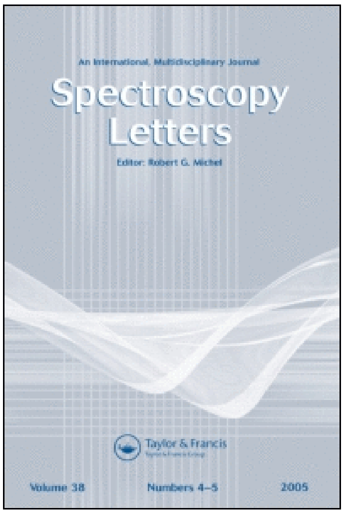

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

# The Rotational Analysis of the Five new Vibronic Bands of $No_2$ in the Range 5050-5200 Å

Cui Zhifeng[a]; Chen Dong[a]; Feng Erying[a]; Ji Xuehang[a]; Lu Tongxing[a]; Zhou Shikang[b]; Li Xuechu[c]
[a] Department of Physics, Anhui Normal University, Wuhu, Anhui, PRC [b] Laser Spectroscopy Laboratory, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei, PRC [c] State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, Liaoning, PRC

**To cite this Article** Zhifeng, Cui , Dong, Chen , Erying, Feng , Xuehang, Ji , Tongxing, Lu , Shikang, Zhou and Xuechu, Li(2000) 'The Rotational Analysis of the Five new Vibronic Bands of $No_2$ in the Range 5050-5200 Å', Spectroscopy Letters, 33: 5, 743 — 753

**To link to this Article: DOI:** 10.1080/00387010009350155

**URL:** http://dx.doi.org/10.1080/00387010009350155

SPECTROSCOPY LETTERS, 33(5), 743–753 (2000)

# THE ROTATIONAL ANALYSIS OF THE FIVE NEW VIBRONIC BANDS OF $NO_2$ IN THE RANGE 5050-5200Å

**Key Words:** VIS-spectra; molecular spectra; rotational analysis

Cui Zhifeng, Chen Dong, Feng Erying, Ji Xuehang and Lu Tongxing

Department of Physics, Anhui Normal University,
WuHu 241000, Anhui, PRC

Zhou Shikang

Laser Spectroscopy Laboratory, Anhui Institute of Optics and Fine Mechanics,
Chinese Academy of Sciences, Hefei 230031, PRC

Li Xuechu

State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of
Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, PRC

## ABSTRACT

The five new vibrational bands in the range 5050-5200 Å of the laser induced fluorescence excitation spectra of $NO_2$ were measured and rotationally assigned at room temperature. Though the spectra were rather congested, we can determine the band origins, and rotational and spin-rotation constants for these bands. All rotational structures analyzed are of the parallel type. It was shown that the electronic excited state $\tilde{A}^2B_2$ were heavily perturbed by the high lying vibration

levels of ground state $\tilde{X}^2A_1$ and that the interactions between these two electronic states was the main rationale for the complexity of $NO_2$ visible spectra.

## INTRODUCTION

The complex spectral structure of $NO_2$ in the visible range remains one of challenging problems of molecular spectroscopy. The 319 vibronic bands of the fluorescence excitation spectra of $NO_2$ in this range were obtained so far, however only a few parts of these bands were assigned rotationally[1-10]. In this paper the five new vibration bands of $NO_2$ were measured in our experiment by using high resolution fluorescence excitation spectrum at room temperature. The rotational analyses of these new bands were made; and the molecular constants, such as, band origins and rotational and spin-rotation constants for these bands, were also obtained. The mechanism of the spectral complexity in the five new vibronic bands was discussed.

