complex, particularly in the presence of light, oxygen, ozone and organic matter. It is however evident that among these oxides, only NO₂ is both present in significant amounts and has a strong absorption of sunlight, the energy source required for the initiation of photochemical air pollution. Furthermore, it photodissociates to give highly reactive fragments of oxygen atoms capable of initiating the thermal reactions responsible for the overt physiological manifestation of smog such as eye irritation and plant damage. While the importance of NO₂ in air pollution was recognized years ago, until recently, the basic information covering the details of its photochemistry in both the mm Hg pressure range and the ppm concentration ranges was relatively scarce [2,3].

6.2. Sources of Atmospheric NO₂

NO x is generated by many man-made processes such as, fuel oil combustion, solid fuel combustion, incineration, agricultural
burning and even, to an extend, by household fires. Though some of these may look insignificant, they have a cumulative effect on the net NO\textsubscript{x} levels. Among these, the major producer of NO\textsubscript{x} is the automobile exhaust of which NO and NO\textsubscript{2} are the main constituents. NO is formed during the high temperature combustion and is subsequently oxidized to NO\textsubscript{2} by a relatively slower reaction which takes place only in the exhaust streams with large concentrations of NO and excess of oxygen. Generally, it is seen that 99\% of the NO\textsubscript{x} in auto exhaust is NO [9], and in Diesel engines, 37\% of the NO\textsubscript{x} is found to be NO\textsubscript{2} [10].

6.3. Photochemistry Of NO\textsubscript{2} In The Visible Region

The vapour phase photochemistry of NO\textsubscript{2} in the visible region of the solar spectrum (\(>435.8\text{nm}\)) is a good example of the mechanism consisting only of photophysical processes. In this region, irradiation of either pure NO\textsubscript{2} or of NO\textsubscript{2} in air with hydrocarbons added does not lead to permanent chemical changes in the system. This is particularly pertinent to air pollution since a large fraction of the sunlight absorbed by NO\textsubscript{2} falls in the region of \(\lambda\geq435.8\text{nm}\) [4] as seen in the fig.6.1. In this region, several mechanisms occur which can be represented as follows;

1. Absorption: The first reaction to occur is the photochemical dissociation of NO\textsubscript{2} by the 300-400nm UV photon

\[
\text{NO}_2 + h\nu \rightarrow \text{NO}_2^* \quad \text{......(6.1)}
\]

2. Collisional de-activation

\[
\text{NO}_2^* + \text{NO}_2 \text{ (or M)} \rightarrow \text{NO}_2 + \text{NO}_2 \text{ (or M)} \quad \text{......(6.2)}
\]
Fig. 6.1. The absorption of sunlight by NO$_2$ at different incidence angles ($z$) of the sun [4].

Fig. 6.2. The various vibrational modes of bent and linear NO$_2$ molecule.
3. Fluorescence

$$\text{NO}_2^* \rightarrow \text{NO}_2 + h\nu' \quad \text{.......(6.3)}$$

4. Resonance Transfer (Intersystem crossing)

$$\text{NO}_2^* \rightarrow \text{NO}_2^{**} + \text{heat} \quad \text{.......(6.4)}$$

5. Collisional de-activation

$$\text{NO}_2^{**} + \text{NO}_2 \text{ (or M)} \rightarrow \text{NO}_2 + \text{NO}_2 \text{ (or M)} \quad \text{.......(6.5)}$$

6. Fluorescence

$$\text{NO}_2^{**} \rightarrow \text{NO}_2 + h\nu'' \quad \text{.......(6.6)}$$

Step 4 is a resonance transfer from a higher excited electronic state to a lower one. It is a general type of process highly important in the photoactivated system. The specimens M in steps 2 and 5 is a third body which may take up the electronic excitation energy of $\text{NO}_2^*$ or $\text{NO}_2^{**}$ and convert it into thermal energy without chemical change and can be any molecule in air. The direct photodissociation of $\text{NO}_2$ in the 300nm region into nitric oxide (NO) and highly reactive oxygen atoms in their ground electronic state ($3p$) takes place as,

$$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} (3p) \text{ (primary process)} \quad \text{.......(6.7)}$$

