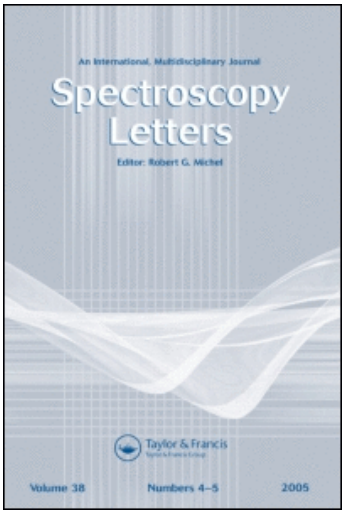

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Observation of Strong Forward Emission Due to UV Multiphoton-Dissociative Excitation of CH_4: N_2 Mixture

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OBSERVATION OF STRONG FORWARD EMISSION DUE TO UV MULTIPHOTON-DISSOCIATIVE EXCITATION OF CH_4:N_2 MIXTURE

Key Words: Raman Scattering, Two-Photon Absorption, Stimulated Emission, Photochemical Mechanism

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Abstract:

The multiphoton dissociative excitation in a high pressure mixture of CH_4:N_2 has been investigated using a third harmonics of a Nd:YAG laser under various experimental conditions, namely at a fixed pump energy (10mJ) and CH_4 pressure (300PSI), varying the N_2 pressure; at a fixed pump energy (10mJ) and N_2 (30PSI), varying CH_4 pressure; at fixed CH_4 and N_2 pressure of 300PSI and 30PSI respectively, varying the pump energy. We have observed the first positive system, $B^3\pi_g \rightarrow A^3\Sigma^+_u$ (v'=10;v"=5) at 544nm; second positive system, $C^3\pi_u$-$B^3\pi_g$ at 434.4nm (v'=0;v"=4) and at 405.9nm (v'=0;v"=3) due to neutral N_2. We also have observed CN band $B^2\Sigma$-$\rightarrow X^2\Sigma$(v'=11;v"=11) at 392nm. These emitted signals have the same spectral directionality as the pump beam. The transition at 434.4nm is due to four photon excitation with a rate-limiting step that scales as a two photon

process. The CN band is due to three photon processes. Spontaneous emission for the (B-A), (C-B) of N_2 and CN (B-X) band systems were observed but the signal was very weak for our optical detection system to record the spectrum.

1. INTRODUCTION:

Multi-photon dissociative excitation and ionization of molecules due to the interaction of short pulse, high peak power Q-switched laser sources have become one of the most fascinating domain of modern molecular physics. Multi-photon processes are spectroscopically important due to their ability to probe high-lying levels, otherwise forbidden for single photon absorption. These processes may result from (i) multi-photon transition via virtual intermediate states; (ii) step-wise transition in which each photon is resonant with a single dipole-allowed transition; (iii) multi-photon transition with one intermediate resonance; and (iv) multiphoton dissociation involving closely spaced "quasi-continuum" intermediate states. These processes (i-iv) are illustrated respectively in Fig.1(a)-(d). In addition, the dissociation products due to photolysis may undergo further excitation.

The $CH(A^2\Delta \rightarrow X^2\pi)$ emission due to sequential two-photon absorption [1,2] and $C_2(d^3\pi_g \rightarrow a^3\pi_u)$ Swan band emission due to three photon absorption [2] in C_2H_2 and the product of $C(^1D_2)$ atoms by multiphoton photolysis of CO, CH_4, C_2H_2, C_3H_8, CH_3OH, and CH_3COCH_3 [3] pumped by a high power ArF laser at 193nm are reported. Multi-photon laser ionization techniques using frequency doubled dye-laser systems [4,5], third and fourth harmonics of Nd:YAG laser [6,7] to excite ground state neutral N_2 to the $B^2\Sigma^+_u$ ionic state have been demonstrated in the past.

