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Radiative lifetime measurement of excited neutral nitrogen atom by Time Resolved Laser-induced breakdown spectroscopy

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Abstract

Lifetimes of the excited $2P_2$ (^{3}P) 3p $^4\mathbf{S_{3/2}}$ level of nitrogen atom corresponding to transitions to different lower states have been estimated by measuring the line intensity of a transition as a function of the delay time between the Q-switching of the laser and the gating of the window of the ICCD. This novel time resolved laser-induced breakdown spectroscopic technique is explained in the paper. The lifetimes of the upper level $2P_2$ (^{3}P) 3p $^4\mathbf{S_{3/2}}$ corresponding to the three transitions to $2P_2$ (^{3}P) 3s $^4\mathbf{P_{1/2}}$ (742.346 nm), $2P_2$ (^{3}P) 3s $^4\mathbf{P_{3/2}}$ (744.27 nm) and $2P_2$ (^{3}P) 3s $^4\mathbf{P_{5/2}}$ (746.851 nm), were measured by this technique. The corresponding average lifetimes (τ) of these transitions were 199 ns, 105 ns and 68 ns. These values compare pretty well with the calculated lifetimes of 203.8 ns, 96.7 ns and 59.2 ns for the above three transitions as reported by Hibbert et al. The plasma temperature (atomic excitation temperature) decay time was found to be 1133 ns. This novel technique of estimating the lifetime of an excited state of an atom/ion is yet another very useful application of the LIBS as a versatile analytical tool.

Key Words: LIBS, upper state, lifetime, atomic excitation temperature, decay time.

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1. Introduction:

Laser-Induced Breakdown Spectroscopy (LIBS) is a versatile, efficient and rapid technique of elemental analysis. By this technique one can also determine the concentration of the constituent elements by analyte additive method [1]. LIBS can be used as a plasma diagnostic tool [2]. LIBS has been applied for measurement of plasma temperature (atomic/ionic excitation temperature) by Saha-Boltzmann plot [3, 4]. This technique can also be applied for electron density measurement [5] of the plasma.

Measurements of lifetimes of atomic and ionic states have been of constant interest in different branches of physics and chemistry, viz., astrophysics, laser physics, plasma physics, meteorology, physical chemistry etc. Lifetimes of upper states were measured by beam-foil method [6, 7], by laser induced fluorescence (LIF) [8, 9], by time-resolved LIF [10-12] and by delayed coincidence techniques [13, 14]. The lifetime of highly ionized atoms with multiple excited levels can be measured by high-frequency deflection method [15]. However, there is no single method for the measurement of lifetime that can be applied to all kinds of states in atoms, ions and molecules over a wide range of wavelengths and lifetimes. Unlike these experimental techniques, Hibbert et al. [16] calculated transition probabilities and associated lifetimes of neutral nitrogen atom based on configuration interaction calculations (performed with the CIV3 code).

In our laboratory, a novel application of LIBS in tandem with time-resolved gated ICCD was developed for the measurement of the lifetime of the excited states of atomic/ionic species [17] and the lifetime of excited states of nitrogen atom was measured by this technique.

2. Experimental setup:

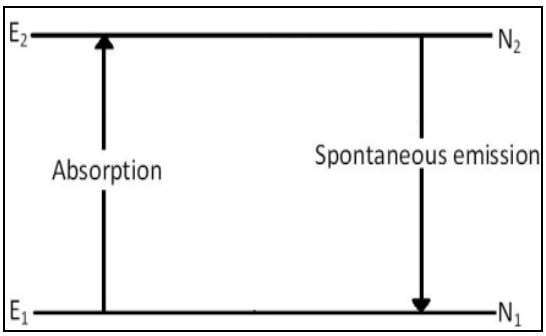
For the LIBS experiment (see figure 1), the 2nd harmonic of a Q-switched Nd:YAG (Spectra-Physics LAB-170-10) laser at 532 nm with pulse duration of 8 ns, repetition rate of 10 Hz and maximum pulse energy of 450 mJ was focused on the target**.** It was also equipped with harmonic generators capable of generating up to fourth harmonics of the fundamental by means of KDP crystals. The actual pulse energy used in the experiment was 40 mJ. At this pulse energy the average plasma temperature (atomic excitation temperature) was around 10000 K for sand plasma [17]. However, the electron temperature could be much higher than this [18, 19]. The beam had a Gaussian profile in the far-field with a beam divergence of less than 0.5 mrad [1]. Pulse to pulse energy stability was better than 99 % (manufacturer supplied data).

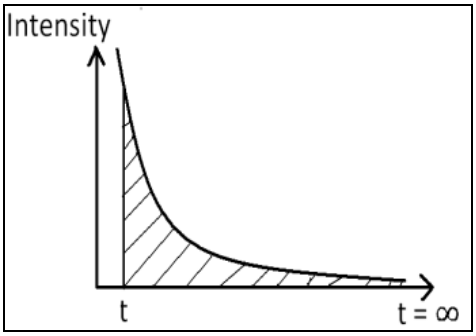
The output of the Nd: YAG laser at the 2nd harmonic was focused on the laboratory air by a convex lens of 100 mm focal length to produce an intense and transient micro-plasma. Near the focus of the high power pulsed laser beam the electric field strength was strong enough to accelerate the electrons (resulting from the primary ionization produced by multi-photon absorption) sufficiently to produce more ionization by secondary and tertiary ionization. The laser ablated plasma is weakly ionized plasma. In this plasma the ratio of electron to other species is less than 10% [18].

