

# Photo-acoustic spectrum and detection of nitrogen dioxide

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The photo-acoustic (PA) spectrum of nitrogen dioxide ( $\text{NO}_2$ ) in the range of 420–520 nm with a Nd:YAG pumped optical parametric generator and amplifier as radiation source is presented. The spectrum has a characteristic of banded structure superimposed on continuum. The banded structure of the spectrum can be assigned to  $\text{NO}_2$   $B^2B_1 \leftarrow X^2A_1$  transition. While the continual one comes from the chaos states of the first excited state  $A^2B_2$  and the high vibration levels of the ground state  $X^2A_1$ . The relationship of PA signal with buffer gas pressure and  $\text{NO}_2$  concentration is measured. The PA signal intensity increases with buffer gas pressure and almost is invariable when the buffer gas pressure is more than  $3.00 \times 10^4$  Pa. The PA signal intensity has linearity with  $\text{NO}_2$  concentration. The detection limit is about  $2 \times 10^{-5}$  on the basis of  $\text{SNR} = 1$ , however lower value of the detection limit can be expected by improving the apparatus properties.

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There has been great interest in laser-based sensitive monitors of pollutants in the atmosphere in recent years, especially the detection and monitoring of nitrogen oxide compounds in the atmosphere.  $\text{NO}_x$ , which plays an important role in the cycle of ozone in the troposphere, is mainly emitted from automobile exhausts. We have already performed detailed study about the optical properties of NO and gotten useful information for its detection<sup>[1–3]</sup>. As for  $\text{NO}_2$ , people have interested in it for many years due to its particular feature. The reported literatures show that there is a mixing of the first excited electronic states  $A^2B_2$  and high-lying vibration states of the ground electronic state  $X^2A_1$ <sup>[4–7]</sup>. This induces that the absorption spectrum in the visible region is very complex and the natural lifetime of its excited levels is anomalously long<sup>[8,9]</sup>. Therefore, the energy transfer from the excited levels by collision process is very efficient. So at present the laser-induced photo-acoustic (PA) technique seems to be one of the most sensitive and versatile methods for the study and detection of  $\text{NO}_2$ . In this letter, the PA spectrum of  $\text{NO}_2$  with pulsed laser as radiation source is presented. The relation between the PA signal intensity and buffer gas pressure and  $\text{NO}_2$  concentration was studied.

The experimental setup is shown in Fig. 1. An optical parameter generator and parameter amplifier (EKSPLA, PG401VIR) pumped with the triple-frequency 355 nm output of a Nd:YAG laser (Quantel, YG900) are used to excite  $\text{NO}_2$ . The laser is operated at 10 Hz with

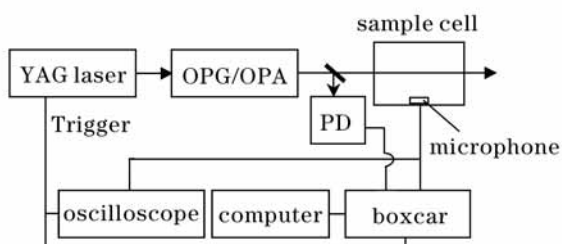


Fig. 1. Experimental setup.

a line width of  $\sim 6 \text{ cm}^{-1}$ . The pulse energies are 0.1–0.4 mJ and the pulse duration is  $\sim 35$  ps. The nonresonant sample cell, which is made of stainless steel with four windows sealed with quartz glass, is a cylinder. The height and diameter are both 10 cm. A capacitive microphone ( $-58$  dB sensitivity) is mounted in the inside wall of the sample cell. It is powered with a 9-V battery. The vertical distance from the microphone to the laser beam is about 0.2 cm. A photo-diode (PD) is used to detect the laser energy. Both of the signals from the microphone and PD are fed into a boxcar (Stanford, SRS280/255) using a gate with width of 100  $\mu\text{s}$ , and a computer connected with the boxcar records the spectrum. A digital oscilloscope (Tektronix, TDS3052) is used to collect the waveform of the PA signal in time.

Figure 2 is a typical PA spectrum of  $\text{NO}_2$  in the region of 420–520 nm under the condition of the pressure of 665 Pa. The spectrum which is normalized with respect to the laser energy is similar to the absorption one<sup>[10]</sup>. It presents a characteristic of banded structure superimposed on a continuum. To give an ascription of the spectrum, we must first confirm the excited states which are correlated with the exciting process.

