The Study on the Excitation Lasers for NO Planar Laser-Induced Fluorescence Imaging
(NO PLIF용 excitation 레이저에 관한 연구)

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Abstract

Excitations of eight pumping transitions for nitric oxide fluorescence imaging are analyzed under equivalent experimental conditions to determine the detection. Frequency mixed dye laser pumping, 1st anti-Stokes H_2 Raman of KrF excimer laser pumping and ArF excimer laser pumping show good sensitivities.

1. Introduction

Since nitric oxide (NO) is one of major air pollutants resulting from combustion, its measurement and control is of global importance. Laser-induced fluorescence(LIF) has proved to be an effective and sensitive tool to measure NO. Many single point LIF and planar laser-induced fluorescence(PLIF) experiments to measure NO have been performed[1-11]. PLIF imaging has been proven as an especially powerful tool for obtaining spatial concentration profiles of NO at a single instant in time. Advances in PLIF that provide more quantitative data have high potential to generate a better understanding of NO production and emission.

Fluorescence is the emission of light from an atom or molecule following promotion to an excited state by various means: electron bombardment, heating, chemical reaction (chemiluminescence) or photon absorption[12]. Here only the last means will be considered. Fluorescence is the sequence of an optical absorption process followed by a spontaneous emission event. A molecule in an excited electronic state may not necessarily emit radiation. Several other pathways of energy loss are available to compete with fluorescence. Some of these are: energy transfer to another molecule, energy transfer to other internal energy states within the same molecule, and chemical reaction. These processes compete with fluorescence, and reduce the amount of fluorescence.

A laser source with an emission frequency tuned to an absorption in the NO molecule excites those molecules to an excited electronic state as shown Fig. 1. Although the transitions, which are shown

in Fig. 1 such as A-X(0,1)[1], A-X(0,0)[2-9], A-X(0,2)[10] and D-X(0,1)[11] have been used to excite NO molecule to emit fluorescence, there has been no detailed comparison of NO excitation schemes except the experimental work[13] for A-X transition using frequency mixed dye laser pumping. In order to compare the eight laser NO excitation techniques[1-11] indicated in table I, the detection limit are compared. The detection limits are estimated under equivalent experimental conditions based on calculation of the Number of Photons per Pixels(NPP) on a two dimensional detector.