The light emitted from the plasma was focused by a fused quartz lens (f=50 mm) at right angle to the laser beam and collected by a 3 m long multimode silica fiber. The output end of the optical fiber was placed at the entrance slit of a 750 mm focal length computerized Czerny-Turner spectrograph (Acton Model SP-2758). The spectrograph is equipped with three ruled gratings: 2400, 600 and 300 grooves/mm blazed at 240, 500 and 300 nm, respectively, which are interchangeable under computer control, providing high and low resolution spectra in the wavelength range of 190–880 nm. If 600 grooves/mm grating is used, a spectrum of about 38 nm in width can be captured without moving the grating, and for the 2400 grooves/mm grating, it is about 9 nm [1]. The resolution of the spectrometer for the 600 grooves/mm is about 0.02 nm and the repeatability and accuracy of the computer-controlled system is ±0.05 nm and ±0.1 nm respectively.

An intensified and gated CCD camera (Princeton PI-MAX with Unigen II coating and programmable delay generator) was coupled to the output end of the spectrograph. The ICCD camera used has 1024X1024 pixels and was cooled to -20 C by Peltier cooling to reduce noise. The ICCD camera was electrically triggered by the synchronous Q switch pulse of the Nd: YAG laser after a software-controlled, adjustable time delay t. In the present experiment, a varying delay time (t) between 200 - 6500 ns and a constant gate width (t_w) of 100 μs were used to measure the line intensities of the emission lines as a function of t. Usually, spectra from a number of laser shots (about 40) were acquired and averaged to increase the signal-to-noise ratio. Three such averages were taken and integrated line intensity was obtained for each delay time t. The spectrum, captured by the ICCD camera, was transferred to the personal computer by USB cable. A software (Win Spec/32) provided by the manufacturer was used to control all the functions of the gated ICCD camera and the Acton spectrograph [1].

3. Theory:





The decay of an excited atom to a lower state is a statistical one shot process emitting a photon. If the number of excited atoms is very large one can apply this statistical method to the decay process and obtain an expression for the fraction of these excited atoms that would decay on an average in a certain interval of time. One then assumes that the disintegration rate of a given number of atoms in an excited state at any time is directly proportional to the number of excited atoms present at that time .That is,

$$\frac{dN_2}{dt} = -\frac{N_2}{\tau} \qquad (1)$$

$$\therefore N_2 = N_2^0 e^{-t/\tau} \qquad (2)$$

This is the well known exponential decay law of the excited state of atoms with time. N_2 and N_2^0 are the numbers of the excited atoms at time t and at time t=0. τ is the spontaneous emission lifetime.

Now the number of excited atoms decaying between t and ∞ is given by

$$N_t = N_2^0 \int_t^\infty e^{-t/\tau}\, dt$$

$$= N_2^0 \tau e^{-t/\tau} \qquad (3)$$

This is equal to the total number of the photons emitted in the interval between t and ∞. This must be proportional to the integrated area under the emission spectrum for this particular transition. Let us term this as I. Then,

$$I \propto N_t$$

$$I = C N_2^0 \tau e^{-t/\tau}$$

or $$I = K\, e^{-t/\tau} \quad , \qquad (4)$$

where C is the proportionality constant that absorbs all the factors involved in the detection system. K is a new constant = $CN_2^0\tau$.

An exponential fit of the experimental values of I as a function of t according to equation (4) will give a value of the spontaneous emission lifetime τ of the upper state of an excited atom/ion corresponding to the transition to a lower state.

Taking natural logarithm on both sides of equation (4) one gets

$$\ln I = \ln K - \frac{t}{\tau} \qquad (5)$$

One can also use a semi-logarithmic plot (where lnI is plotted as a function of the delay time t between the Q-switching of the laser pulse and the opening of the ICCD gate), to estimate the lifetime of the excited state of any atom/ion corresponding to the transition to a lower state. The negative of the reciprocal of the slope of the resulting straight line gives the desired measure of the lifetime.

4. Results & discussion:

The measurement of the lifetimes of the excited states of atomic/ionic species was possible because of the precise control of the delay between the Q-switch pulse and the gating (opening) of the window of the ICCD by a programmable delay generator. Emission lines were chosen in the spectral region where the plasma background is minimal.

The plasma was checked for optical transparency (optical thinness) for the emission lines used in the experiment by comparing the ratios of the theoretical line intensities and the experimental line intensities [20]. An excellent agreement between these two ratios confirmed the optical thinness of the plasma which is a necessary condition in LIBS experiments involving line intensities.

At the laser pulse energy used in the experiment, the delay between the Q-switching and the initiations of the plasma (as evidenced from the plasma background emission) was measured to be 100ns and that between Q-switching and the onset of emission of spectral lines was 170 ns respectively. This was determined by using a very narrow temporal window (of the order of few tens of nanoseconds) and varying the delay time t between the Q-switching of the laser and the gating of the window of the ICCD and observing the plasma background emission and the emission of the spectral lines.

