

Variation of electronic transition moment versus internuclear distance for NO ($A^2\Sigma \rightarrow X^2\Pi$) transition

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Two-photon laser-induced fluorescence spectrum (TP-LIF) of NO is obtained with a Nd:YAG pumped optical parametric generator and amplifier as radiation source. Spectral intensity distribution shows that the electronic transition moment for NO ($A^2\Sigma \rightarrow X^2\Pi$) transition varies significantly with inter-nuclear distance. The variation relationship of the electronic transition moment versus inter-nuclear distance is deduced with polyminal fit procedure. The spontaneous radiative coefficients for NO ($A^2\Sigma \rightarrow X^2\Pi$) transition from $v' = 0, 1$ are obtained by combing this transition moment variation with the measurements of spontaneous radiative lifetime.

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NO is a special diatomic molecule. It is the unique chemical stable open-shell molecule with an unpaired outer electron^[1]. Because of its special properties, there are many reports about its researches^[2-10]. A few of them discuss whether or not the NO ($A^2\Sigma \rightarrow X^2\Pi$) electronic transition moment varies significantly with inter-nuclear distance. The conclusion is different from one to the other. M. Khalil and G. P. Lawrence have shown evidence of a significant variation about the transition moment^[3,4], otherwise, H. P. Broida and M. Jeunehomme have disputed this contention^[5,6]. Up to now, there is no consistent conclusion about this subject. The general recognition seems to be that no significant transition moment variation occurs for electronic transition. Recently, while studying the laser induced fluorescence spectrum about NO ($A^2\Sigma \rightarrow X^2\Pi$) transition, inconsistencies are founded in the distribution of spectral intensity if adopting a constant transition moment. The observed band intensity ratios for transitions from a common vibration level in the upper state cannot be explained by variation in the Frank-Condon factors. Observation shows that variation of the electronic transition moment is more than 60% in the inter-nuclear distance 0.096–0.114 nm. Combing this variation with the spontaneous radiant lifetime measurement, the spontaneous radiative coefficients from the upper vibration level are calculated.

The experimental setup is shown in Fig. 1. The optical parameter generator and amplifier (PG401) pumped by the triple-frequency 355 nm output of a Nd:YAG laser (France Quantel 900) is used as exciting source. The output wavelengths at 429.4 nm and 452.4 nm are used to excite NO $A^2\Sigma(v' = 0, 1) \leftarrow X^2\Pi(v'' = 0)$ transition. The laser operates at 10 Hz with a line-width of $\sim 6 \text{ cm}^{-1}$. The pulse duration is $\sim 35 \text{ ps}$. After being focused by a lens with 15-cm focal length, the power density of the laser beam in the focal region is of the order of $\sim 10^{10} \text{ W/cm}^2$. The sample cell is made of stainless with four windows sealed with quartz glass. The fluorescence focused is directed into a mono-chromator equipped with a photo-multiplier tube (PMT). The sig-

nal from the PMT is fed into a boxcar averager. The resulting fluorescence spectrum is recorded at resolution $\Delta\lambda=0.1 \text{ nm}$ in 210–370 nm wavelength range. When measuring the fluorescence lifetime, the fluorescence that passed through a filter with central wavelength $\sim 235 \text{ nm}$ was sent into a PMT. The response time about the PMT is smaller than 1 ns. A Tektronix digitizer oscilloscope is used for the measurement of lifetime. The outputs of Boxcar averager and digitizer oscilloscope are stored in a laboratory computer for later analysis.

Figure 2 shows the fluorescence emission spectrum of NO excited by laser wavelengths of 452.4 nm and 429.4 nm at 1064 Pa pressure. The fluorescence forms a progression by $A^2\Sigma(v' = 0) \rightarrow X^2\Pi(v'' = 1 - 8)$ transition in the spectral region 210–370 nm excited by wavelength of 452.4 nm. Otherwise, with excitation wavelength of 429.4 nm, the fluorescence forms a progression by $A^2\Sigma(v' = 1) \rightarrow X^2\Pi(v'' = 1 - 10)$ transition in the observation wavelength region. The intensities of each band are listed in Table 1.