The potential curve of  $\text{NO}_2$  is shown in Fig. 3. There are four electronic states  $X^2A_1$ ,  $A^2B_2$ ,  $B^2B_1$ , and  $C^2A_2$

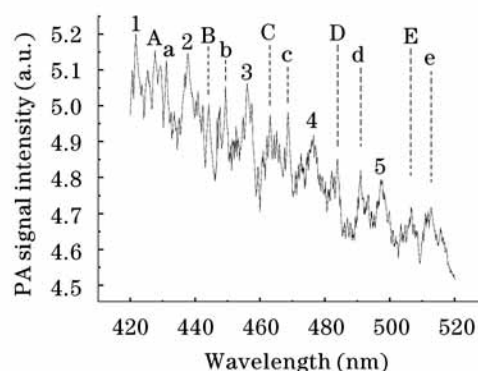


Fig. 2. PA spectrum of  $\text{NO}_2$  in the 420–520 nm region.

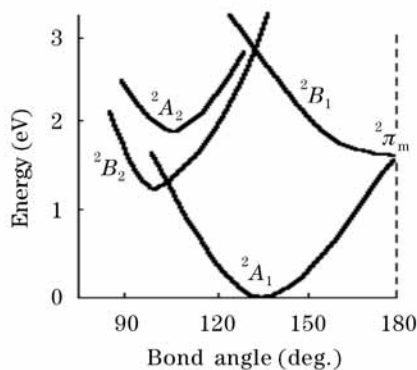


Fig. 3. Potential curve of NO<sub>2</sub> in bond angle coordinate.

in the exciting wavelength range. The vertical excitation energy of  $C^2A_2$  excited electronic state is higher than 2 eV, and the  $C^2A_2 \leftarrow X^2A_1$  transition is forbidden according to the symmetry selection rules of the polyatomic molecules. NO<sub>2</sub> can only be excited to the higher vibration levels of the excited states  $A^2B_2$  and  $B^2B_1$  due to the selection rules together with Frank-Condon principle. But we can see from Fig. 3 that there is a conical intersection in the potential curves of the ground and the first excited states. This induces a mixing of the first excited state  $A^2B_2$  and the higher vibration levels of the ground electronic state  $X^2A_1$ , and  $X^2A_1$  state are no Born-Oppenheimer one. The transition spectral lines that follow the selection rules increased.  $X^2A_1$  state can borrow oscillation strength from  $A^2B_2$  state and become the terminal state of a transition from the ground vibration level. Thus NO<sub>2</sub> can be excited to the higher vibration levels of the ground electronic state. As is known, the higher vibration levels of polyatomic molecules are very dense. The continuum structure of the PA spectrum is formed when the excited molecules de-excite through collision process.

The band origin of the transition from  $X^2A_1$  state to the second excited electronic state  $B^2B_1$  is about  $13389 \text{ cm}^{-1}$  (1.66 eV)<sup>[11]</sup>. There are enough NO<sub>2</sub> to be excited to  $B^2B_1$  state when the exciting wavelength is in the region of 420 – 520 nm. The banded structure of the spectrum comes from the vibration energy of this state transformed into the translation one.

Under the first approximation, the wave number for vibration transition of undegenerate level is

$$\tilde{\nu} = \tilde{\nu}_{00} + \Sigma \omega'_{ei} v'_i - \Sigma \omega''_{ei} v''_i, \quad (1)$$

where  $\tilde{\nu}$  is a transition wave number and  $\tilde{\nu}_{00}$  is a band origin, whose unit is  $\text{cm}^{-1}$ .  $\omega'_{ei}$  and  $\omega''_{ei}$  are vibration constants of the excited and the ground electronic states, respectively,  $v'_i$  and  $v''_i$  are vibration quantum numbers. NO<sub>2</sub> has three vibration modes, symmetry stretching, bending, and asymmetry stretching vibration. The vibration frequencies of these modes are  $\omega_1$ ,  $\omega_2$ , and  $\omega_3$ , respectively. Usually the asymmetry stretching vibration modes can not be excited. So one can let  $v'_3 = v''_3 = 0$ . At room temperature, most of the molecules are in the ground vibration levels of  $X^2A_1$  ground electronic state. For the transition between (0, 0, 0) of ground electronic state and ( $v'_1, v'_2, 0$ ) of the excited state, Eq. (1) can be

Table 1. Assignment of the PA spectrum

Peak No.	Wavelength (nm)	Assignment ( $v_1, v_2, v_3$ )
1	421.8	(0, 11, 0)
2	438.0	(0, 10, 0)
3	456.0	(0, 9, 0)
4	475.8	(0, 8, 0)
5	497.5	(0, 7, 0)
a	431.4	(1, 9, 0)
b	449.4	(1, 8, 0)
c	468.7	(1, 7, 0)
d	489.7	(1, 6, 0)
e	512.7	(1, 5, 0)
A	427.9	(2, 8, 0)
B	444.9	(2, 7, 0)
C	463.5	(2, 6, 0)
D	483.9	(2, 5, 0)
E	506.4	(2, 4, 0)