Lifetimes of the upper state ($2P_2$ (^{3}P) 3p $^4\mathbf{S_{3/2}}$) of the excited neutral nitrogen atom (NI) making transition to different lower states (see figure 6), giving rise to the emission lines at 742.346 nm, 744.27 nm and 746.851 nm were estimated by monitoring the intensities of these emission lines as a function of the delay time t between the Q-switching of the laser and the gating of the window of the ICCD. The width of the temporal gate of the ICCD was 100μs, which is effectively infinity with respect to the lifetime of the upper states involved in the transition (which is a mathematical requirement of equation 3).

The decrease of intensity of spectral lines of neutral nitrogen atom (NI) with the increase of delay time is evident from Fig 2(a)-(c). Figure 3(a) shows the plot of intensity of NI emission line at the wavelength of 746.851 nm vs. delay time (in the range of 200-6500 ns). In order to guess the nature of the decay process, the data was fitted with mono-exponential (R^2= 0.978) and then with bi-exponential (R^2 = 0.986) fit as shown in Figures 3(b) and Fig 3(c) respectively using the Origin software. Comparison between these two graphs shows that in the bi-exponential fit, the value of the χ^2 ($5.93\text{x}10^7$) is lesser and the value of the R-square (0.986) is greater than those for the mono-exponential fit (χ^2=$8.8\text{x}10^8$ and R^2=0.978). It appears that the bi-exponential fit is better than the mono-exponential fit.

One can confirm whether a data set is bi-exponential or not by making a semi-logarithmic plot of the respective data set. The bi-exponential plot becomes linear with two distinct straight lines in a semi-logarithmic plot. This is exactly what we obtained for NI line at 746.851 nm in the delay range of 200-6500 ns (Fig. 3(d)). Similarly, figure 4(a) and 4(b) represent the semi-logarithmic

plots (lnI vs. delay time t) for the emission lines of NI at 744.27 nm and 742.346 nm respectively. Each of these three graphs clearly shows that two decay processes are involved here having two distinct straight lines with different slopes in two delay regions. The faster process is in the delay range of 200-800 ns and the slower decay process is in the delay range of 850-6500 ns. The faster decay is the lifetime of the upper state and the slower decay time is related to the atomic excitation temperature decay time of the hot plasma. This is defined as the time during which the atomic excitation temperature decay by a factor of e [19].

The lifetimes of the upper state $2P_2$ (^{3}P) 3p $\mathbf{^4S_{3/2}}$ of NI atom corresponding to the branching transitions to the lower states $2P_2$ (^{3}P) 3s $\mathbf{^4P_{1/2}}$, $2P_2$ (^{3}P) 3s $\mathbf{^4P_{3/2}}$ and $2P_2$ (^{3}P) 3s $\mathbf{^4P_{5/2}}$ were obtained by the bi-exponential fitting of the experimental points of integrated line intensity I as a function of the delay time t between the Q switching of the laser and the opening of the window of the ICCD (equation 4) for the emission lines at wavelengths of 742.346, 744.27 and 746.851 nm respectively (see figures, 5(b), 5(a) and 3(c). The lifetimes of the upper state corresponding to these transitions were 199 ns, 105 ns and 68 ns respectively (Table 1).

Figures 3 (e) and 3 (f) show the semi logarithmic plot of *l*nI vs. delay t in the time domain of 200-750 ns and 850-6500 ns respectively for the transition from $2P_2$ (^{3}P) 3p $\mathbf{^4S_{3/2}}$ to $2P_2$ (^{3}P) 3s $\mathbf{^4P_{5/2}}$ of NI atom resulting in the emission line at 746.851 nm. The negative of the reciprocal of the slopes of these two straight line graphs gives the lifetime of the upper excited state $2P_2$ (^{3}P) 3p $\mathbf{^4S_{3/2}}$ corresponding to the transition to the lower state $2P_2$ (^{3}P) 3s $\mathbf{^4P_{5/2}}$ (figure 3(e)) and the atomic excitation temperature decay time of the plasma (figure 3(f)). However, in order to determine the correct value of the exponential decay constant for the faster decay process, the contribution of the slower decay process had to be subtracted from the faster decay process. To do so, the straight line graph for the slower decay process was extrapolated in the delay region of 200-800ns (Figure 3(d)). Then the contribution of slower decay process was subtracted from that of faster decay process and the corrected semi logarithmic graph for NI emission line (at 746.851 nm) in the delay region of 200 - 800ns was re-plotted (figure 3 (g)). Similar corrections to the semi logarithmic plot were done for the other two transitions resulting in the emission lines at wavelengths of 742.346 nm and 744.27 nm. Using the corrected semi logarithmic plot the upper state lifetimes of different transitions of the excited neutral nitrogen atom (NI) were obtained as 199 ns, 93 ns, and 74 ns for the emission lines at wavelengths of 742.346 nm, 744.27 nm and 746.851 nm respectively as shown in Table 1. The results obtained by the semi logarithmic plot compare well with the results obtained by the bi-exponential plots of figures 5(b), 5(a) and 3(c), (also see Table 1).