The intensity of fluorescence is in direct proportion to the product of the number density $N_{v'}$ in the upper state, the Frank-Condon (F-C) factor $q_{v',v''}$, the quartic of the transition frequency $\nu_{v',v''}$, and the square of the electronic transition moment $R_e(r)$ ^[11]. That is

$$I_{v',v''} = N_{v'} A_{v',v''} h\nu_{v',v''} \propto N_{v'} q_{v',v''} \nu_{v',v''}^4 R_e(r)^2. \quad (1)$$

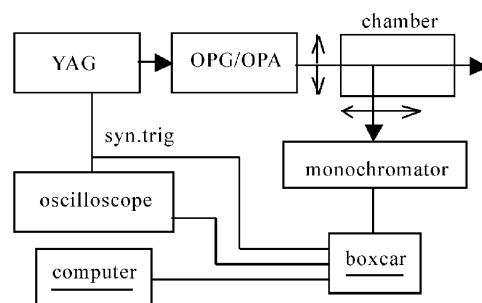


Fig. 1. Experimental setup.

Table 1. Some Parameters for NO ($A^2\Sigma \rightarrow X^2\Pi$) Transition

Band v''	Wavelength λ (nm)	Relative Intensity	$q_{v'v''}$	$r_{v'v''}$ (nm)	$R_e(r)$	$A_{v'v''}$ (s^{-1})
$v' = 0 \rightarrow$						
0	226.243	0.000	0.1670	0.1109	0.950	1.004×10^6
1	236.271	1.369	0.2635	0.1087	0.958	1.415×10^6
2	247.058	1.259	0.2365	0.1067	0.994	1.196×10^6
3	258.700	1.000	0.1596	0.1048	1.052	7.875×10^5
4	271.264	0.891	0.0905	0.1030	1.129	4.463×10^5
5	284.915	0.504	0.0457	0.1014	1.221	2.278×10^5
6	299.744	0.202	0.0213	0.0998	1.325	1.073×10^5
7	315.923	0.098	0.0094	0.0983	1.439	4.710×10^4
8	333.636	0.073	0.0040	0.0968	1.562	2.007×10^4
$v' = 1 \rightarrow$						
0	214.862	0.000	0.3335	0.1136	0.985	2.363×10^6
1	223.887	0.631	0.1030	0.1111	0.951	6.008×10^5
2	233.550	0.000	0.0010	0.1092	0.954	5.073×10^3
3	243.919	1.000	0.0723	0.1075	0.976	3.442×10^5
4	255.071	1.567	0.1338	0.1055	1.028	6.182×10^5
5	267.090	2.032	0.1326	0.1037	1.099	6.028×10^5
6	280.080	1.953	0.0978	0.1020	1.185	4.480×10^5
7	294.155	1.112	0.0606	0.1004	1.282	2.802×10^5
8	309.452	0.556	0.0334	0.0989	1.391	1.562×10^5
9	326.130	0.327	0.0170	0.0975	1.508	8.027×10^4
10	344.377	0.164	0.0082	0.0961	1.632	3.870×10^4