In the far UV, the oxygen atom formed is in the first excited state $\text{O}(^1D)$. It is important to note that there is significant difference in the reactivity of the oxygen atoms in the ground state triplet ($3p$) and the singlet excited state ($^1D$). The atomic oxygen produced in this process is highly reactive which
combines through collisions with molecular oxygen present in abundance to give ozone and NO in the case of traces of NO₂ as,

\[ O + O_2 \rightarrow O_3 + M \quad \text{(secondary process)} \quad \ldots \ldots \quad (6.8) \]

\[ O + NO_2 \rightarrow NO + O_2 \quad \text{(secondary process)} \quad \ldots \ldots \quad (6.9) \]

The ozone produced in the above reaction (8) is relatively stable to thermal decomposition and exist long enough to form or be a precursor to many of the host of compounds that characterize a typical photochemical 'smog' [13]. The ozone reacts very rapidly with NO originally produced in the primary process to yield,

\[ O_3 + NO \rightarrow NO_2 + O_2 \quad \ldots \ldots \quad (6.10) \]

In these cases also, M is the third body which must be present to siphon away the energy formed in the highly exothermic reaction process, otherwise, the hot \( O_3 \) molecule would immediately disintegrate into O and \( O_2 \) [11]. The rates of these reactions will depend on the intensity of the UV radiation and thus the altitude of the sun and the atmospheric UV absorption. The reactions 6.9 and 6.10 play a vital role in the ozone layer depletion. The high altitude aircrafts flying in the stratosphere (~18kms) release NO as exhaust, which reacts with the ozone present there. The NO is not consumed in these reactions and thus there is a net depletion of the ozone and the atomic oxygen in the upper atmosphere, thus contributing to create the 'ozone hole' [12].

6.4. Detection Of Nitrogen Dioxide

There are many methods to estimate the NO\(_x\) or NO\(_2\) concentrations in trace amounts [34], and a few commonly used ones are described
Various estimation techniques for NO₂ have evolved over the years and they include photometric (absorption, fluorescence etc.), calorimetric, adsorption and chemiluminiscence.

The most common and easiest method to estimate NO₂ is by photometric methods, though it is not very sensitive. The NO present in the NOₓ is completely converted to NO₂ by bubbling it through potassium permanganate solution [30]. The NO₂ is then bubbled through the Greiss-Ilosvay reagent as modified by Saltzman [31]. The intensity of the pink color of the reagent is indicative of the concentration of NO₂. High concentrations of NO₂ can be directly measured by monitoring the absorption of a particular wavelength of visible light in comparison to a standard sample. Another commonly used technique for NOₓ determination is the phenoldisulfonic acid method, which measures the total combined nitrogen oxides or compounds (except nitrous oxide) whether it be HNO₃, NO₂, NO, any organic nitrogen compound or an inorganic nitrate [32]. A NO₂ detector based on the chemiluminescent reaction between NO₂ and 'luminol' (5-amino-2,3-dihydro-1,4-phthala-zinedione) in alkaline solution capable of detecting both NO and NO₂ in the sub ppb region has been reported [27,28,8]. The total NO₂ in NOₓ can also be determined by oxidizing all the NO to NO₂ and then bubbling it through water. NO₂ is easily absorbed by water and the estimation of the acid content in the resulting solution can give a rough estimation of the NO₂ concentration. Adsorption of NO₂ on substances like silica gel have been used to determine NO₂ concentrations though it is not efficient at low concentrations [33]. The gas chromatography technique is yet another method to determine NO₂ concentrations accurately. This method does not have a large dynamic range and moreover, each test sample requires a standard reference sample of comparable concentrations to obtain the results and is thus inconvenient. The differential
absorption technique was employed to determine remotely in ppm concentration, the \( \text{NO}_2 \) distribution over a chemical factory using a tunable dye laser and a LIDAR setup [35].