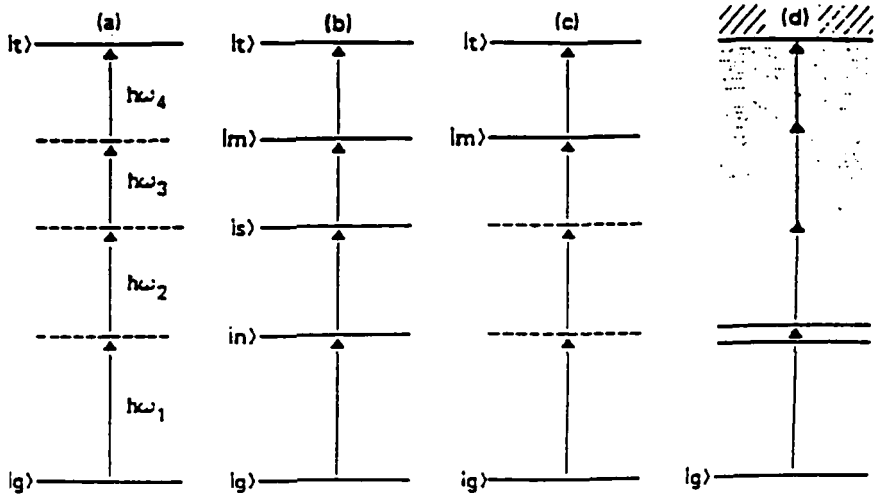

Fig.1. Various multi-photon absorption processes

The previous work was involved with gas phase molecules in a low pressure environment (few tens of mTorr - a few of Torr,except in [4,6], atmospheric pressure), and the emissions were detected in a direction perpendicular to the pump beam. However, in the present work, we have investigated the multi-photon dissociative excitation of CH_4:N_2 mixture in a high pressure Raman cell pumped by the third harmonics of a Nd:YAG laser. In addition to various Stokes and anti-Stokes radiation, we have observed the first ($B^3\pi_g$->$A^3\Sigma^+_u$), the second ($C^3\pi_u$->$B^3\pi_g$) positive systems of N_2 and probably the excited radical of CN ($B^2\Sigma$ ->$X^2\Sigma$) in the same direction as the pump beam.The various experimental conditions are given in Table.1.

2. EXPERIMENTAL:

The experimental set-up used in the present investigation is shown in Fig.2. The pump beam used is

Table 1. Experimental Conditions of the Pump Energy, N_2 Pressure, and CH_4 Pressure.

Pump Energy [mJ]	N_2 Pressure [PSI]	CH_4 Pressure [PSI]
2.5	5	200
8	10	300
10	15	400
12	20	500
	25	600
	30	

the third harmonic of a Nd:YAG laser at 355nm (JKJ model HY 500). The Raman cell of length 40cm is made up of stainless steel tubing of 25mm inner diameter. A constricted tubing of 6.4mm inner diameter, also made of stainless steel tubing, is welded inside the main cell with clear access to the gas fillings and measuring the pressure inside the constricted tubing. Both ends of the Raman cell are attached with thick quartz (6.35nm) windows and Viton O-rings. The gas pressure is controlled by a set of pressure valves and is measured accurately using a carefully calibrated pressure gauge.

The pump beam is focused at the center of the Raman cell by a lens of focal length 20cm. The beam from the exit window of the Raman cell is collimated by another lens of focal length 20cm in the same direction as the pump beam. These collimated beam consists of emission from the excited states of neutral N_2 and CN radicals, due to the multiphoton dissociative excitation and also various Stokes and anti-Stokes radiation due to the stimulated Raman and four-wave mixing processes. The

