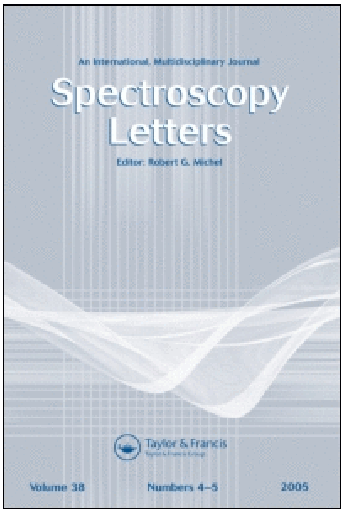

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NEW BANDS IN THE SHOCK EXCITED NbO BLUE/VISIBLE AND NEAR INFRARED SYSTEMS

Key Words: Electronic bands, NbO, Shock tube spectroscopy

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Abstract

Band systems of the astrophysically important molecule Niobium Oxide (NbO) have been excited in helium-driven shock waves through argon containing powdered Nb_2O_5. Of the 25 bands of the $\Delta v = +3, +2, +1, 0, -1, -2$ and -3 sequences of the $C^4\Sigma^- - X^4\Sigma^-$ blue/visible system which were excited between 4220Å and 5608Å, 16 are newly reported here. The $\Delta v = +3$ and -3 sequences are completely new. 12 new bands were also excited in the near infrared region 7952Å – 8450Å.

1 Introduction

The spectra of the transition metal monoxides are of astrophysical importance because of the occurence of these species in the atmospheres of cool stars, the temperatures of which are a few thousand K. In particular NbO is present in the atmospheres of M stars[1], and probably in the atmospheres of S stars[2]. These spectra are used diagnostically in the astrophysical study of stellar atmospheres. Such work requires information on location of spectral features, molecular structure constants and intensity parameters. New observations on spectral features of NbO in the blue - visible region (4220Å - 5608Å) and near infrared region (7952Å - 8450Å) are reported below.

2 Experimental

The most common compounds of the transition metals are the multi-oxides which are often powdered solids. In order to excite the emission spectra of the monoxides (eg. NbO) it is convenient to use a shock tube as a transient furnace of controllable temperature thermally to dissociate the multi-oxide powdered materials to form monoxide species in the vapour phase[13]. Accordingly we subjected samples of Nb_2O_5 to helium driven shock waves (Mach numbers $\cong 4.0$) into argon produced in a $5cm$ diameter $4.7m$ long spectroscopic shock tube. Gas dynamic conditions were arranged so that temperatures of about $2000K$ were produced in the reflected shock wave at the end of the test section for a few ms. Under these circumstances the NbO species is abundant, and easily excited. The emission spectrum of the resulting flash of light has been recorded photographically at low and medium resolution by use of four spectroscopic instruments, three for survey work and one for the principal work.

Low resolution surveys of NbO spectra were made of the visible region using a fast $0.5m$ spectrograph with reciprocal dispersion of 12.5 Å$/mm$

and a 1.5m spectrograph with reciprocal dispersion of 15 Å/mm. The 0.5m spectrograph recorded the spectrum of a single shock flash on polaroid film and the 1.5m spectrograph recorded the spectra of 20 flashes on Kodak 2485 high speed film.

Near infrared survey spectra of 120 shock flashes were recorded on hypersensitized Kodak 2481 high speed infrared film using a fast 0.65m spectrograph with reciprocal dispersion 12.7 Å/mm. Hypersensitization involved storing the film in its aluminum container in a mixture of 92% H_2, 8% N_2 for 24 hours before use.

After the surveys had been made, higher resolution spectra were recorded at 2.5 Å/mm using a Baird Atomic 3m Eagle mounted spectrograph. Visible spectra of between 100 and 250 shock flashes were recorded on Kodak 2485 film. Infrared spectra of 450 shock flashes were recorded on hypersensitized Kodak 2481 film. Band head positions were located using a Brower and Grant optical comparator.

3 Observations and Analysis

Early work on the NbO spectrum[7,8,9,10,11,12] has led to the present understanding of the known electronic systems. Figure (1) shows a comparative term value diagram of the reported electronic levels. The observed transitions are also indicated. A detailed study[9] confirmed the $^4\Sigma$ nature of the ground state of NbO. This led to the designation of the blue system as $C^4\Sigma^- - X^4\Sigma^-$. The work described here has significantly extended this system into the visible (see table 1), and in this paper we refer to it as the blue/visible system.