## EXPERIMENTAL

The experimental block diagram is shown in Fig.1. We made the gas sample of $NO_2$, and the sample was introduced into the reaction cell by use of a micro-valve. The pressure of $NO_2$ in the cell can be varied in the range $6\times10^{-5}$-$1\times10^{-1}$Torr and the background pressure was $2\times10^{-6}$Torr. An Excimer, pumped dye laser with a 10 ns pulse duration, and 0.01 Å line width, was used as the excitation source. The energy of a single pulse monitored by an energy meter was about 10 mJ. The wavelength of the dye laser was monitored by a Wsp-I plane-graded spectrograph with wavelength resolution and deviation of 0.01 Å, and 0.009 Å, respectively. The standard emission lines from Hg, Ne, Kr, and Xe discharge lamps calibrated the absolute wavelength of the spectrograph. The laser beam was focused to a diameter of 0.5mm at the center of the cell. Light baffles were used to decrease the scattered laser light. The fluorescence was collected with two f/67mm condense lens and then imaged at the photocathode of the cooled photomultiplier

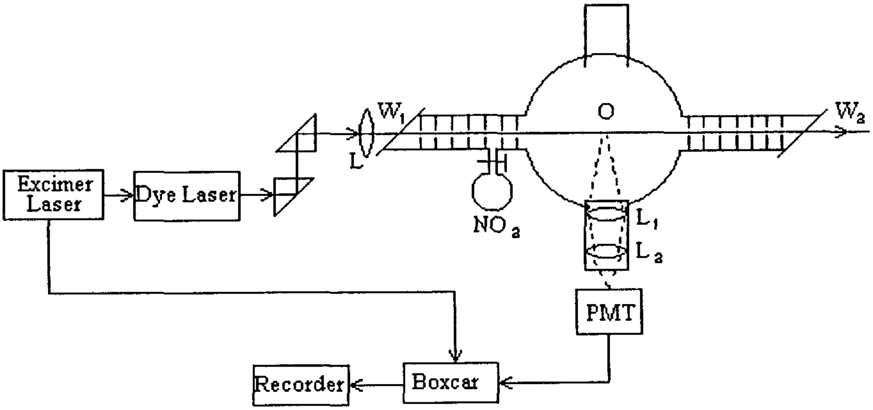

Fig. 1. The block diagram of experimental setup

(C31034A). The output of the PMT was fed into the input of the R250 Boxcar averager and the spectra were recorded by a strip chart recorder. The intensity of all the spectrum lines is normalized to the same laser power to prevent an error caused by laser power fluctuation.

## EXPERIMENTAL DATA AND ANALYSIS

We have measured the high-resolution excitation spectra of $NO_2$ in the range 5050-5200 Å at room temperature. A part of the spectra was shown in Figure 2. In this region the spectral structure is far more complex than the ones in long wavelength region[5]. Particularly in the range 5050-5130 Å, the spectra structure is so complex that only a few parts of the bands could be recognized. We have assigned 25 vibronic bands rotationally in this region. The five new vibronic bands in the range 5050-5200 Å were recorded with high resolution and the band origins were: 5069.63Å, 5084.78Å, 5092.91Å, 5096.22Å, and 5151.34Å, respectively. The spectra in this region correspond to the transition $\tilde{X}^2A_1 - \tilde{A}^2B_2$. The spectroscopic parameters of these vibonic bands are given in Table 1.