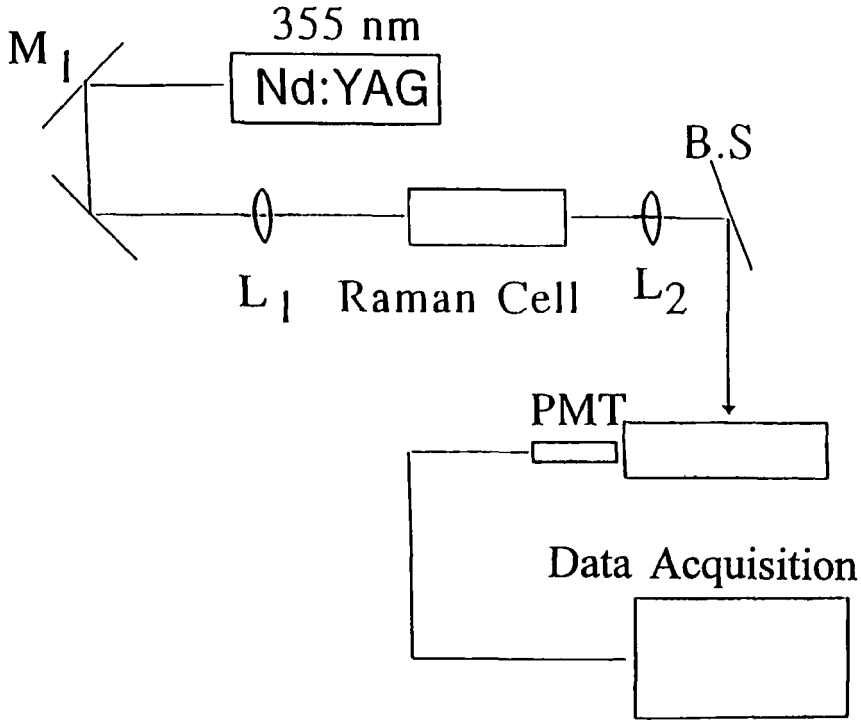

Fig.2. Experimental set-up used in the present study.

collimated beam is split by a beam splitter which reflects about 4% of the total beam in order to avoid the damage of either the grating, or the PMT. The reflected beam is dispersed by a 0.2m scanning monochromator (0.5nm spectral resolution), detected by a Photo Multiplier Tube (PMT) at room temperature, and recorded using a Multi-Channel Analyzer(MCA). We have used Multi-Channel Analyzer(MCA) in the Multi-Channel Scaling (MCS) mode for data collection and spectral recording. Multi-Channel Scaling(MCS) is a time sweep of the channels in the MCA, with each channel being an interval of time equal to the total sweep time/total channel swept. For example, we have set the time per

channel equal to 1 second and the number of channels 1024, to give a total sweep time of 2040s (34 minutes).

During each channel time interval (1s) in our case, the memory contents for that channel is available for input data counting in the form of serial digital pulses. Thus, the resulting display is frequency /wavelength histogram. The background count recorded with an evacuated cell was subtracted in measuring the relative intensity of various band systems.

3. RESULTS AND DISCUSSION:

The Stokes and anti-Stokes radiation from CH_4 (N_2 pressure is well below the stimulated Raman scattering threshold to generate neither its Stokes nor anti-Stokes), emission from the first ($B^3\pi_g \rightarrow A^3\Sigma^+_u$), the second ($C^3\pi_u \rightarrow B^3\pi_g$) positive systems of N_2, and the excited state CN radical ($B^2\Sigma \rightarrow X^2\Sigma$) are observed in the same direction as the pump beam. The physical processes responsible for the generation of various Stokes and anti-Stokes radiation in CH_4, such as stimulated Raman scattering, cascade Raman scattering, and four-wave mixing have been already reported by us [8]. The intense radiation at 391.44nm associated with the transition [$B^2\Sigma^+_u$ (v'=0) $\rightarrow X^2\Sigma^+_g$ (v"=0)] in the first negative band of N_2^+ pumped by the third harmonics of a Nd:YAG laser reported in Ref.6 is absent in this investigation. This may be due to the fact that, six photons at 355nm, are required for the excitation of the $B^2\Sigma^+_u$ state and the pump energy used in the present study is insufficient to cause six photon absorption. In the same line of reasoning, the transitions at 391.4nm (v'=0;v"=0), 427.8nm (v'=0;v"=1), and 407.9nm (v'=0;v"=2) in the first negative system of N_2^+ ($B^2\Sigma^+_u \rightarrow X^2\Sigma^+_g$) pumped by the fourth harmonics of a Nd:YAG laser reported in Ref.7 is not observed in the present investigation. However, the