6.4.1. Calorimetric Detection Techniques For \( \text{NO}_2 \)

The two mainly used calorimetric techniques for \( \text{NO}_2 \) detection are the photoacoustic and the photothermal deflection (Thermal lens) techniques. The various advantages of these techniques for trace analysis and pollution monitoring of \( \text{NO}_2 \) over other conventional techniques are listed in chapter 1.

i. Thermal Lens Technique

The thermal lens technique (PTD technique) has also been used by several workers to detect the \( \text{NO}_2 \) species. Tran and Franko used the dual wavelength, differential thermal lens technique to detect 300ppb of \( \text{NO}_2 \) for a 30mW multiline argon laser pump source. Essentially, in the thermal lens technique, the deflection of a weak probe beam due to the refractive index gradient produced by the absorption of the stronger pump beam by the sample is monitored and this technique is also a calorimetric technique like the PA detection technique. Higashi et al [23] used this technique to detect 5ppb of \( \text{NO}_2 \) using the 488nm line of the argon ion laser since it gave the largest signal due to its large output power and large molar absorptivity (\( \varepsilon = 60 \)). Pulsed thermal lens was used to detect the atmospheric traces of \( \text{NO}_2 \) using an excimer pumped dye laser and a trace detection limit of 4ppb was obtained [24,25,26].
ii. PA Detection Of NO₂

The major advantage of the PA detection scheme, as mentioned in earlier chapters, is its in situ monitoring capability. Though other gases have been extensively detected and studied in detail using the PA technique, not many workers have used this technique to actually study this gas. The first reported study of NO₂ using PA detection technique was by Harshbarger and Robin who used a white light source-monochromator setup to record the visible PA spectrum of NO₂. It was observed that the PA spectrum follows the absorption spectrum up to the neighbourhood 400nm at which point the absorption peaks and then begins to decrease slowly, whereas the heat amplitude suffers a dramatic reduction to about two-thirds of its peak intensity in the same wavelength region. It is at 400nm that the dissociation limit of NO₂ is reached (Equ.6.7). Even though the dissociation limit of NO₂ is 398.6nm, the fall-off in the PA signal begins at only 420nm [14,46]. The PA signal falls due to the fact that the absorbed energy finds an alternative decay route in the process of photodissociation. The use of high resolution dye laser for exciting the NO₂ reveals extensive fine structure in the PA spectrum, but in spite of this, there is still no sharp onset for the dissociation. Kreuzer et al used the CO₂ laser at powers of ~1watt to detect 0.1ppb of NO₂ in nitrogen buffer using the PA technique [15]. Agnus et al used the modulated cw dye laser to detect 10ppb of NO₂ [16] and Claspy et al used a 250mW pulsed dye laser to detect ≈10ppb of the same using the PA detection technique [17]. Using a resonant PA cell, the PA spectrum in low resolution was observed in the 580-610nm region. Since the molar extinction coefficient of NO₂ in this region is less than 20, this technique has obvious applications for the analytical determination of not only NO₂, but of any gas having even an extremely weak absorption in the wavelength region.
of the laser. A fibreoptic sensor based resonant PA cell was used to detect traces of NO$_2$ [18]. A fibreoptic interferometer, constructed in the Mach-Zehnder arrangement replaces the microphone in the cavity and a detection limit of $\sim$ 50ppb was obtained for a laser power of 500 mW using the argon ion laser. The continuous products of the photolysis of nitromethane and the subsequent formation of NO$_2$ was studied by PA techniques by Colles et al, in which they monitored the levels of NO$_2$ after a flash photolysis of nitromethane [19]. Poizat and Atkinson used the differential PA technique to detect NO$_2$ concentrations of the order of 2ppb, and a linear dependence of the PA signal on the NO$_2$ concentrations for over 6 orders of magnitude was obtained using the various wavelengths of a krypton ion laser [20]. PA detection technique using argon laser was used to monitor the evolution of NO$_2$ in the NO-O$_3$ reaction, which essentially are the critical components involved in the chemistry and physics of the troposphere and the stratosphere [21]. The concentration changes in NO and NO$_2$ agreed well with other detection techniques. NO$_2$ has been used frequently to calibrate PA systems due to its high absorption in the visible region. Since the NO$_2$ group exists in most of the organic explosives, PA detection can be effectively used to detect the explosive vapours by using a broad-band tunable laser to probe the absorption due to the asymmetric stretching near 6$\mu$m or the -O-N stretching mode near 11$\mu$m, the specific location being determined by the basis molecule to which this group is attached [44]. The peak asymmetric stretch absorptions in -NO$_2$ group occur at 6.039 and 6.086$\mu$m in ethylene glycol dinitrate (EGDN), and at 5.97, 6.046 and 6.079$\mu$m in nitroglycerine (NG). The -O-N absorptions occur at 11.148, 11.628 and 11.877 $\mu$m in EGDN and at 11.099 and 11.905$\mu$m in NG [45]. By looking for these signature absorptions, these molecules can be traced using PAS, but the effects of interfering species are more severe in this wavelength region.
Nitrogen dioxide is one of the few relatively stable gaseous molecules with an odd number of electrons. Furthermore, it is one of the few well known triatomic molecules that absorbs in the visible region. The whole spectrum of this molecule is extremely complex and its analysis has frustrated experimentalists and theoreticians ever since it was first observed by Brewster in 1834. The unusual complexity in the visible absorption spectrum of NO$_2$ is attributed to the following: the fine structure due to the spin $S=1/2$ of the unpaired electron, and the hyperfine structure due to the nuclear spin $I=1$ of the $^{14}$N atom, and the overlapping of the excited electronic states. The coupling between the four electronic states, each of which can interact with the other three states through various perturbation mechanisms also plays an important role in its highly irregular spectrum. The visible absorption spectrum of NO$_2$ is so dense (approximately 19000 lines in the 553-648nm region) that a very high resolution is necessary to separate single vibrational-rotational lines. Although partial analysis of some select bands have been performed on the basis of high resolution fluorescence and absorption measurements, wide range, very high resolution spectra are still necessary for a thorough understanding of the complete visible spectrum. The absorption lines of NO$_2$ in the visible region have been listed as an atlas in two books, both of which present absorption and fluorescence data in a very detailed manner [36,37]. Many workers [38,39,43,47,48] in the past have investigated the visible absorption, fluorescence, and Raman spectra of NO$_2$ in the past starting from Broida [43] in 1969 who
observed the fluorescence of NO$_2$ under argon ion laser excitation.