The association of the faster decay times with the spontaneous decay of the upper state ($2P_2$ (^{3}P) 3p $\mathbf{^4S_{3/2}}$) to different lower states ($2P_2$ (^{3}P) 3s $\mathbf{^4P_{1/2}}$, $2P_2$ (^{3}P) 3s $\mathbf{^4P_{3/2}}$ and $2P_2$ (^{3}P) 3s $\mathbf{^4P_{5/2}}$) obtained by the bi-exponential plot is consistent with the values of 203.8 ns, 96.7 ns, 59.2 ns respectively as calculated by A. Hibbert et al. [16] for the identical transition from the excited levels of NI. The average of the measured values of the decay constants for the atomic excitation temperature of the

plasma is 1133 ns (Table 1) and it is consistent with the cooling rate of laser induced plasma (atomic excitation temperature) reported in literature [18] which is of the order of microsecond.

5. Conclusion:

A novel technique based on LIBS and time-resolved gating of ICCD has been employed for the first time to determine the lifetime of the excited states of neutral nitrogen atom. Lifetimes of the upper state of NI corresponding to different lower states were estimated by monitoring the intensities of these emission lines as a function of delay time between the Q-switching of the laser and the gating (opening) of the window of the ICCD. The faster decay processes are due to the spontaneous decay of the upper state $2P_2$ (^{3}P) 3p $^4\mathbf{S_{3/2}}$ to three lower states viz., $2P_2$ (^{3}P) 3s $^4\mathbf{P_{1/2}}$ (742.346 nm), $2P_2$ (^{3}P) 3s $^4\mathbf{P_{3/2}}$ (744.27 nm) and $2P_2$ (^{3}P) 3s $^4\mathbf{P_{5/2}}$ (746.851 nm). The results of the bi-exponential fit of the experimental data points show that the decay times of the excited state $2P_2$ (^{3}P) 3p $^4\mathbf{S_{3/2}}$ of the neutral nitrogen atom resulting in the emission lines at wavelengths of 742.346 nm, 744.27 nm, and 746.851 nm were 199 ns, 105 ns, and 68 ns respectively (Table 1). These measured lifetimes compare very well with those calculated by Hibbert et al. [16]. We have also checked our results with semi logarithmic plots. This method can be applied for the efficient determination of the lifetime of the excited states of atoms and ions in laser-induced plasma.

The laser-induced atomic excitation temperature decay time constant of the plasma was also estimated. Using the bi-exponential fit of the experimental points, the atomic excitation temperature decay time (the longer decay time) was obtained from the three emission lines of neutral nitrogen atom at wavelengths of 742.346 nm, 744.27 nm and 746.851 nm. These decay times were 1053 ns, 1105 ns and 1242 ns, respectively. The average of which was 1133 ns and it compares pretty well with the results obtained by Boltzmann method [18].

However, the method is better suited for transitions involving emission in the spectral region where the plasma background is minimal. It was also assumed and experimentally verified that the plasma was optically thin enough to neglect self absorption and radiation trapping. The contribution to the population of the upper state of the transition due to the recombination of nitrogen ions during the decay process was also neglected. This approximation is a reasonable one as the laser induced plasma is weakly ionized plasma and most of the laser energy is spent on the excitation of the neutral species in the sample.

The accuracy of the measurement will depend on shot to shot stability of the laser pulse energy (as mentioned earlier, pulse to pulse energy stability was better than 99%) and the setting of laser for constant output per pulse for different delay times. Deviation from any or all of these will introduce error in the measurement. This is because the delay between the triggering of the laser pulse and the initiation of the laser plasma is strongly dependent on laser pulse energy. Any variation of this delay due to lack of constancy of laser pulse energy will introduce error in the measurements because opening of the ICCD window was controlled by the synchronous Q-switched pulse and not by the initiation time of the laser plasma (because it was not possible either

by hardware of software). Also subsequent plasma expansion, cooling and atom/ion density are all strongly dependent on laser pulse energy. [21]. Therefore the control of the laser pulse energy is very vital in this sort of measurements.

Finally, we would like to emphasize that, within the above limitations, our method of measurement of radiative lifetime is quite general and, in principle, it should be possible to measure the radiative lifetimes of most excited species (neutral and ionic) in the plasma by this technique. This is yet another useful application of LIBS. However there are scopes of improvement of this method (e.g. working with a shorter temporal window of the ICCD, to avoid possible convolution effect, if there is any) which will be done in future experiments.

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Table 1: Measured values of upper state lifetimes of N I for different transitions

Obser-ved lines (nm)	Transitions		By semi logarithmic fit			By bi-exponential fit			Transition lifetimes reported by Hibbert et. al. (ns)
	Upper state (Term value with J)	Lower state (Term value with J)	Spontan-eous emission lifetime (**ns**)	Plasma temperature (excitation temperature) decay time constant (**ns**)	Average plasma temperature (excitation temperature) decay time constant (**ns**)	Spontan-eous emission lifetime **(ns)**	Plasma temperature (excitation temperature) decay time constant (**ns**)	Average of plasma temperature (excitation temperature) decay time constant (**ns**)	
742.346	$1s^2 2s^2 2p^2\ 3p^1$ $^4S_{3/2}$	$1s^2 2s^2 2p^2 3s^1$ $^4P_{1/2}$	199	1203	1225 ± 20	**199**	1053	**1133 ± 51**	**203.8**
744.27		$1s^2 2s^2 2p^2 3s^1$ $^4P_{3/2}$	93	1240		**105**	1105		**96.7**
746.851		$1s^2 2s^2 2p^2 3s^1$ $^4P_{5/2}$	74	1233		**68**	1242		**59.2**

Figure Captions:

Figure 1:

Schematic diagram of the LIBS experimental setup.