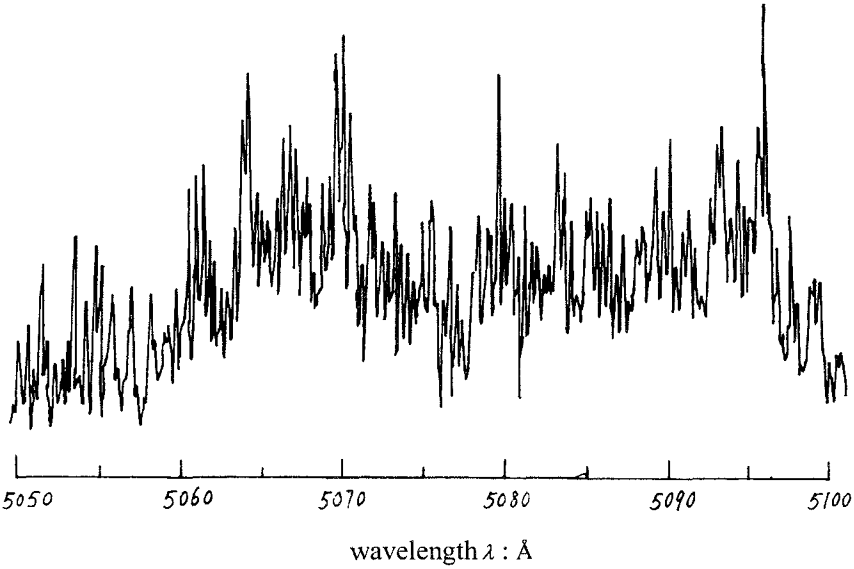

Fig.2. Laser induced fluorescence excitation spectra from 5050 Å to 5100 Å

The vibration energies $T_v'$ of these new bands were calculated by

$$T_v' = R(0)_\alpha - \frac{1}{2}\left|\tilde{\varepsilon}'\right| - 2B'$$

where $R(0)_\alpha$ is the frequency of the longer wavelength component of R(0) doublet. The spin-rotation interaction factors of the excited states $\tilde{\varepsilon}'$ were calculated from R(0) or R(2) splitting, the rotational constants $\tilde{B}'$ of the electronic excited states were obtained from R(2)-P(2) or R(4)-P(4), and the rotational constants $\tilde{B}''$ of the ground state were obtained from R(0)-P(2). The constants $\tilde{B}'$ depends slightly on the sign of $\tilde{\varepsilon}'$ and we chose $\tilde{\varepsilon}'>0$ in all cases. The spin-rotational interaction factors of the ground states were small enough that we can omit them.

The assigned rotational structure at the excitation wavelengths 5151.34Å was shown in Fig.3. The dominant structure originated from the $\Delta N = \pm 1$ transition in

TABLE 1

Spectroscopic Constants for the five new vibration bands of $NO_2$ in 5050-5200Å

| N | $T_v'(cm^{-1})$ | $\tilde{B}''(cm^{-1})$ R(0)-P(2) | $\tilde{B}'(cm^{-1})$ R(2)-P(2) | $\tilde{B}'(cm^{-1})$ R(4)-P(4) | $\tilde{\varepsilon}'(cm^{-1})$ From R(0) | $\tilde{\varepsilon}'(cm^{-1})$ From R(2) |
|---|---|---|---|---|---|---|
| 14 | 19412.43 | 0.420 | 0.389 | 0.388 | 0.27 | |
| 17 | 19622.40 | 0.423 | 0.390 | | | |
| 18 | 19635.13 | 0.423 | 0.409 | 0.408 | | |
| $20^a$ | 19666.52 | 0.423 | 0.392 | 0.395 | | |
| $24^a$ | 19725.31 | 0.422 | 0.450 | 0.448 | | 0.07 |

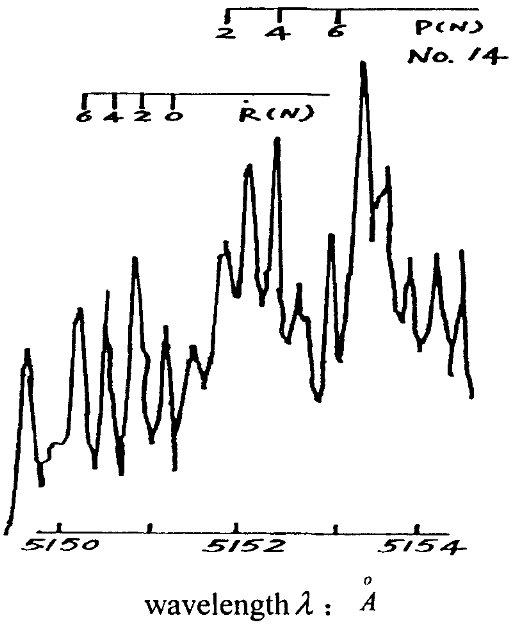

Fig.3. Laser induced fluorescence excitation spectra of $NO_2$ from 5150 to 5154 Å