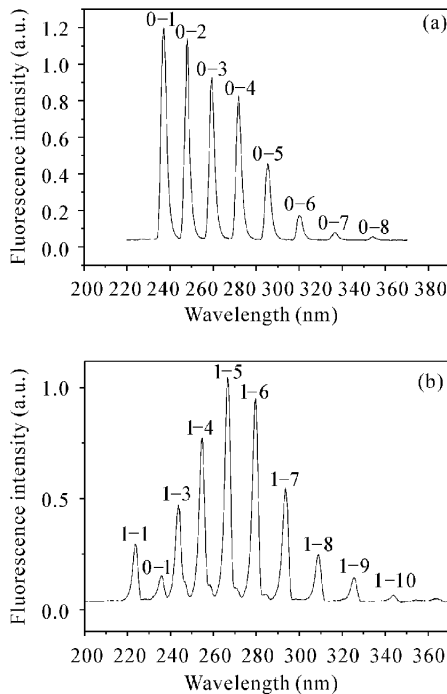


Fig. 2. Two-photon laser-induced fluorescence spectrum (TP-LIF) of NO. (a) With excitation wavelength 452.4 nm; (b) with excitation wavelength 429.4 nm.

The relative intensity is

$$\frac{I_{v'v''}}{I_{v'v''}} = \left(\frac{\lambda_{v'v''}}{\lambda_{v'v''}} \right)^4 \cdot \frac{q_{v'v''}}{q_{v'v''}} \cdot \left[\frac{R_e(r_{v'v''})}{R_e(r_{v'v''})} \right]^2$$

The F-C factor is transition probability of the upper and lower vibration states. It can be calculated by

$$q_{v'v''} = \left| \int \varphi_{v'} \varphi_{v''} dr \right|^2, \quad (2)$$

where $\varphi_{v'}$, $\varphi_{v''}$ are vibration wave functions of the upper and lower vibration states respectively. They can be obtained by solving Schrödinger-equation^[7]. The calculation results about F-C factor are listed in Table 1. The value of relative electronic transition moment can be calculated with the experimental results about band position and corresponding intensity. Figure 3 shows the value of the electronic transition moment relative to its value for the $\Delta v = -3$ sequence. In the calculation about F-C factor and inter-nuclear distance^[12], a Morse potential function^[11] is adopted.

Fitting the data to a quadratic function of inter-nuclear distance $r_{v'v''}$, the electronic transition moment can be written as

$$R_e(r_{v'v''}) = 41.809 - 74.051r_{v'v''} + 33.551r_{v'v''}^2. \quad (3)$$

The value of the electronic transition moment versus inter-nuclear distance was calculated according to this formula. The results are given in Table 1 also. As seen, the variation of the electronic transition moment is small for the transition of low ($v'' \leq 3$) vibration levels (for $v' = 0 \rightarrow v'' = 0 - 3$ transition, $\frac{1.052-0.95}{1.052} \approx 10\%$; for $v' = 1 \rightarrow v'' = 0 - 3$ transition, $\frac{0.976-0.951}{0.976} \approx 2.6\%$), but rises much more sharply for the transition of high ones

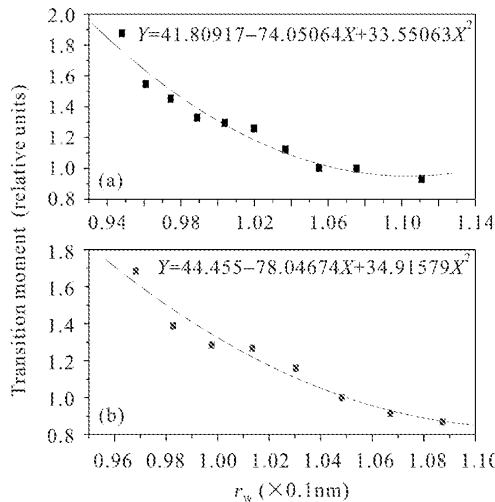


Fig. 3. Variation for electric transition moment versus inter-nuclear distance.