Figure 2 (a)-(c):

Spectral emission lines of neutral nitrogen atom (NI) used for the determination of the lifetimes of the upper state at three different delay times t of (a) 350 ns, (b) 400n s, (c) 450 ns.

Figure 3 (a) - (c):

Plot of the integrated intensity vs. delay time (in the range of 200 – 6500 ns) of the emission line of NI (at 746.851 nm) with (a) no fit, (b) mono-exponential fit (R^2= 0.978), (c) bi-exponential (R^2 = 0.986).

Figure 3 (d) - (g):

Semi logarithmic plots (i.e. lnI vs. delay time) of NI emission line (at 746.851 nm) with linear fits in the range of (d) 200-6500 ns, (e) 200-800 ns, (f) 850-6500 ns, (g) 200-800 ns (corrected).

Figure 4 (a) - (b):

Semi logarithmic plots (i.e. lnI vs. delay time) with linear fits in the range 200-6500 ns of the emission lines of N I at wavelength of (a) 744.27 nm and (b) 742.346 nm.

Figure 5(a) – (b):

Bi-exponential fit of integrated intensity I vs. delay time t (in the range of 200-6500 ns) of NI line at (a) 744.27 nm and (b) 742.346 nm.

Figure 6:

Relevant energy levels of the transitions with associated lifetimes (not to scale).

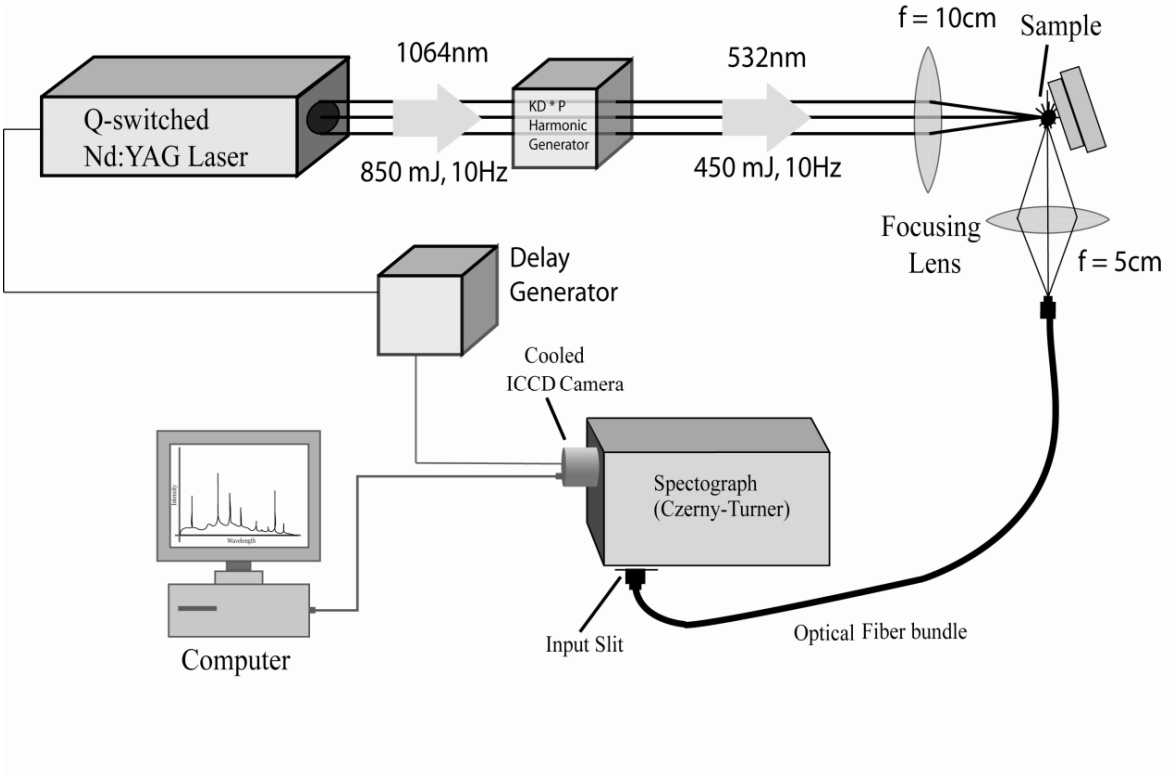
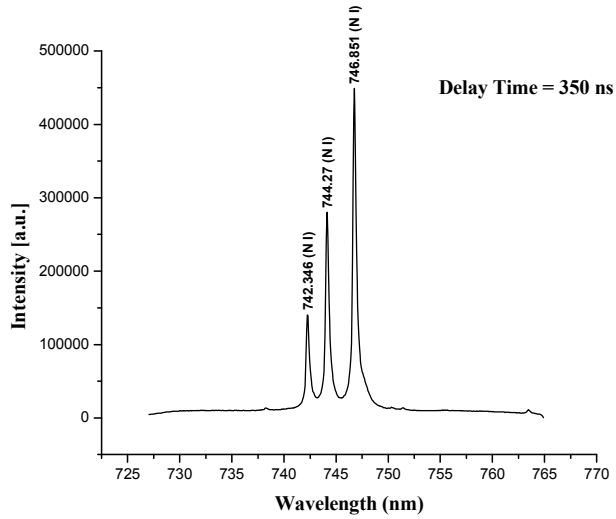
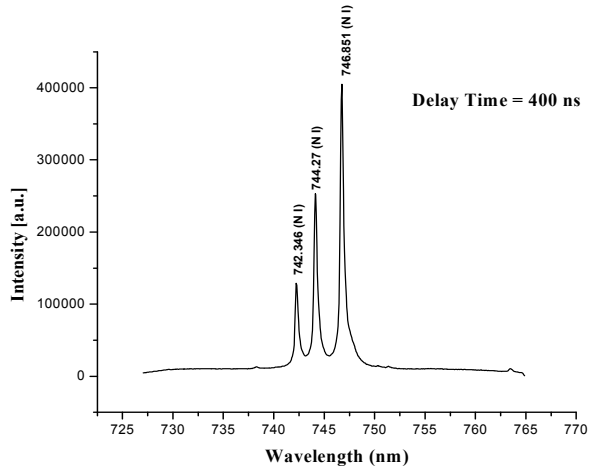