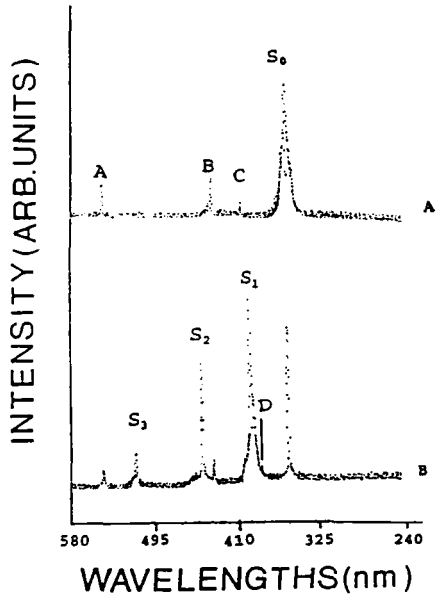

Fig.3A. Multi-photon excitation spectra of pure N_2 at a pressure of 30PSI and pump energy of 2.5mJ recorded in the wavelength range of 580-240nm. The notations A, B, C, and S_0 are first positive system $B^3\pi_g \rightarrow A^3\Sigma^+_u$ (v'=10;v"=5) at 544nm, second positive system $C^3\pi_u \rightarrow B^3\pi_g$ (v'=0; v"=4) at 434.4nm (v'=0;v"=3) at 405.9nm, and the pump beam at 355nm, respectively. Spectra not corrected for optical detection efficiency.

Fig.3B. Electronic emission spectra of CH_4 at a pressure of 300PSI, air at atmospheric pressure, and a pump energy of 10mJ recorded in the wavelength range of 580 - 240nm. The notations A, B, C, and S_0 has the same meaning as in Fig.3.A. S_1, S_2, and S_3 are the first, second, and the third Stokes lines of CH_4, respectively. D is the CN band violet system $B^2\Sigma \rightarrow X^2\Sigma$ (v'=11;v"=11) at 392nm. Spectra not recorded for optical detection efficiency.

absence of the two strong transitions in the second positive system of N_2 [($C^3\pi_u$-$B^3\pi_g$) at 337.1nm (v'=0;v"=0)], and 357.7nm(v'=0;v"=1) is due to the fact that a set of glass plates used to protect the PMT and the grating of the monochromator from damaging due to the intense pump beam significantly reduces the signal intensity at 337.1nm and 357nm.

The multi-photon excitation spectra of N_2 at 30PSI pressure and 2.5mJ pump energy recorded in the wavelength range of 580-240nm is shown in Fig.3A. The transition at 544nm denoted by A in the figure is due to the first positive system, $B^3\pi_g$->$A^3\Sigma^+_u$(v'=10;v"=5). The notations B and C are the transitions in the second positive system $C^3\pi_u$-$B^3\pi_g$ at 434.4nm(v'=0;v"=4) and at 405.9nm (v'=0;v"=3) respectively. The lowest state of N_2, $A^3\Sigma^+_u$ occurs at 6.2ev from the ground state. The probability coefficients for the transition from this state to the ground state $X^1\Sigma^+_g$ known as Vegard-Kaplan are extreamly low both as a single and two process. The $B^3\pi_g$ state lies at 7.4ev from the ground state and hence the first positive system $B^3\pi_g$->$A^3\Sigma^+_u$ observed is due to three photon process. The $C^3\pi_u$ state lies at about 12ev from the ground state for the neutral N_2 molecule. In order to attain this state, four photons are necessary. The notation S_0 denotes the pump beam.

The spectrum recorded by dispersing the output from the Raman cell containing CH_4, at 300PSI pressure and air at atmospheric pressure is shown in Fig.3B. The energy of the pump beam is 10mJ. In addition to the first(S_1), second(S_2), and third Stokes(S_3) of CH_4, we observed the above mentioned three transitions due to N_2. This indicates that the transitions due to N_2 could readily be observed in air. The strong CN band head(D) observed is due to violet system $B^2\Sigma$->$X^2\Sigma$ (v'=11;v"=11).