Triatomic molecules of the type YXY have three normal modes viz, $v_1$ the symmetric stretch, $v_2$ the bending vibration and $v_3$ the asymmetric stretch. The energy ordering of the vibrational modes is usually $v_3 \geq v_1 \geq v_2$. The various vibrational modes of the linear and bent NO$_2$ molecules are represented in fig.6.2. The direction of the arrows indicate the nuclear motion whereas the magnitude indicates the displacements. The centre of mass does not move for normal mode vibrations. The absorption in the visible region of NO$_2$ is due to the $^2B_2 \rightarrow ^2A_1$ transition as shown in fig.6.3. The $^2B_2$ state is obtained from the $^2A_1$ state by promotion of an electron from the $3b_2$ to the $4a_1$ orbital. It has been known from calculations that the $^2B_2$ state is expected to be more bent than one in the ground state. Thus, excitation to the $^2B_1$ state should make the molecule somewhat linear [37]. It is seen from the calculations of Gillispie et al that the $^2B_2$ to $^2A_1$ states may readily interact with each other, because of the potential surfaces are close to each other and hence are said to have favourable Franck-Condon overlap factors.

ii. Pulsed PA Spectrum Of NO$_2$

Here we describe the experimental procedure and the results of pulsed PA spectrum of NO$_2$ gas in the 560-580nm region of the visible spectrum. The experimental setup for the pulsed PAS of NO$_x$ is as mentioned in Chapter 3. The advantage of using the visible wavelength for NO$_x$ detection is that NO, which is a part of the NO$_x$ species, does not have any interference in the visible region, whereas, it interferes in both the UV as well as the IR regions. The single cavity PA cell was used for these studies. The gas is filled into the cell at the required pressure (no
Fig. 6.3. The schematic of the allowed NO₂ electronic transitions
buffer gas was used) and the pulsed dye laser is tuned across the wavelength. The spectrum observed is basically the \( ^2B_2 \rightarrow ^2A_1 \) band system of \( \text{NO}_2 \) in the visible region. The energy profile of the dye laser is compensated by the ratioing technique. Figure 6.4. shows the normalized PA spectrum of high concentration \( \text{NO}_2 \) in the visible region. The UV-VIS-NIR absorption spectrum of \( \text{NO}_2 \) in this wavelength region (fig.6.4.) shows only a broadband structure peaking at 564 nm which corresponds to the peak output wavelength of the pulsed dye laser. From the above figure, it can be seen that at the wavelength where the absorption of \( \text{NO}_2 \) shows a maximum, the PA signal tends to show a dip, indicating the possibility of an alternate radiative path of de-excitation occurring at this wavelength, thus causing a decrease in the PA signal. This dip in the PA spectra can be used as a signature of the presence of \( \text{NO}_2 \) in trace analysis studies since this signature is clearly evident at all the pressure and laser energy ranges that were studied.