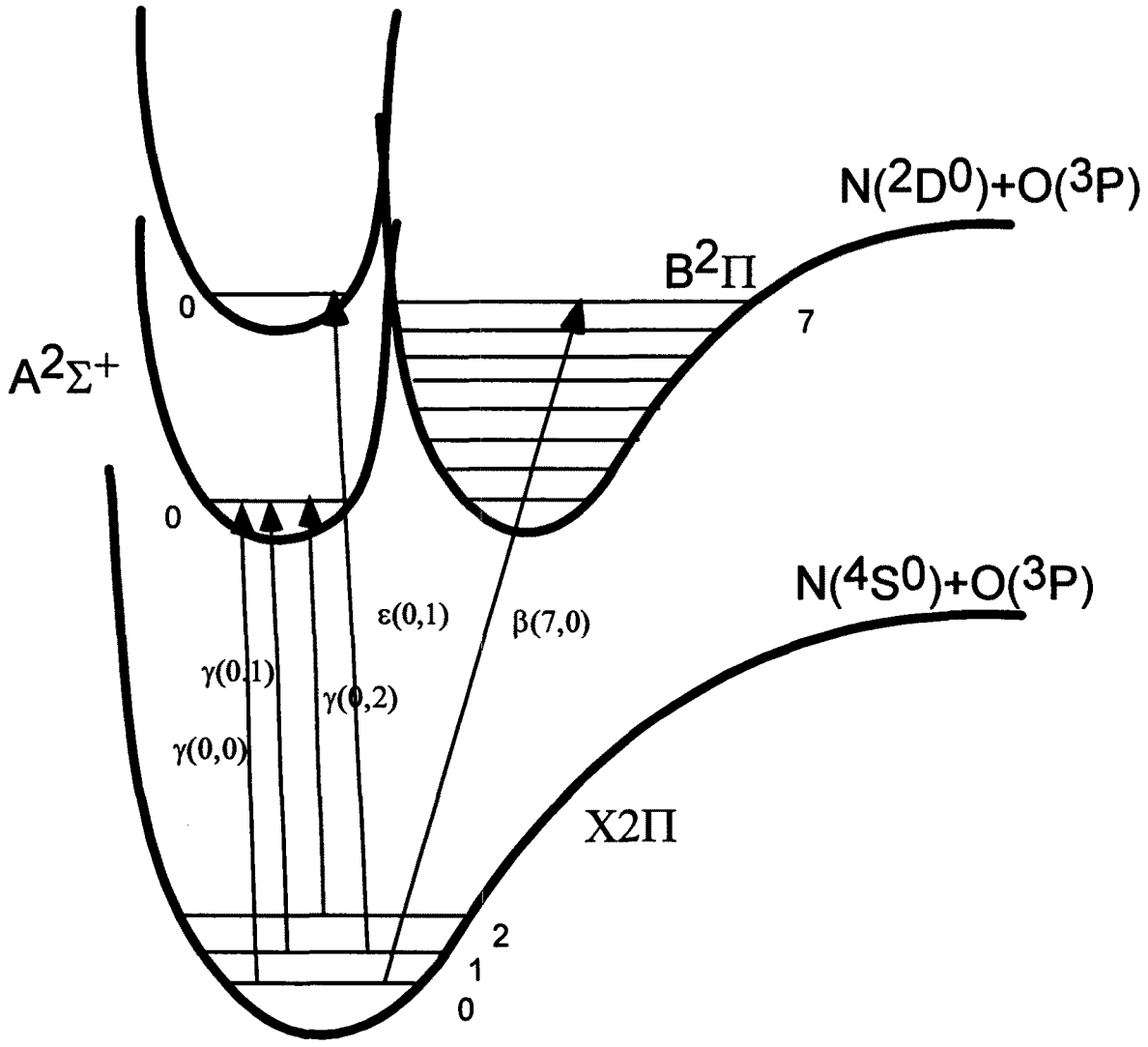

Figure 1 Ptential energy diagram of NO

Oxygen molecules, which can be much more abundant than nitric oxide, can also absorb light at wavelength where NO is excited. Strong oxygen LIF signals are also observed in some nitric oxide LIF detection bands. Oxygen absorption and LIF interference are discussed in section 3(b).

Table 1. Comparison of various laser excitation scheme for NO PLIF

Case No.	Laser	Excitation scheme [cm^{-1}]	Excitation band	A 10^6 s^{-1}	Q 10^8 s^{-1}	NPP (100ppm)	Detection limit [ppm]	Reference
(a)	Mixed IR Nd:YAG and doubled dye laser pumped by 2nd Nd:YAG laser	$A^2\Sigma^+ - X^2\Pi$ γ (0, 1) 42239.11	$Q_{22}+R_{12}(7.5)$ $+P_{22}+Q_{12}(14.5)$ $+ P_{12}(24.5)$	0.184	0.584	31.3	28	(1)
(b)	Mixed IR Nd:YAG and doubled dye laser pumped by 2nd Nd:YAG laser	$A^2\Sigma^+ - X^2\Pi$ γ (0, 0) 44202.09, 44185.76	$Q_{11}+P_{21}(6.5)$, $P_{11}(14.5)$	0.198	0.584	61.7	14	(2)
(c)	Mixed IR Nd:YAG and doubled dye laser pumped by 2nd Nd:YAG laser	$A^2\Sigma^+ - X^2\Pi$ γ (0, 0) 44275.98	$Q_{11}+P_{21}(18.5)$	0.221	0.584	64.2	13.6	(3)
(d)	Mixed IR Nd:YAG and doubled dye laser pumped by 2nd Nd:YAG laser	$A^2\Sigma^+ - X^2\Pi$ γ (0, 0) 44330.19	$Q_{22}+R_{12}(26.5)$	0.228	0.584	103	8.5	(4)
(e)	Doubled dye laser pumped by XeCl excimer laser	$A^2\Sigma^+ - X^2\Pi$ γ (0, 0) 44108.09	$Q_{22}+R_{12}(6.5)$	0.199	0.584	37.1	23	(5)
(f)	Doubled dye laser pumped by XeCl excimer laser	$A^2\Sigma^+ - X^2\Pi$ γ (0, 0) 44241.14, 44241.48	$Q_{22}+R_{12}(20.5)$, $Q_{11}+P_{21}(14.5)$, $P_{11}(22.5)$	0.214	0.584	220	4.0	(6)
(g)	1st anti-Stokes Raman of H_2 cell pumped by KrF excimer laser	$A^2\Sigma^+ - X^2\Pi$ γ (0, 0) 44404.38	$Q_{11}+P_{21}(28.5)$	0.231	0.584	111	7.8	(7, 8)
(h)	KrF excimer laser seeded by doubled dye laser pupmed by XeF excimer laser	$A^2\Sigma^+ - X^2\Pi$ γ (0, 2) 40355.13	$P_{22}+Q_{12}(5.5)$	0.260	0.584	33.0	26.4	(9)