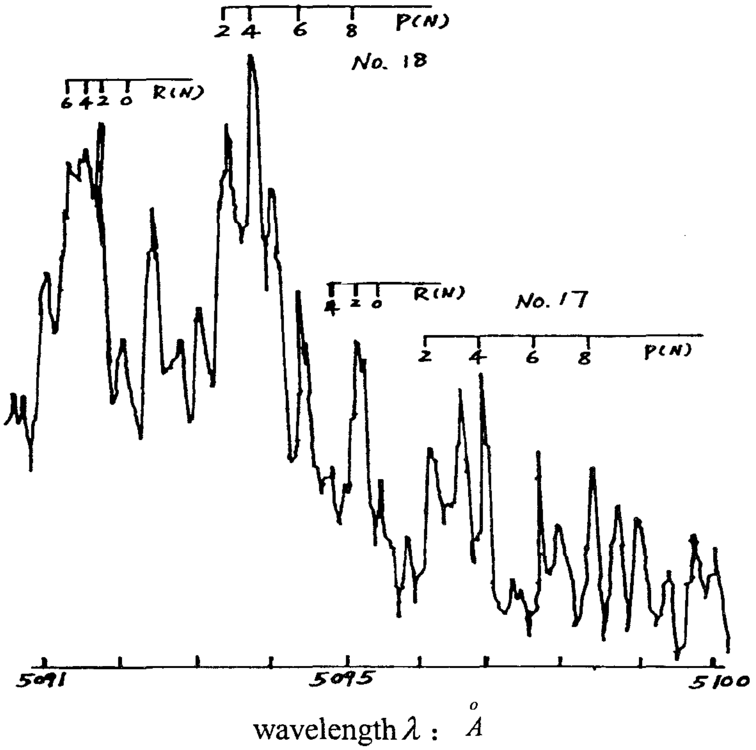

Fig.4. Laser induced fluorescence excitation spectra of $NO_2$ from 5091 to 5100 Å

$N''$=0,2,4,6, of the $K''$=0 manifold of the ground states $\tilde{X}^2A_1$, and their rotational assignment is listed in Table 2. The rotational structure of the other two bands at 5096.22Å and 5092.91Å were not clear, as shown in Fig.4. There are some spectral lines with observable intensity unassigned. The spectra lines of these two bands overlapped each other. The bands at 5084.78Å and 5069.63Å shown in Fig.5,6 and assigned in Table 2 have the most complex spectra structure. Some intense spectral lines couldn't be assigned. It probably originated from $K''$=1,2 manifolds of the ground states or the forbidden transition $\Delta K = \pm 2$, and $\Delta N = \pm 3$.

Generally the band head is formed in the R branch, but in the band at 5069.22Å the band head is formed in the P branch, inversely. Thus, the rotational

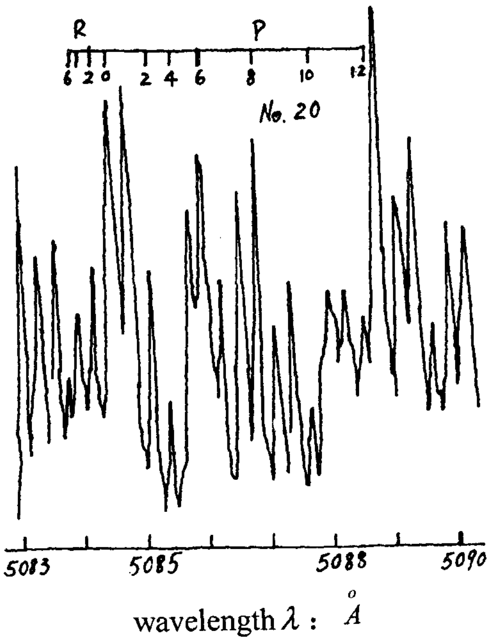

Fig.5. Laser induced fluorescence excitation spectra of $NO_2$ from 5083 to 5090 Å

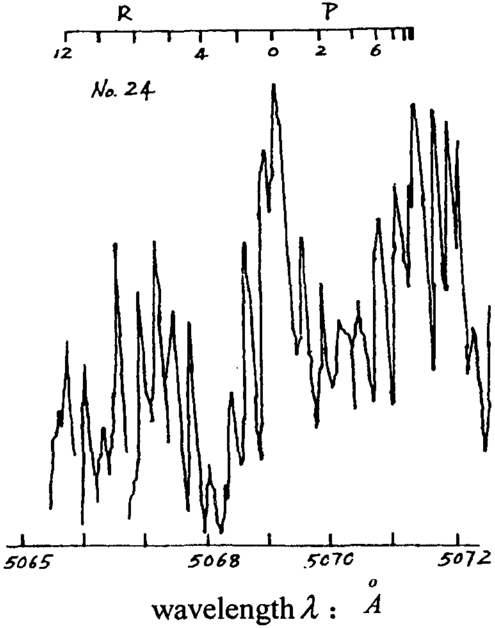

Fig.6. Laser induced fluorescence excitation spectra of $NO_2$ from 5065 to 5072 Å

TABLE 2.

