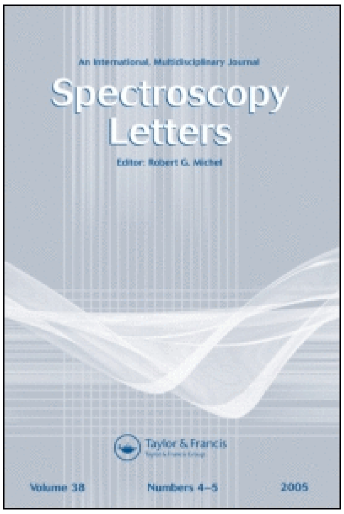

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THE ROTATIONAL ANALYSIS OF THE THREE NEW VIBRATIONAL BANDS OF NO_2 IN THE RANGE 5680-5720 Å

Key Words: VIS-spectra; Molecular spectra; Rotational analysis

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ABSTRACT

The three new vibrational bands in the range 5680-5720 Å of the fluorescence excitation spectra of NO_2 were measured at the normal temperature and were assigned with the rotational quantum numbers. In these bands there are strong spin and rotational forbidden transitions which express the complexity of NO_2 spectra.

INTRODUCTION

The complex structure of NO_2 spectra in the visible range remains one of challenging problem of molecular spectroscopy.

The 144 vibrational bands of the fluorescence excitation spectra of NO_2 in this range were observed so far, however only few bands of these bands were assigned rotationally[1-5]. The three new vibrational bands of NO_2 were measured in our experiment of the high resolution fluorescence excitation spectrum at the normal temperature[6]. The rotational analyses of these new bands were made and the mechanism of the spectral complexity in the three new vibrational bands was discussed in this paper.

EXPERIMENTAL DATA AND ANALYSIS

The experimental setup is the same as in the reference 6. The difference is that the pressure of NO_2 in the cell was $5X10^{-4}$ Torr.

The three new vibrational bands in the range 5680-5720 Å were recorded, at the normal temperature, with the high resolution fluorescence excitation spectra of NO_2 and the laser excitation wavelengths 5715.2 Å, 5708.0 Å and 5686.3 Å respectively. The spectra of NO_2 in this range correspond to the transition $^2B_2$—$^2A_1$. The spectroscopic parameters of these vibrational bands are given in Table 1.

The vibrational energies T'_V of these new bands were calculated by

$$T'_V = R(0)_\alpha - \frac{1}{2}\left|\varepsilon'_{bb}\right| - 2B'$$

here $R(0)_\alpha$ is the frequency of the long wavelength component of R(0) doublet. The spin-rotational interaction factors of the

TABLE 1

The three new vibrational bands in 5680—5720 Å

N	T_v'(cm^{-1})	I (relat. intensity)	$\overline{B}'$(cm^{-1})	$\overline{B}''$(cm^{-1})	$\overline{\varepsilon}'_{bb}$(cm^{-1})
1	17497.2	0.90	0.423	0.421	0.52
2^a	17520.0	1.00	0.423	0.421	0.30
3^b	17586.7	1.30	0.472	0.422	0.22

excited states $\overline{\varepsilon}'_{bb}$ were calculated from R(0) splitting, the rotational constants B' of the electronic excited states were got from R(2) - P(2) and the rotational constants B'' of the ground state were got from R(0) - P(2). The constants B' depends slightly on the sign of $\overline{\varepsilon}'_{bb}$ and we chose $\overline{\varepsilon}'_{bb} > 0$ in all cases.

The assigned rotational structure at the excitation wavelength 5715.2 Å is shown in Fig.1. The dominant structure was originated from $\Delta N = \pm 1$ transitions in $N'' = 0, 2, 4, 6, 8, 10$ levels of the K'' manifold of the ground state $^2A_1$ and their rotational assigment is listed in Table 2. The rotational structure of other two bands at 5708.0 Å and 5686.3 Å are not clear as shown in Fig.3, 4. The forbidden transitions $\Delta K = \pm 2$ and $\Delta N = \pm 3$ are listed in Table 3 and 4. The strong perurbed structure of these bands imply that it is impossible for unique assignment of

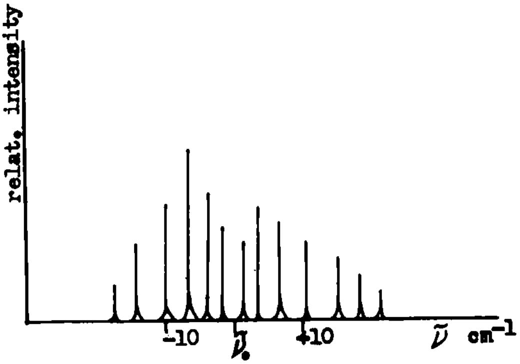

Fig.1 The vibrational band at 5715.2 Å

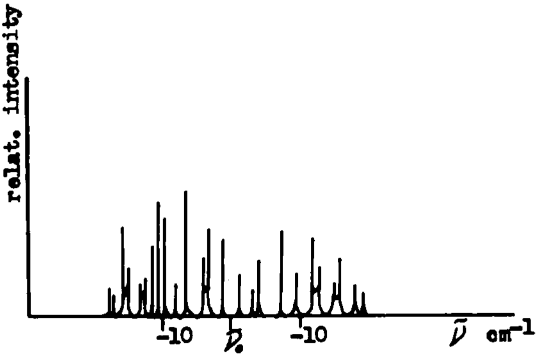

Fig.2 The vibrational band at 5708.0 Å

TABLE 2

Rotational assignment of the band at 5715.2 Å

N'	K'	N"	K"	$\tilde{\nu}$ (cm^{-1})
1	0	0	0	17497.78
3	0	2	0	17500.14
5	0	4	0	17503.34
7	0	6	0	17507.41
9	0	8	0	17513.54
1	0	2	0	17494.81
3	0	4	0	17492.12
5	0	6	0	17488.72
7	0	8	0	17484.47
9	0	10	0	17479.37