(i)	ArF excimer laser	$D^2\Sigma^+ - X^2\Pi$ ε(0, 1) 51712.5	R_{11} (26.5) $+Q_{11}$(32.5) $+P_{11}$(39.5)	2.53	2.08	3610	0.33	(10, 11)

2. Theory

We assume that fluorescence light emerging from a portion of the plane of illumination (height H) is focused, using a lens (focal length f=5.8cm, diameter d = 7.2cm and effective f number $f\#$ = 0.8), onto one of the elements of a square N x N pixel array, each side of which is of length l. The distance between the collection volume and the lens is $D+f$.

The number of photon per pixel(NPP) is given by[14]

$$NPP = \frac{1}{16}\eta\left(\frac{d}{f}\right)^2 \frac{M}{(M+1)^2}\frac{Rl}{N^2}\frac{E_p}{c\cdot\Delta\nu}\left(\frac{A}{A+Q+P}\right)BF_pN_T \qquad (1)$$

where η is the optical collection efficiency; M, magnification($=l/H=f/D$) ; R, the ratio of active to total pixel area; N, the number of pixel (assumed square) ; E_p, the laser energy per pulse; c, the speed of light; $\Delta\nu$, the bandwidth of laser; A, B, the Einstein coefficients; Q, the quenching rate constant; P, predissociation rate constant; F_p, the absorbing state population fraction; and N_T, the absorbing species number density. For the calculation of the Einstein coefficients A and B, vibrational Einstein coefficients[15], the Hönl-London factors[1] and the electronic transition energies (cm^{-1})[4,16-18] are used. The quenching rate constant Q is calculated for a ϕ=0.8 lean premixed methane/air flame. Equilibrium composition and the quenching cross-sections of A(0) state at 2000K are taken from Gray et al[19]. The spectral width $\Delta\nu$, are assumed to be greater than the absorption linewidths.

The quenching cross-sections for the D(0) state at 2000K are not available[20], those of the D(0) state at 300K from Asscher and Haas[21] were used instead. The quenching cross section by H_2O on the D(0) state is assumed to have the same value as that by CO_2 on the D(0) state since they have similar values in the A(0) state and follow similar quenching mechanism like collision complex mechanism and harpoon mechanism[19]. The population of the absorbing state population and the dependence of the quenching cross-sections on temperature[19] are also considered only for A(0) state to estimate the temperature dependence of NPP.

The detection limit is given by Paul et al.[22] considering the signal to noise ratio(*SNR*) and quantum efficiency.

$$NPP = \frac{a}{\varepsilon}(SNR)^2 \qquad (2)$$

where ε is the quantum efficiency of photo detector and a is noise factor for electronic gain. *SNR* is assumed to be 1 at the detection limit.

3. Results and Discussion

3.(a) Detection limit

Table I shows excitation schemes and the calculated detection limits. All excitation schemes are assumed to be applied under the same two dimensional imaging experimental conditions, even though some of them were used in point LIF measurements in the references. The laser energies are assumed to be at maximum available energy within the linear fluorescence regime, and for the purpose of comparison the laser bandwidths are assumed to be the same. In order to verify that all are in linear regime, the ratios of laser spectral intensity to saturation spectral intensities for no relaxation case and completely relaxed case are presented. Cases (d), (f), (g), and (i) show good detection limits, under 10 ppm. Table I shows that D-X transitions such as that of case (i) has one order of magnitude stronger laser energy, bigger Einstein coefficient A, and bigger quenching rate constant Q. The first and second factors provide an explanation for the detection limit advantage of case (i), however, the latter, the bigger Q has an adverse effect on the detection limit because the detection limit can be depend on $\frac{A}{Q}$ instead $\frac{A}{A+Q}$ due to Q >> A. As described in section two, quenching data for the D(0) state at high temperature range are not to our knowledge available in the literature. It is worth noting that the quenching cross–section of N_2 on the D(0) state is much larger than that on A(0) state[19, 21]. These values are 6.8 $Å^2$ and 0.007 $Å^2$ respectively. An increase in the quenching cross–section of N_2 for the A(0) state from 0.007 $Å^2$ to 0.7 $Å^2$ is seen as the temperature rises from 300K to 2000K[19]. If the quenching cross–section of N_2 in the D(0) has similar temperature dependency as that of the A(0) state, the quenching rate

constant of the D(0) state at 2000K can be approximately one order of magnitude larger than that at 300K because of large population of N_2 in air breathing combustion environments.