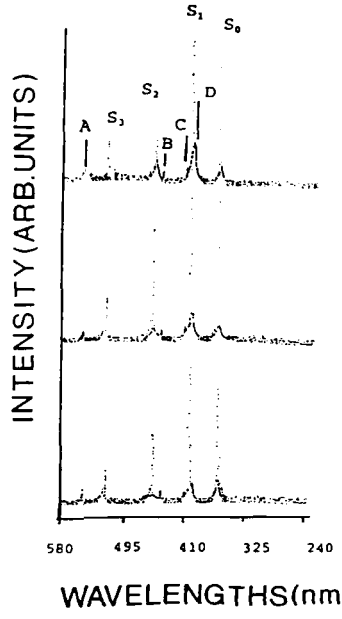

Fig.4. Electronic emission spectra of CH_4:N_2 mixture with a fixed CH_4 pressure of 300PSI and pump energy 10mJ at various N_2 pressures. The notations A, B, C, D, S_0, S_1, S_2, and S_3 has the same meaning as in Fig.3.B. The lower, middle, and uper traces are at 10PSI, 15PSI, and 20PSI of N_2 pressure, respectively.

This agrees well with the largest Frank-Cordon factor for this band head [9]. The electronic emission spectra recorded in the range 580-240nm, by dispersing the radiation from the output window of the cell containing CH_4:N_2 mixture in the forward direction same as the pump beam, is given in Fig.4. The spectra corresponds to a fixed CH_4 pressure of 300PSI, pump energy of 10mJ, and at various N_2 pressures. It is interesting to note that the spectra for CH_4:air mixture given in Fig.3B and for

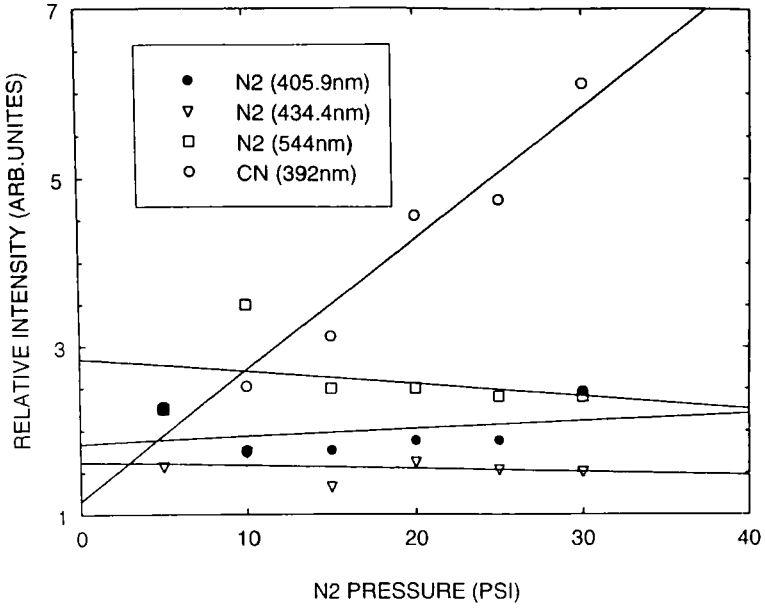

Fig.5. The relative intensity of the first positive system $B^3\pi_g \rightarrow A^3\Sigma^+_u$ at 544nm (v'=10;v"=5), the second positive system $C^3\pi_u \rightarrow B^3\pi_g$ at 405.9nm (v'=0;v"=3), 434.4nm (v'=0;v"=4), CN band $B^2\Sigma \rightarrow X^2\Sigma$ (v'=11;v"=11) at 392nm at a fixed CH_4 pressure of 300PSI and pump energy of 10mJ at various N_2 pressure.

CH_4:N_2 mixture are identical. This is another evidence that the transitions due to the first and second positive systems of N_2 in air. The relative intensity of the first positive system $B^3\pi_g \rightarrow A^3\Sigma^+_u$ at 544nm (v'=10;v"=5), the second positive system $C^3\pi_u$-$B^3\pi_g$ at 405.9nm (v'=0;v"=3) and 434.4nm (v'=0;v"=4), and CN band $B^2\Sigma \rightarrow X^2\Sigma$ (v'=11;v"=11) at 392nm at a fixed CH_4 pressure of 300PSI and pump energy of 10mJ at various N_2 pressures is given in Fig.5. The saturation of the relative intensity at high N_2 pressure is observed for