TABLE 3

Rotational assignment of the band at 5708.0 Å

N'	K'	N"	K"	$\tilde{\nu}$ (cm^{-1})
1	0	0	0	17519.31
3	0	2	0	17521.67
5	0	4	0	17524.87
7	0	6	0	17528.94
9	0	8	0	17535.07
1	0	2	0	17516.84
3	0	4	0	17514.15
5	0	6	0	17510.75
7	0	8	0	17506.50
9	0	10	0	17501.40
5	0	2	0	17528.37
1	0	4	0	17510.66
3	2	2	0	17528.49
1	0	2	0	17524.68
7	0	4	0	17533.38

TABLE 4

Rotational assignment of band at 5686.3 Å

N'	K'	N"	K"	$\tilde{\nu}$ (cm^{-1})
1	0	0	0	17587.48
3	0	2	0	17589.70
5	0	4	0	17592.66
7	0	6	0	17596.37
9	0	8	0	17600.82
1	0	2	0	17584.12
3	0	4	0	17581.19
5	0	6	0	17577.11
7	0	8	0	17571.99
9	0	10	0	17565.94
3	2	2	0	17594.29
5	0	6	0	17593.31
7	0	4	0	17593.11
5	0	2	0	17589.49
1	0	2	2	17593.66

of the R(2), R(4), P(2), P(4) and P(6) lines, if the assignment for the lines bases only on their relative intensities and positions. 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 display within ± 4 Å region around the transition R(0), when the number added no superscript in Table 1. Within experimental error, the following relations was used:

1. $\bar{\varepsilon}'_{bb}$(for P(2)) $=$ ε'_{bb}(for R(0))

   $\bar{\varepsilon}'_{bb}$(for P(4)) $=$ ε'_{bb}(for R(2))

2. $B'' = 0.422 \pm 0.004\ \text{cm}^{-1}$ (for R(0)-P(2))

   $B'' = 0.422 \pm 0.003\ \text{cm}^{-1}$ (for R(2)-P(4))

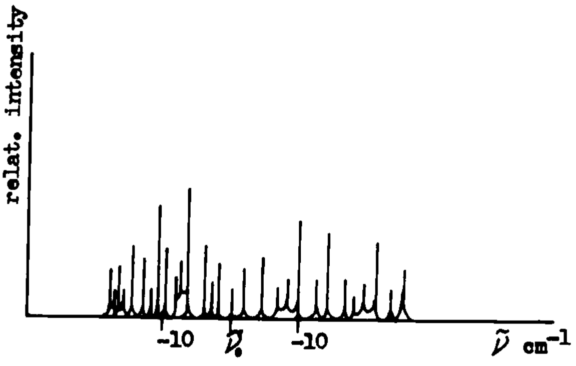

Fig.3 The vibrational band at 5868.3 Å

The superscript "a" adding to the number in Table 1 shows that more set of the transitions than one satisfies above relations within ± 4 Å around the R(0) transition and the overlap between one set of the transitions and other one occurs. The superscript "b" shows that the only transitions R(0) and P(2) meet above relations within ± 4 Å around expected transition R(0).

DISCUSSION

It is the same as the previous analysis[6] for the high resolution excitation spectra of NO_2, its fluorescence excitation spectra corresponding to the transition $^2B_2$—$^2A_1$ are parallel transitions with $\Delta K = 0$ and $\Delta N = \pm 1$. The absence of any Q branch transition implies that the whole assigned vibrational bands present parallel polarization, so upper state has the B_2

vibrational symmetry. This accounted for almost all transitions observed in this region without respect to some weak unassigned lines which might have originated from other excited vibrational states.

In contrast with the vibrational band at 5715.2 Å which has regular structure, the bands at 5708.0 Å and 5686.3 Å are not regular as shown in Fig.2 and 3, and the most complex spectra were from the transition at 5686.3 Å. As shown in Fig.3 only a few of the transitions can be assigned with the vibrational and 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 vibrational levels of the excited $^2B_2$ state and the ground electronic state. The band No.3 which has the excitation energy 17586.1cm^{-1} is located in the region where the vibrational levels of the excited states and the ground state become degenerated and the density of the vibrational levels in this region is so large that the interaction between these levels is very strong. The perturbation theory is not applicable to the analysis of this kind of the interaction. We discussed this interaction by new statistic theory and the calculated level density 1/D is 1.54 cm^{-1} which is conformed with the experiment result very well[7]. This demonstrate that the spectra of NO_2 in this region has a typical random-matrix spectral fluctuations.

The derivation of the excited state $^2B_2$ from the symmetry of symmetric top makes the forbidden transition $\Delta K = \pm 2$ with the interaction between K and K ± 2 vibrational and rotational levels. The Femi-contact term in the high-lying levels of the ground state induces the possibility of $\Delta N = \pm 3$ transitions.

From the above mentioned analysis for the three new vibrational bands of NO_2 we come to the conclusion that the high resolution excitation fluorescence spectra of NO_2 at the normal tempreture have the complex structure for the bands 5708.0 Å and 5686.3 Å, and the band at 5715.2 Å has the simple and regular structure. Moreover the complex structure of the molecular spectra can be explained well by the GOE statistic theory instead of the perturbation theory.

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