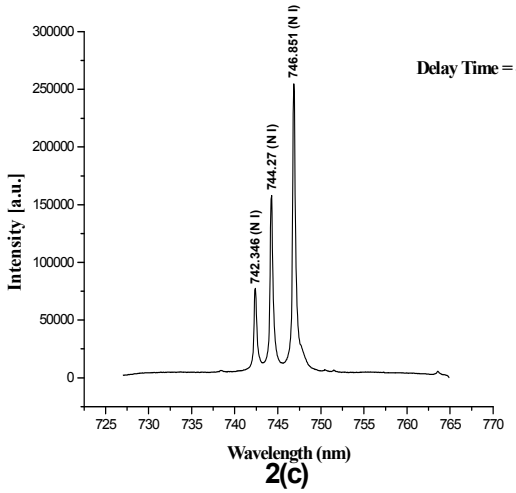
Fig: 1



2(a)

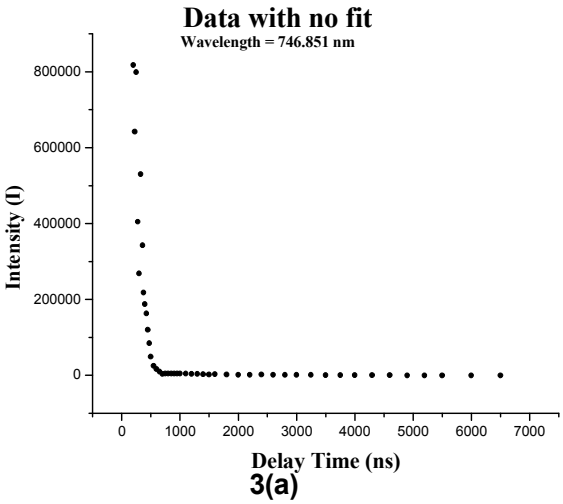


2(b)



2(c)

Fig. 2(a)-(c)



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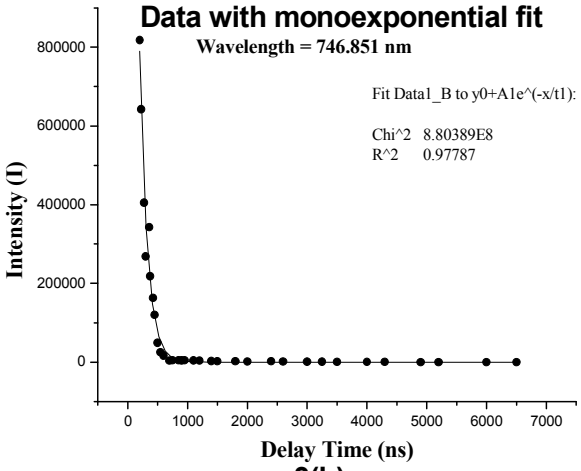
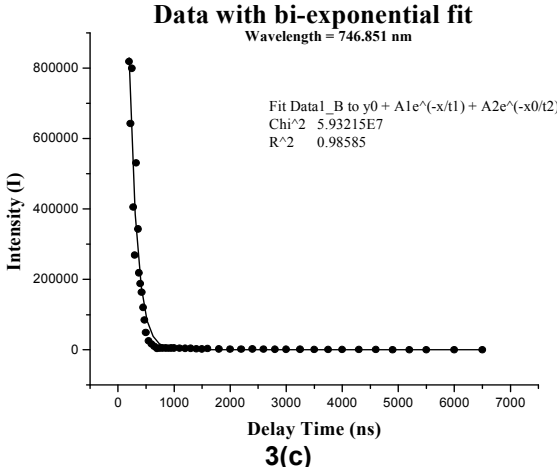
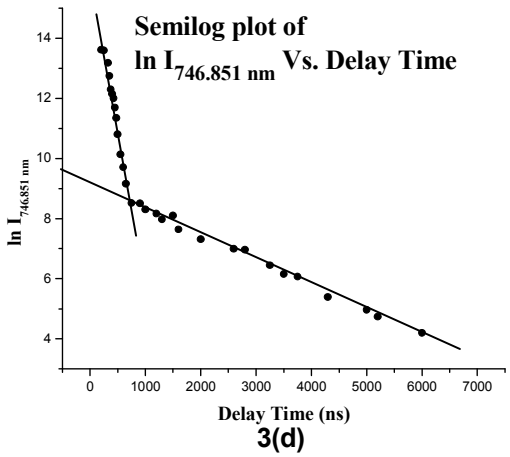