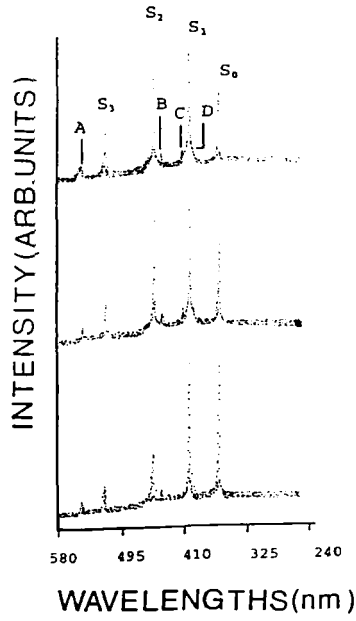

Fig.6. Same meaning as in Fig.4 except at a fixed N_2 pressure of 10PSI, a pump energy of 10mJ and at various CH_4 pressures. The lower, middle, and uper traces are at 200PSI, 300PSI, and 400PSI of CH_4 pressure, respectively.

both the first and second positive systems in contrast to no saturation of intensity for CN band. The highly non-linear behavior of the relative intensity indicates the collisional process. This process not only will significantly change the photochemical process, but also affect the dynamics of the relaxation of excited recombination process. A detailed investigation on the collisional process and the dynamics of the relaxation process is underway and will be published elsewhere.

The spectra displayed in Fig.6 has the same meaning as of Fig.4, and Fig.7,has the same meaning as that of

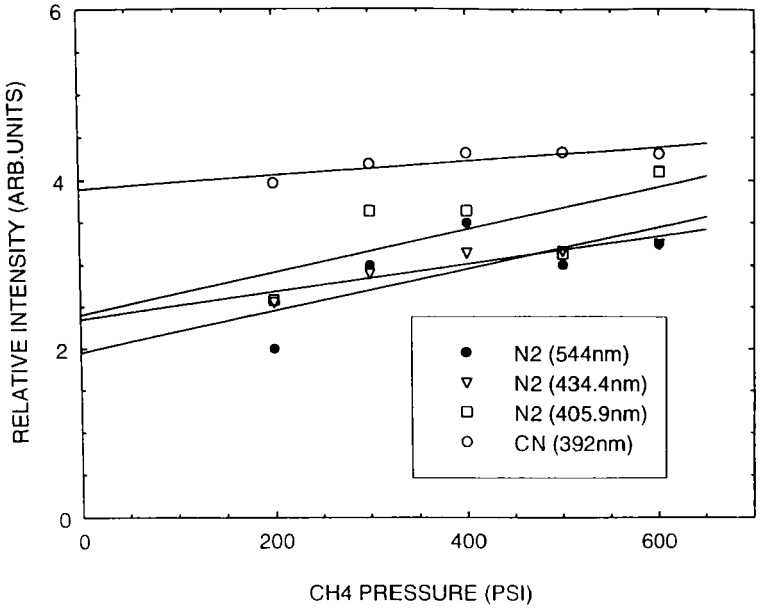

Fig.7. Same meaning as in Fig.5. except at a fixed N_2 pressure of 10PSI, a pump energy of 10mJ and at various CH_4 pressures

Fig.5 except at a fixed N_2 pressure of 10PSI and a pump energy of 10mJ at various CH_4 pressures. It is clear from the spectra (Fig.6) that the transition at 405.9nm (v'=0;v"=3) decreases, and the intensity of 434.4nm (v'=0;v"=4) increases at higher CH_4 pressures. At a fixed N_2 pressure the reduction in intensity of v'(0)-v"(3) transition and the increases in intensity of v'(0)-v"(4) at higher CH_4 pressure may be due to collisional process, some of the N_2 molecules in the v'(3) state are excited to the v'(4) state. The absence of the v'(0)-v"(2) transition at 380.5nm shows that no cascading from v"(3) to v"(2) vibrational energy ladder. At higher CH_4 pressure, a saturation in intensity of CN