Rotational assignment of the five new Vibrational bands 0f $NO_2$ in 5050-5200 Å

| Band No. | N'' | R branch($cm^{-1}$) | P branch($cm^{-1}$) | Band No | N'' | R branch($cm^{-1}$) | P branch($cm^{-1}$) |
|---|---|---|---|---|---|---|---|
| No.14 | 0 | 19413.201 | | No.17 | 0 | 19623.184 | |
| | 2 | 19414.583 | 19410.705 | | 2 | 19624.549 | 19620.640 |
| | 4 | 19415.361 | 19408.406 | | 4 | | 19618.604 |
| | 6 | | 19405.829 | | 6 | | 19616.315 |
| | | | | | 8 | | 19613.754 |
| No.18 | 0 | 19635.976 | | No.20 | 0 | 19667.448 | |
| | 2 | 19637.502 | 19633.416 | | 2 | 19668.688 | 19664.785 |
| | 4 | 19638.403 | 19631.526 | | 4 | 19669.878 | 19662.540 |
| | 6 | 19640.658 | 19629.316 | | 6 | 19670.951 | 19660.063 |
| | 8 | | 19627.841 | | 8 | 19672.195 | 19657.703 |
| | | | | | 10 | | 19655.258 |
| | | | | | 12 | | 19652.338 |
| No.24 | 0 | 19726.710 | | | | | |
| | 2 | 19728.251 | 19723.680 | | | | |
| | 4 | 19730.431 | 19722.372 | | | | |
| | 6 | 19732.720 | 19721.158 | | | | |
| | 8 | 19735.340 | 19720.075 | | | | |
| | 10 | 19737.802 | | | | | |
| | 12 | 19740.260 | 19718.503 | | | | |
| | 14 | 19743.663 | | | | | |

constants vary much from band to band. The strong perturbed structure of these bands imply that if the assignment for the lines is based only on their relative intensity and position, it is impossible for the unique assignment of the R(2), R(4), P(2), P(4), and P(6) lines. The additive superscripts in column 1 of Table 1 note this unclear assignment. The transitions of R(0), R(2), P(2), and P(4) are displayed within ±3Å region around the transition R(0), when the number added no superscript in Table 1. Within experiment error, the following relationships were used:

1. $\tilde{\varepsilon}'$ from P(2)= $\tilde{\varepsilon}'$ from R(0)

   $\tilde{\varepsilon}'$ from P(4)= $\tilde{\varepsilon}'$ from R(2)

2. $\tilde{B}''$ from R(0)-P(2)=$0.424\pm0.004cm^{-1}$

   $\tilde{B}'$ from R(2)-P(2)=$0.4 \pm0.1cm^{-1}$

   $\tilde{B}'$ from R(4)-P(4)=$0.4\pm0.1cm^{-1}$

The superscript "a" added to the numbers in Table 1 indicates that more than one of the transitions satisfies the above relationships within ±3Å around the R(0) transition, and that overlap between one set of the transitions and another set occurs.

## DISCUSSION

It is the same as the previous analysis for the high-resolution excitation spectra of $NO_2$[7], its fluorescence excitation spectra corresponding to the transition $\tilde{X}^2A_1 - A^2B_2$ are a parallel transition with $\Delta K = 0$, and $\Delta N = \pm 1$. The absence of any Q branch transition implies that the whole assigned vibronic bands present parallel polarization, so the upper state has the $^2B_2$ electronic-vibration symmetry. This has accounted for almost all transitions observed in this region without respect to some unassigned lines.