### iii. Laser Energy And Pressure Variations Of The PA Signal

The PA spectrum at different laser energies is given in fig.6.5. The pressure variation of the PA spectrum is shown in fig.6.6. It can be seen that though the baseline of the PA signal increases with pressure, the spectrum is not resolved at low or high pressures. This is due to the pressure saturation of the PA signal induced by the increased collisional energy transfer in the sample which in turn reduces the energy available for the non-radiative de-excitation, thus reducing the PA signal. The collisional effects and the variation of the microphone response at high gas pressures could also induce such a pressure variation [29]. Pressures of less than 200 Torr was found to give well resolved spectra. The PA signal variation with gas pressure is represented in fig.6.7. The PA signal initially increases with
Fig. 6.4. Normalized pulsed PA spectrum of NO$_2$ and the absorption spectrum recorded with a UV-VIS-NIR spectrophotometer in the same wavelength region. Pressure $\sim$ 150 Torr, Laser energy $\sim$ 2.5mJ/pulse.
Fig. 6.5. Pulsed PA spectrum of NO$_2$ at different laser energies.

Fig. 6.6. Pulsed PA spectrum of NO$_2$ at different gas pressures.
Fig. 6.7. The variation of the PA signal with gas pressure at some of the spectral peak points (Laser energy ~ 3.3 mJ/pulse).

Fig. 6.8. The variation of the PA signal with laser energy at some of the spectral peak points (Pressure ~ 100 Torr).
the pressure of the gas and then decreases with further increase in pressure. This is seen for all the peak positions at all the laser energies studied. The laser energy variation of the PA signal at few of the prominent peak positions is given in fig.6.8. The PA signal is linear up to a laser energy of 10mJ after which PA saturation, which is characterized by a decrease in the PA signal is observed. The decrease in PA signal is due to the $1/I_0$ dependence of the PA signal at high laser intensities ($I_0$) which is quite well predicted in the PA theory.

PART B : CW PAS

i. CW PAS of NO$_2$

Since NO$_2$ has high absorption in the wavelength region of the argon ion laser, it is best suited for the detection of NO$_x$ species. The absorption coefficient of NO$_2$ at different Argon ion laser wavelengths have been reported by Sakurai and Broida [43]. Fig.6.9. shows the absorption coefficient of NO$_2$ at some of the argon and krypton ion laser wavelengths [43]. The absorption coefficient was found to be linear with respect to the gas pressure in the region of pressure investigated. NO$_2$ exists in equilibrium with N$_2$O$_4$, the mole fraction of N$_2$O$_4$ at 1 Torr total pressure being less than 0.015. The radiative lifetime of the excited NO$_2$ was also estimated as $10^{-5}$ secs. To be able to apply this technique to trace analysis of the gas sample, it is essential to obtain not only the signature spectrum, but also the variation of the signal with the input laser power and the gas pressure, which determines the concentration of the gas. The following studies are all done in the regions of tens of Torr pressure (typically 25-300 Torr). The non-availability of standard certified gas samples and an alternate efficient method
Fig. 6.9. The variation of absorption coefficient of NO\textsubscript{2} with gas pressure for some of the lasing wavelengths of argon and krypton ion lasers [43]
to analyze the prepared gas samples, very low pressure studies on the gas samples have not been carried out. It has been reported however, that the PA signal is linear in the low pressure regions also. The PA signal response for different pressures of both low and high concentration NO\textsubscript{2} at different laser powers of the multiline output as well as the various discrete lasing lines of the argon ion laser, viz, 514.5, 496, 488, 476 and 458 nm was studied. In all the cases, the PA signal shows a linear variation with pressure and laser power for low pressures and moderate laser powers. In high concentration samples, this linearity ceases to exist (ie, saturation of the PA signal sets in) at lower laser powers and pressures as compared to the low concentration samples. The details of the results of these studies are described below.