3(b)



3(c)

Fig. 3(a)-(c)



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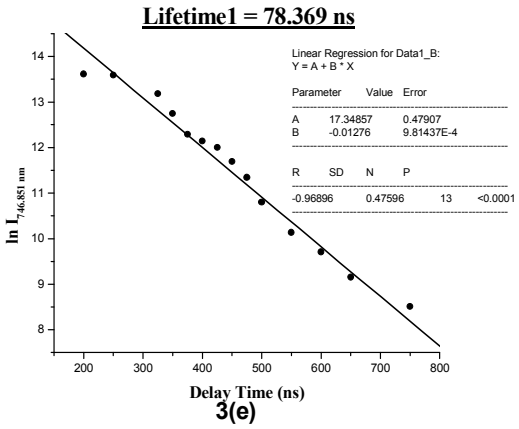

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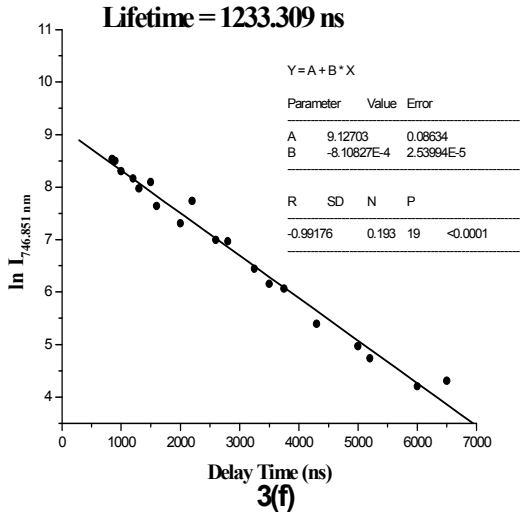

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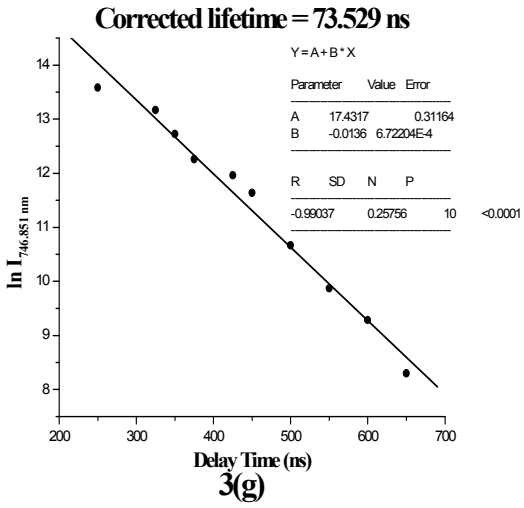


3(g)

Fig. 3(d)-(g)

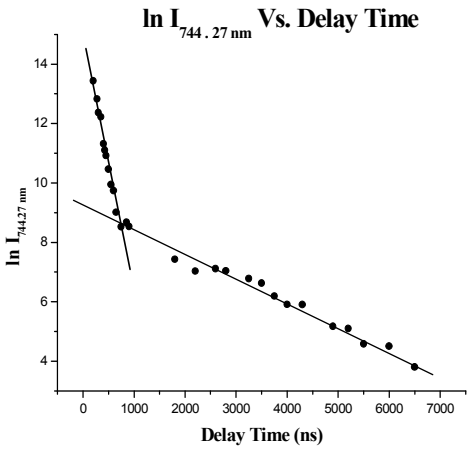


Fig 4 (a)

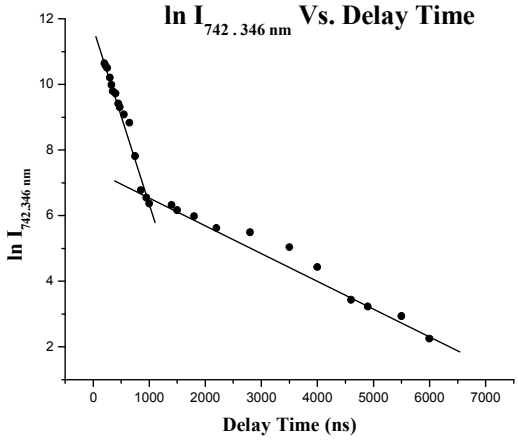


Fig 4(b)