In contrast with the vibration bands at 5151.34Å that have regular structure, the bands at 5096.22Å, 5092.91Å, 5084.78Å, and 5069.63Å are not regular (as shown in Figs. 4 and 5). The most complex spectra are the bands at 5084.78Å and 5069.63Å (as shown in Figs. 5 and 6). Only a part of the transition can be assigned with the rotational quantum numbers within the definite error, while other lines with averaging intensity couldn't be assigned rotationally. We consider that the complexity of the visible spectra of $NO_2$ rise, at least partially, from the interaction between the vibration levels of the excited $\tilde{A}^2B_2$ state and the high lying vibration levels of the ground state. The bands at 5084.78Å and 5069.63Å are located in the region where the vibration levels of the excited and the ground state almost become degenerated and the density of the vibration levels in this region are so large that the interaction between these levels is very strong. The perturbation theory is not applicable to the analysis of this kind of interaction. With our Statistical theory[8], we calculated the level density (1/D) and the obtained value is 1.78 line/$cm^{-1}$ which is conformed with the experiment result

(1.75 line/cm$^{-1}$), very well. This demonstrates that the spectra of $NO_2$ in this region have typical random-matrix spectral fluctuations.

From the above mentioned analysis for the five new vibration bands of $NO_2$ we come to the conclusion that the high resolution excitation fluorescence spectra of $NO_2$ at room temperature have the complex structure for the bands at 5069.63Å, 5084.78Å, 5092.91Å, and 5096.22Å, and the band at 5151.34Å have a simple and regular structure. Moreover the complex structure of the molecular spectra can be well explained by the GOE statistic theory instead of the perturbation theory.

## ACKNOWLEDGEMENTS

This research was supported by the National Natural Science Foundation of China (Grant No.29873051), and the Science Foundation of Anhui Normal University, China.

## REFERENCES

1. D.L.Monts, B.Soep, R.N.Zare, Rotational analysis of the $NO_2$ 6125- Å region. J.Mol.Spectrosc. 1979; 77:406.

2. N. Sugimoto, S.Takezawa, Rotational analyses and vibrotional assignments of the 463- and 474-nm bands of $NO_2$. J.Mol.Spectrosc., 1984; 106:306.

3. Th.Zimmermann, L.S.Cederbaum, H.-D.Meyer, H.Koppel, Statiscal Properties of energy levels. J.Chem.Phys., 1987; 91:4446.

4. K.Shibuya, T.Kusumoto, H.Nagai, K.Obi, Rovibronic levels of $NO_2$ excited at 514nm and probed by an optical-optical bouble-resonance method. Chem.Phys.Lett., 1988; 152:129.

5. X.Z.Zhao, T.X.Lu, Z.F.Cui, The fluorescence excitation spectrum of $NO_2$ Rev.Roum.Phys., 1989; 34:1049.

6. X.Z.Zhao, T.X.Lu, Z.F.Cui, An experiment study of the lifetimes of excited electronic states of $NO_2$. Chem.Phys.Lett., 1989; 162:140.

7. X.Z.Zhao, T.X.Lu, Z.F.Cui, The rotational analysis of the three new vibrational bands of $NO_2$ in the range 5680-5720Å. Spectrosc.Lett., 1990; 23:1159.

8. T.X.Lu, X.Z.Zhao, Z.F.Cui, Theretical Calculation of the spectral fluctuation of the molecular $NO_2$ spectrum. Phys.Lett.A., 1991; 158:63.

9. A.Delon, R.Jost, Laser induced dispersed fluorescence spectra of jet cooled $NO_2$: The complete set of vibronal levels up to 10000 $cm^{-1}$ and the one of the $\tilde{X}^2A_1 - A^2B_2$ vibronic interaction. J.Chem.Phys., 1991; 95:5686.

10. B.Kirmse, A.Delon, R.Jost, The $NO_2$ vibronic levels near the $\tilde{X}^2A_1 - A^2B_2$ conical intersection observed by laser induced dispersed fluorescence. J.Chem.Phys., 1998; 108:6638.

Date Received: March 15, 2000
Date Accepted: July 8, 2000