ii. Laser Power Variations Of The PA Signal

The laser power variations of the PA signal for different pressures of high concentration NO\textsubscript{2} using the multiline output of the argon ion laser is shown in fig.6.10. The PA signal remains linear with the laser power up to \( \sim 125 \text{mW} \) after which the PA signal is saturated and it decreases with further increase in laser power. This is typically the kind of PA saturation mentioned earlier in Chapter 2. Similar studies on the low concentration NO\textsubscript{2} (fig.6.11.) show that the PA saturation occurs only at laser powers greater than 1watt. In both these cases, the variation of the PA signal with laser power in the low laser power region is linear. The variation of the PA signal with laser power of the different lasing wavelengths of the argon ion laser at a gas pressures 400 Torr of low concentration NO\textsubscript{2} are represented in fig.6.12.a. It can be seen that the absorption of NO\textsubscript{2} is maximum for the 496nm and minimum for the 488 and 514nm wavelengths. Within the laser power range employed, no PA
Fig. 6.10. The variation of the PA signal with the power of the multiline output of the argon ion laser at different gas pressures of high concentration NO₂.

Fig. 6.11. The variation of the PA signal with the power of the multiline output of the argon ion laser at different gas pressures of low concentration NO₂.
saturation was observed. Similar observations were obtained for different gas pressures also.

iii. Gas Pressure Variations Of The PA Signal

Figure 6.12.b shows the variation of PA signal with the gas pressure at different laser powers of the 514nm wavelength of the argon ion laser for low concentration NO$x$. The saturation behaviour of the PA signal is clearly seen from this graph. Similar results were obtained for all the other lasing wavelengths of argon ion laser. The gas pressure variations of the PA signal for high and low concentration NO$_2$ at different laser powers of the argon multiline laser output are shown in fig.6.13. and fig.6.14. respectively. It is interesting to note that in the case of the low concentration NO$_2$, the PA signal is linear up to the measured maximum gas pressure of 300 Torr while in the case of the high concentration NO$_2$, there is a periodic variation of the signal with pressure as the pressure is increased. The PA signal peaks at a gas pressures of ~75 Torr, ~175 Torr, and 275 Torr. One possible reason for such a behaviour of the PA signal could be that there can be altered equilibrium values in the $\text{N}_2\rightarrow\text{N}_2\text{O}_4$ reaction rates which results in an enhanced concentration of N$_2$O$_4$ at gas pressures beyond 75, 175 and 275 torr resulting in a decreased absorption and thus the PA signal. Another possibility is the formation of dimers of NO$_2$ at higher concentrations. The existence of such dimer formation in NO$_2$, formed by the bi-molecular collision between an electronically excited NO$_2$ and a ground state NO$_2$ molecule has been reported by Butler et al [47] resulting in the emission of continuum in the fluorescence spectrum.

Observations similar to (fig.6.7. and 6.13.) the variation of the PA signal with gas pressure were made in mixtures of CH$_4$
Fig. 6.12. The variation of the PA signal with (a) power of the discreet lasing lines of argon ion laser and (b) gas pressure of low concentration NO₂ at 514nm wavelength.
Fig. 6.13. The variation of the PA signal with gas pressure for different laser powers of the multiline output of the argon ion laser for high concentration NO$_2$.

Fig. 6.14. The variation of the PA signal with gas pressure for different laser powers of the multiline output of the argon ion laser for low concentration NO$_2$. 
and different buffer gases detected at the 3.39 μm He-Ne laser wavelength by Wake and Amer [50,51] in the process of the study of the non-resonant and resonant PA signals with respect to pressure and buffer gas. Starting from the thermodynamic solid-gas theory of Kerr and Atwood [52], which provides a suitable starting point to analyze the PA signal strength in the case of a weakly absorbing gas confined to a cylindrical cavity excited by a radiation passing through the axis of the cavity, one may analyze these results. Taking the expression for the first harmonic lock-in amplifier output,

\[
V = S(P_o, \gamma, T) \beta(P_o) \frac{P_o}{4\pi LkT} \left\{ \sum_m D_m \exp(i\theta_m) \right\}
\]

\[
= \frac{S(P_o, \gamma, T) \beta(P_o) P_o}{4\pi LkT} \left\{ \sum_m \frac{D_m \exp(i\theta_m)}{1 + \left( \frac{\omega^2 a^4}{\alpha^2 \xi_m^4} \right)^{1/2}} \right\}
\]

\[
\cdots \cdots (6.11)
\]