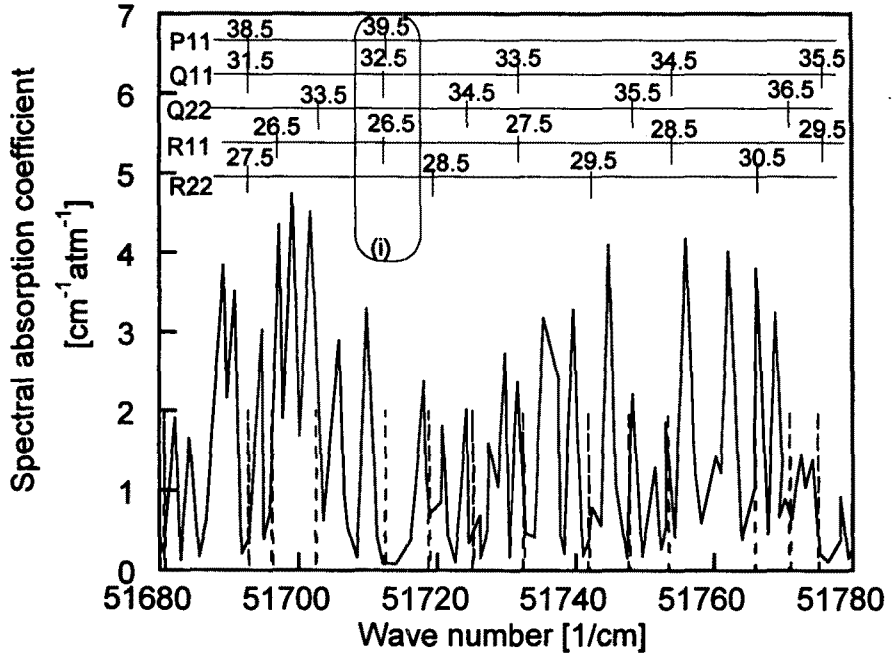

Figure 2 Spectral absorption coefficient of O_2 at 2000K(solid line)[23] and NO D-X(0,1) absorption frequency (dashed line)

3.(b) Oxygen Interferences in NO excitation wave length

Another problem related to ArF excimer laser pumping is that the laser wavelengths used for NO excitation are also absorbed by oxygen molecules. Figure 2 shows that spectral absorption coefficient of oxygen at 2000K under 1 atm environment[23] as a fraction of excitation frequency in 193nm ArF excimer laser spectral range. It shows that few NO excitation bands including case (i), have small oxygen absorption coefficient. Therefore, oxygen absorption can pose problems for ArF excimer laser pumping PLIF schemes. Absorption coefficient decrease, however, by three order of magnitude as excitation wavelength increase from 190nm to 260nm[24]. Cases (a) and (h) show fewer problems caused by oxygen absorption as they are at relatively longer wavelength than others considered here in.

Another problem related ArF excimer laser pumping is many O_2 transitions that are observed with strong LIF signals despite the fast predissociations of the excited electronic state[24]. However, with narrow-band ArF excimer laser pumping at case (i), O_2 LIF signal can be suppressed by from 50% of total measured fluorescence to 1.3% of the total fluorescence[10]. According to Battles et al.[25] for NO A-X(0,0) band has three general broadband O_2 fluorescence, which consist of many spectra l lines, in the ranges 44318.28 cm^{-1} to 44305.62 cm^{-1} , 44251.70 cm^{-1} to 44228.22 cm^{-1} , and 44202.80 to 44182.3 cm^{-1}. So cases (b) and (c) can have a problem related O_2 LIF interference. Case (d) minimize inadvertent O_2 excitation except $Q_{22}(25.5)$ according to Partridge et al.[26]

4. Conclusion

Each laser excitation scheme has advantages in specific applications. Cases (d) and (g) are good excitation schemes for quantitative NO concentration imaging. ArF Excimer pumping case (i), is most valuable for probing hot NO production regions in a combustion environment. These results are valid for atmosphere pressure flames. Consideration of the effect of pressure on quenching rates, rotational energy transfer (RET) and line broadening would be required for extrapolation to higher pressure regimes.

Acknowledgments

Kyung-Tae Kang would like to thank Drs. John A. Shirley, Michael Winter and Alan Eckbreth for their kind discussion. Kyung-Tae Kang were supported by Korea Sciences and Engineering Foundation and United Technologies Corporation.

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