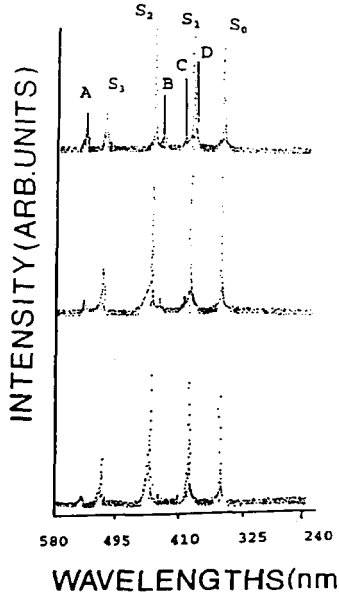

Fig.8. Same as in Fig.4. except at a fixed N_2 pressure of 10PSI and CH_4 pressure of 300PSI with various pump energies. The lower, middle, and uper traces are at 8mJ, 10mJ, and 12mJ of the pump energy, respectively.

band is observed. The electronic emission spectra of fixed N_2 pressure of 10PSI and CH_4 pressure of 300PSI at three different pump energies is shown in Fig.8.

In order to understand the possible photo-chemical mechanism the variation of line intensity at 434.4nm $C^3\pi_u$-$B^3\pi_g$ (v'=0;v"=4) and CN $B^2\Sigma$->$X^2\Sigma$(v'=11;v"=11) at 392nm with pump laser energy was measured. A quadratic dependence of 434.3nm intensity with a laser power was observed. In general, such a quadratic dependence indicates two photon process. However, to excite $C^3\pi_u$ state one needs four photons at 355nm. This suggest that there is a rate limiting step that scales as two photon

process. The $A^3\Sigma^+_u$-$X^1\Sigma^+_g$ excitation may be that rate limiting process. The standard enthalpy of formation of CN (g) obtained from photo-dissociation method is 101kcal/mole [10]. Scaling this value to our experimental temperature and pressure using thermodynamical data and applying non-identity correction, the number of photons absorbed corresponding to this energy is three. This agrees with our experimental results based on nearly cubic dependence of the CN band intensity with laser pump power.

4. CONCLUSION:

We have investigated the multi-photon excitation of high pressure CH_4:N_2 mixture using the third harmonics of a Nd:YAG laser. In addition to various Stokes and anti-Stokes of CH_4, we have observed strong emission in the forward direction due to the first positive system at 544nm, second positive system at wavelengths 405.9nm and 434.4nm of neutral N_2 and the CN band at 392nm. The transition at 434.4nm is due to four photon excitation with a rate-limiting step that scales as a two photon process. The CN band at 392nm is due to three photon process.

Spontaneous emission for the N_2 (B-A), (C-B) and CN (B-X) band system were observed but the signal was very weak for our optical detection system to record the spectrum. These emissions were confirmed by minimizing the background count as low as possible and setting the monochromator for the specific transition, for example, for the (B-A) transition at 544nm and checking the photon count.

The forward emission which has the same directionality as the pump beam is suggestive that the emission may be due to stimulated process. In order to confirm that the observed signal is Stimulated Emission

(SE), further investigation such as (a) divergence measurements, (b) threshold behaviour, © amplification of the signal by introducing resonant cavity mirrors, (d) monitoring the signal at various Raman cell lengths (the spontaneous LIF photon provides seeding for the amplification of the Stimulated Emission(SE)), and (e) detection of the signal in the backward direction are necessary.

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REFERENCES:

[1] W.M.Jackson, J.B.Halpern and Chung-San Lin, Chem. Phys. Letters 55 (1978) 254.

[2] J.R.McDonald, A.P.Baronavski and V.B.Donnelly, Chem. Phys. 33(1978) 161.

[3] R.C.Sausa, A.J.Alfano and A.W.Miziolek, Appl. Opt. 26 (1987) 3588.

[4] M.Alden and W.Wendt, Opt. Comm. 69 (1988) 31.

[5] A.Fujii, T.Ebata and M.Ito, J. Chem. Phys. 88 (1988) 5307.

[6] G.Laufer, R.H.Krauss and J.H.Grinstead, Opt. Letters 16 (1991) 103.

[7] W.B.Lewis and W.R.Wadt, Chem. Phys. Letters 78 (1981) 266.

[8] K.Sentrayan, L.Major, A.Michael and V.Kushawaha, Appl. Phys. B55 (1992) 311.

[9] R.W.B.Pearse and A.G.Gaydon, The Identification of Molecular Spectra (John Wiley & Sons, New York, 1976).

[10] H.Okabe, Photochemistry of Small Molecules (John Wiley & Sons New York, 1978).

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