Here, \( S(P_o, \gamma, T) \) is the sensitivity of the microphone, and

\[
\tan (\theta_m) = \left( \frac{\omega a^2}{\alpha \xi_m^2} \right)^{-1}
\]

\( I_o / L \) is the laser power incident/unit length, \( \beta(P_o) \) is the fraction of \( I_o / L \) absorbed, \( P_o \) and \( T \) the equilibrium pressure and temperature of the gas, \( k \) and \( \alpha \) the effective thermal conductivity and effective thermal diffusivity respectively, \( \xi_m \) is the \( m \)th root of the 0th order Bessel function \( J_0(\xi) = 0 \). \( D_m(b) \) the numerical coefficient that depends on \( b \), the ratio of the Gaussian beam waist to the cell radius \( a \). \( D_m \) is difficult to estimate for small values of \( b \) due to round-off errors and can be verified as,

\[
\sum_m D_m(b) = 1 - b^2 + \frac{b^2 - (2b)^{-2}}{\exp(1/b^2)}
\]

\[
\cdots \cdots (6.12)
\]

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The variation in the PA signal can be described on the basis of the above equation as,

(a) The initial rise in the PA signal is due to a direct consequence of the increase in pressure $P_0$ and a decreasing $k$.

(b) The term $\left(\frac{\omega^2 a^4}{a^2 \xi_1^2}\right)$ becomes greater than unity near the peak of each curve allowing the $1/P_0$ dependence to cancel the $P_0$ factor and thus limits any further increase in the PA signal.

(c) The high pressure fall in the PA signal is due to a decreasing power absorption, $\beta(P_0)$ and a decreasing microphone sensitivity at high pressures.

Wake and Amer [50], using different buffer gases showed that noble gases produce the largest PA signal. Those gases with large thermal diffusivities yield largest signals at high pressure than those with smaller diffusivities. A practical consequence of this behaviour is that if one were to optimize the SNR of the system, the following should be taken into account: the term $\left(\frac{\omega^2 a^4}{a^2 \xi_1^2}\right)^{1/2}$ of Equ.6.11 must be kept of the order of unity or smaller for as high a pressure as possible. Since $\alpha$ is proportional to $k(P_0 C_v)^{-1}$, $C_v$ being the specific heat at constant pressure, the first term eventually drops out, the $P_0$ and $k$ dependence cancels out and the signal becomes proportional to $1/C_v$. Until this happens, however, the PAS signal rises with pressure. Ideally, then, one requires a buffer gas of small $k$ and high $\alpha$ values. Both this factor and the high pressure dependence mentioned above point to as small a $C_v$ as possible indicating the selection of a noble gas as buffer. One may also moderate the increase of $\left(\frac{\omega^2 a^4}{a^2 \xi_1^2}\right)^{1/2}$ by varying other factors. One should use as low a modulation frequency as possible, although the $1/f$ noise of the electronics sets the limit.
Fig. 6.15. The 3-D representation of the laser power and gas pressure variation of the PA signal for high concentration NO$_2$ using the multiline output of the argon ion laser.
of this approach. A reduction in the cell radius would benefit since this enters as a factor in the fourth power. Here too, a tradeoff exists as $D_m$ falls with increasing $b$ value. Also reducing the temperature enhances the signal as well as lowers the electrical noise to a limit [50]. In general, higher signal may be obtained with an absorber-buffer mixture than with any amount of the absorber alone.

The pressure and laser power variations of the high concentration NO$_2$ using the multiline output of the argon laser are summarized in the 3-D plot given in fig.6.15. From these data, the pressure corresponding to the lowest signal detectable can be calculated. This was done by monitoring the PA signal at a fixed laser power while the cell was being evacuated. The residual gas in the cell after the cell is pumped down can still give a signal which was detected to be 10µV at a laser power (multi-line output) of 35mW which corresponds to a pressure of $\sim 7 \times 10^{-3}$ Torr of high concentration NO$_2$ which means that detection limits of a few tens of ppb can easily be achieved in a gas mixture. Thus the potentiality of this technique for monitoring of NO$_2$ in the context of atmospheric pollutants is obvious.