(for $v' = 0 \rightarrow v'' = 3 - 6$ transition, $\frac{1.325-1.052}{1.052} \approx 26\%$; for $v' = 1 \rightarrow v'' = 3 - 6$ transition, $\frac{1.185-0.976}{0.976} \approx 21\%$). The variation is obvious. $R_e(r)$ varies from 0.95 to 1.632 when r changes from 0.096 to 0.114 nm. On the whole, the result is consistent with the one of Lawrence G. P. who excited NO molecules by the method of energy transfer^[4], but the variation of $R_e(r)$ versus r is more obvious in our work. The possible reason is that in our experiment, there is error in measuring the fluorescence intensity about transitions $v' = 0 \rightarrow v'' = 8$ and $v' = 1 \rightarrow v'' = 10$ because of low ratio of signal to noise. One can find in Fig. 3, the variation of $R_e(r)$ versus r will be slower if these bad points are abandoned.

The Einstein coefficient for spontaneous radiation is^[11]

$$A_{v'v''} = \frac{64}{3h} \pi^4 \nu_{v'v''}^3 R_e^2(r_{v'v''}) q_{v'v''}. \quad (4)$$

The radiative lifetime of the upper vibration level

$$\frac{1}{\tau_{v'}} = \sum_{v''} A_{v'v''} = \frac{64\pi^4}{3h} \sum_{v''} \nu_{v'v''}^3 R_e^2(r_{v'v''}) q_{v'v''}. \quad (5)$$

Let Eq. (4) divided by Eq. (5), then

$$A_{v'v''} \tau_{v'} = \frac{\nu_{v'v''}^3 R_e^2(r_{v'v''}) q_{v'v''}}{\sum_{v''} \nu_{v'v''}^3 R_e^2(r_{v'v''}) q_{v'v''}}. \quad (6)$$

If we know the radiative lifetime of upper vibration level, the Einstein coefficient for spontaneous radiation can be calculated.

The lifetime of $A^2\Sigma(v' = 0, 1)$ state of NO molecule is measured. A typical time waveform is shown in Fig. 4 with 429.4-nm excitation wavelength and pressure of 931 Pa. The radiative lifetime of NO $A^2\Sigma(v' = 1)$ state is about 23 ns under this conditions. The spontaneous radiative lifetime of $A^2\Sigma(v' = 0, 1)$ state can be deduced by measuring variation of the lifetime versus pressure, which is about 190 ns and 180 ns respectively. The Einstein coefficients $A_{v'v''}$ for each band are listed in the right of Table 1. These values agree basically with Ref. [4].

By measuring the spectral intensity of TP-LIF about

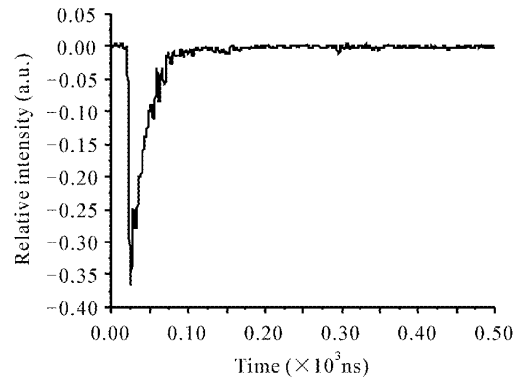


Fig. 4. A typical time waveform of fluorescence signal with 429.4 nm excitation wavelength.

NO molecule, variation of the electronic transition moment for the NO ($A^2\Sigma \rightarrow X^2\Pi$) transition with inter-nuclear distance is observed. The electronic transition moment $R_e(r)$ varies from 0.950 to 1.632 in the inter-nuclear distance 0.096 – 0.114 nm. Combing this transition moment variation with the measurements of spontaneous radiative lifetime, the spontaneous radiative coefficients for NO ($A^2\Sigma \rightarrow X^2\Pi$) transition from $v' = 0, 1$ are obtained. This is significant. Because when calculating the gain for various transitions in the NO ($A - X$) laser, correct NO ($A \rightarrow X$) transition probabilities are needed. In addition, the technique of laser-induced fluorescence is an important tool for probing the quantities of NO in air pollution monitor and chemical reaction. Incorrect NO ($A \rightarrow X$) transition probabilities will invalidate the results of these measurements.

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