simplified as

$$\tilde{\nu} = \tilde{\nu}_{00} + \omega'_1 v'_1 + \omega'_2 v'_2. \quad (2)$$

The values of  $\omega'_1$  and  $\omega'_2$  of  $B^2B_1$  electronic state are 960 and  $1192 \text{ cm}^{-1}$ <sup>[11]</sup>, respectively. According to these constants of NO<sub>2</sub>, the banded structure can be assigned to NO<sub>2</sub>  $B^2B_1 \leftarrow X^2A_1$  transition. The results of the assignment are shown in Table 1. The stretching and bending vibration frequencies of  $B^2B_1$  electronic state are obtained, which are  $\omega_1 = (1188 \pm 47) \text{ cm}^{-1}$  and  $\omega_2 = (905.8 \pm 10.7) \text{ cm}^{-1}$ . The results are consistent with Ref. [11] very well. This indicates that PA technique is a suitable method for studying the properties of NO<sub>2</sub> molecule. In addition, the inharmonic vibration coefficient of  $B^2B_1$  electronic state can be obtained from the spectrum, which is  $\chi_{22} = -4.2 \text{ cm}^{-1}$ . There is not concern for the inharmonic vibration coefficient of NO<sub>2</sub>  $B^2B_1$  electronic state until now.

From Fig. 2, it is obvious that the PA signals of (0,  $v$ , 0) series are stronger, so the corresponding wavelengths can be used as optimum exciting ones when performing the detection of NO<sub>2</sub> with PA technique. The wavelength of the radiation source is fixed at 438.0 nm in the experiments.

Figure 4 is a plot of PA signal intensity as a function of buffer gas pressure. Air is used as buffer gas. The NO<sub>2</sub> pressure maintains 665 Pa during the measurement. The result indicates that PA signal intensity increasing with the buffer gas pressure and is almost invariable when the buffer gas pressure is more than  $3.00 \times 10^4 \text{ Pa}$ . This is because the enhancement of  $V-T$  transfer energy with buffer gas pressure and the quantity of NO<sub>2</sub> is invariable. The oscilloscope cursor is optimized to maximum signal during the measurement since the shape of the waveform of the PA signal varies with the pressure. The width and the delay time of the PA signal decrease with increasing the pressure.

A sensitivity plot for NO<sub>2</sub> under the condition of atmospheric pressure is shown in Fig. 5. The PA signal

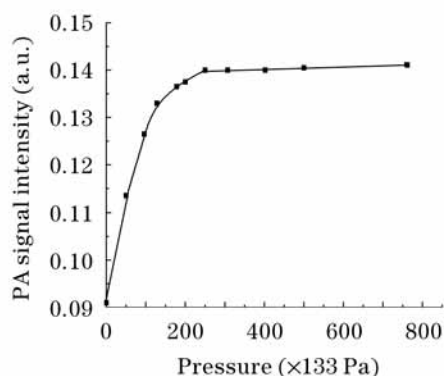
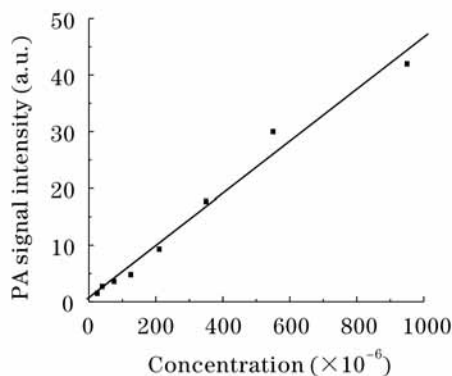


Fig. 4. PA signal intensity versus buffer gas pressure.

Fig. 5. PA signal intensity versus NO<sub>2</sub> concentration.

decreases with decreasing NO<sub>2</sub> concentration. Measurements show that the PA signal is covered up by the background noise when NO<sub>2</sub> concentration is lower than  $2 \times 10^{-5}$ . Radiation absorption by the windows and scattered light contacting the microphone contributed to the noise mostly. We can conclude that on the basis of SNR = 1, the detection limit in the experiment is about  $2 \times 10^{-5}$  when the exciting wavelength is 438.0 nm. One can insure that the detection limit can be improved further by optimizing the experimental properties<sup>[13]</sup>, such as increasing laser energy, reforming the sample chamber, and

selecting microphone with higher sensitivity.

The absorption properties of NO<sub>2</sub> in the range of 420 – 520 nm are studied with PA technique and some molecular constants of NO<sub>2</sub>  $B^2B_1$  state are obtained. The PA signal intensities versus buffer gas pressure and NO<sub>2</sub> concentration are detected also. The detection limit is about  $2 \times 10^{-5}$  in this experiment. Indeed the apparatus is complex and expensive. Its sensitivity is lower also owing to the lower output energies of the exciting source and nonresonant sample chamber. Based on these results, we design a set of detection apparatus with low cost, which use an appropriate output wavelength of a common flash as radiation source. The detection limit can reach  $6 \times 10^{-6}$ .

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