### iv. CW PA Spectrum Of NO$_2$

The absorption spectrum of NO$_2$ recorded using a UV-VIS-NIR spectrophotometer in the visible region of 570-600nm region is given in fig.6.16. The complex nature of the absorption of NO$_2$ is clearly evident from this spectrum. To record the PA spectrum of NO$_2$, the ring dye laser is tuned across the wavelength region and the PA signals obtained from the differential PA cell is normalized against the variation in laser power across the dye laser output profile. The normalized PA spectrum of NO$_2$ is shown in fig.6.17. The spectrum, quite different from the absorption
Fig. 6.16. The absorption spectrum of NO₂ in the 570-620nm region recorded using a UV-VIS-NIR spectrophotometer.

Fig. 6.17. The normalized cw PA spectrum of high concentration NO₂ in the wavelength region 575-609nm (Pressure ~ 100 Torr, pre-amp gain ~ 40dB, Average laser power ~ 150mW).
spectrum obtained for the same wavelength region, shows four bands of the $^2B_2 \rightarrow ^2A_1$ band system of the visible region. Spectra with similar features of NO$_2$ in the visible region have been reported by many workers employing different detection techniques like absorption [37,39], fluorescence by supersonic beam technique [48], opto-galvanic detection technique [49], polarization spectroscopy [53,54,55] and by calorimetric techniques like PA and PTD methods. Most of the work other than absorption and fluorescence of NO$_2$ does not detail spectroscopy of the sample but has concentrated on the detection of the sample. The PA spectra of the different bands in the $^2B_2 \rightarrow ^2A_1$ transition in the wavelength region of the dye laser are given in the expanded form in fig.6.18.a,b,&c. The noise reduction capability of the dual cavity differential cell used for these studies is evident from the noise level indicated in the above spectra. The noise level was recorded by plotting the PA signal versus time at a particular wavelength. Typically, a total noise of 3.3mV in a signal of 700mV was observed at a wavelength of 568nm with the amplifier gain at 40dB, and 2.6mV at 588nm, where the total signal is ~ 400mV. The fine structure of all the bands is clearly resolved in the present PAS mainly due to the narrow linewidth of the ring dye laser (≈ 30GHz). Such resolved features have been detected for the first time in the case of NO$_2$ PA spectrum in the visible region.

6.5. Conclusions

The significance of studies on NO$_2$ specially in the context of atmospheric pollution and the detection of NO$_2$ by PA technique using both pulsed and cw dye lasers have been described. The signature spectrum of NO$_2$ in the 560-600nm has been established and the nature of variation of the PA signal with the gas pressure and laser energy/power has been determined. It is seen that the
Fig. 6.18(a) The cw PA spectrum of NO$_2$ in the (a) 566-575nm wavelength region.
Fig. 6.18(b) The cw PA spectrum of NO$_2$ in the (b) 577-594 nm wavelength region.
Fig. 6.18(c) The cw PA spectrum of NO$_2$ in the (c) 589-604 nm wavelength region
PA signal tends to saturate easily for high concentration samples. The differential PA detection technique employed here has a very low noise level as is evident from the spectra recorded.

6.6. References


[8] USEPA "Air Quality Criteria for Oxides of Nitrogen", National Air Pollution Control Administration, USA, Publication # AP-84, 1971


[38] Abe K et al, J.Mol.Spectrosc., 38, 552, (1971)

6.7. Symbols and Notations

- \( a \) radius of the PA cell
- \( \alpha \) Effective thermal diffusivity
- \( b \) Ratio of the Gaussian beam waist and the cell radius
- \( C_v \) Specific heat at constant volume
- \( D_m(b) \) Numerical coefficient dependent on \( b \)
- \( \gamma \) Ratio of specific heats
- \( I_0 \) Incident laser power
- \( k \) Effective thermal conductivity
- \( L \) Length of the cell
- \( \omega \) Modulation frequency
- \( P_0 \) Gas pressure
- \( S \) Sensitivity of the microphone
- \( T \) Temperature
- \( \nu \) Normal vibrational modes of \( \text{NO}_2 \)
- \( V \) First harmonic output of LIA
- \( \zeta_m \) \( m \)th root of the \( 0 \)th order Bessel fn. \( J_n(\zeta) = 0 \)

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