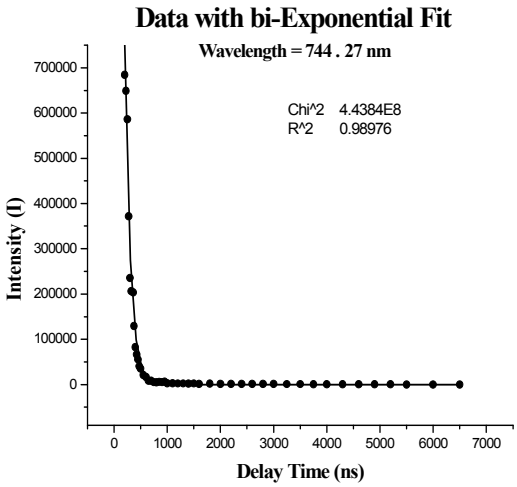
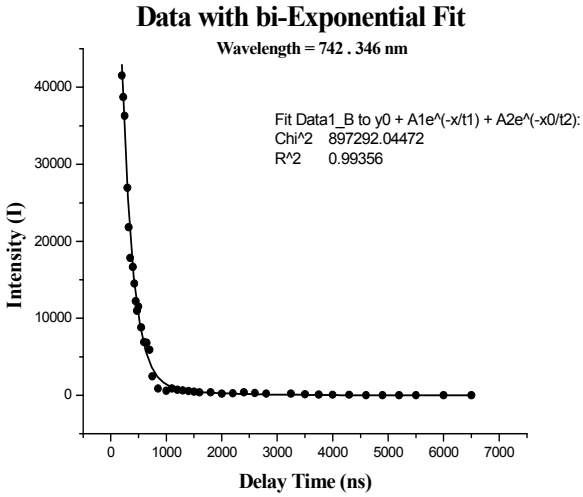


Fig 5 (a)



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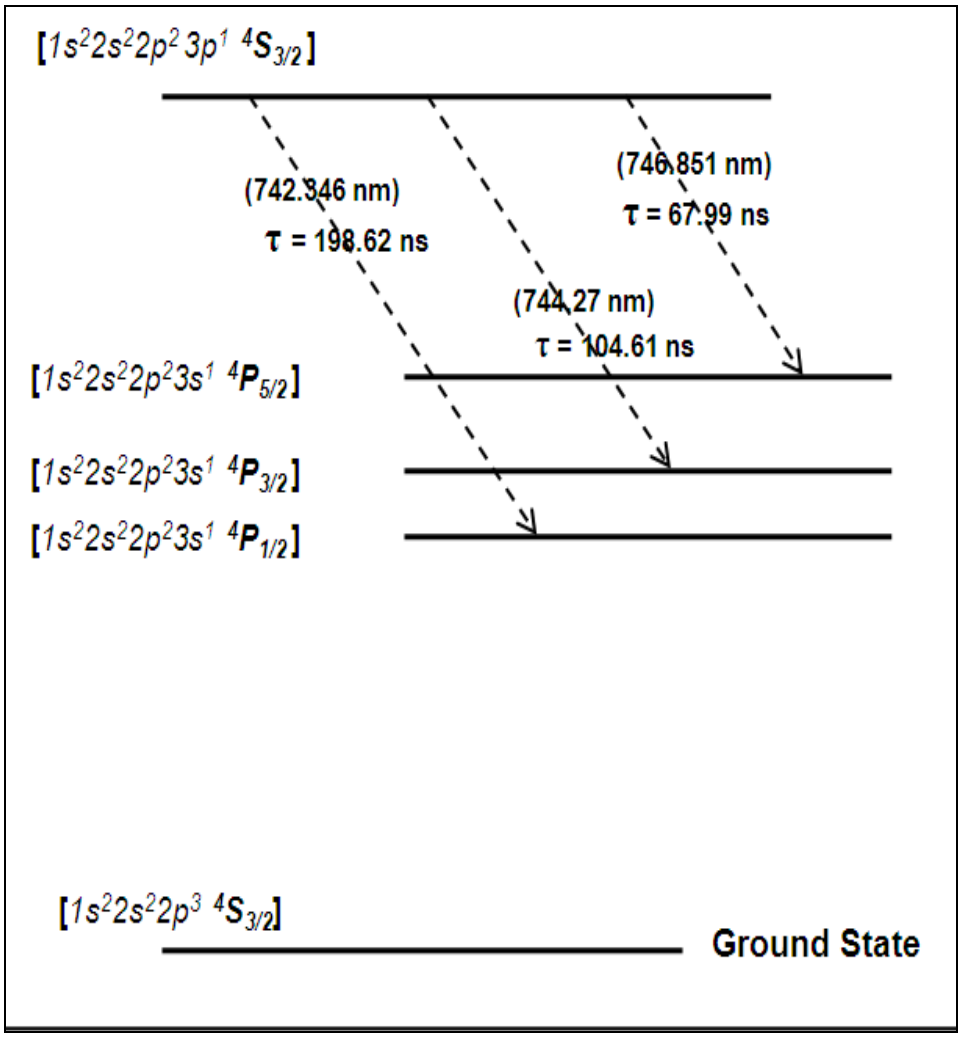

Fig.6

Lifetimes of excited $2P_2(^3P)3p\,^4S_{3/2}$ level of nitrogen atom for transitions to lower states were measured by time-resolved laser-induced breakdown spectroscopy.

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