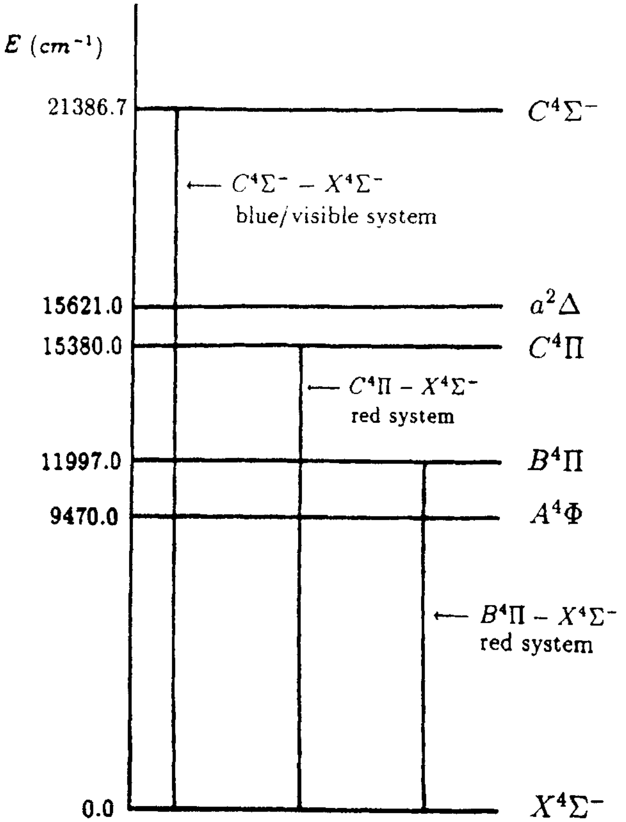

Figure 1: Term value diagram of electronic states of NbO and observed transitions between them

The red region is particularly complicated. There are at least five band systems between 530*nm* and 740*nm*[9]. Two of these, the $B^4\Pi - X^4\Sigma^-$ and the $C^4\Pi - X^4\Sigma^-$ transitions, both of which are heavily overlapped, have been widely studied[1,4]. They are in the 5800Å - 7500Å wavelength range. In particular, two bands at 695.5*nm* and 735.1*nm* have been assigned to the

Table 1: Déslandres table of wavelengths, Franck-Condon factors and Condon loci of the band heads of the $C^4\Sigma^- - X^4\Sigma^-$ Blue/Visible system of NbO. Data for new bands are displayed in bold print and underlined

v' \ v''	0	1	2	3	4	5	6	7	8
0	4688.6 0.445	4914.7 0.372	5161.7 0.143	**5432.7** **0.033**					
1	4510.3 0.347		4946.5 0.279	**5194.8** **0.245**	**5467.2** **0.091**				
2	4346.3 0.148	4539.9 0.230			**5228.1** **0.263**	**5501.8** **0.152**			
3		4375.0 0.221		**4780.9** **0.126**		**5261.5** **0.218**	**5536.5** **0.199**		
4		**4222.9** **0.109**	4404.0 0.200		**4812.1** **0.161**		**5295.1** **0.144**	**5571.3** **0.222**	
5			**4251.0** **0.156**			**4843.4** **0.137**			**5606.3** **0.218**
6				**4279.4** **0.169**					

Legend

Upper entry: $\lambda\,(\text{Å})$

Lower entry: FC factor $q\left(v',v''\right)$

$C^4\Pi - X^4\Sigma^-$ transition, and two bands at 650.9nm and 666.6nm have been assigned to the $B^4\Pi - X^4\Sigma^-$ transition[4].

In further work on the $B^4\Pi - X^4\Sigma^-$ system, an unusual intensity cancellation effect in the hyperfine structure of certain lines was discussed[5]. Some later work by the same group[1] revealed an unexpected Hund's case *a*) coupling for low rotation in the $^4\Sigma^-$ ground state.

Theoretical calculations of some important parameters of the known electronic states of NbO were later provided[6]. An $A^4\Phi$ state which was not previously reported was also proposed in this work.

3.1 Blue/Visible Region $C^4\Sigma^- - X^4\Sigma^-$

The $C^4\Sigma^- - X^4\Sigma^-$ blue/visible band system consists of red degraded bands with sharp band heads. At the resolutions of our work, bands of this $^4\Sigma - ^4\Sigma$ transition were recorded as single headed.

In this work, 25 vibrational bands have been shock-excited in the wavelength region 4220Å - 5608Å. They are displayed with their Franck-Condon factors in the Déslandres array of table (1). 16 of these bands, which lie in the sequences $\Delta v = +3, 0, -2$ and -3 have not been previously reported. The previously reported bands occur in the $\Delta v = +2, +1, 0, -1$ and -2 band sequences. The $\Delta v = +3$ and -3 sequences are completely new.

The longest wavelength band that was previously reported is the (0,2) band at 5161.8Å[7]. We have augmented the $\Delta v = -2$ sequence with the (1,3), (2,4), (3,5) and (4,6) bands. Bands identified in the $\Delta v = -3$ sequence are the (0,3), (1,4), (2,5), (3,6), (4,7) and (5,8) bands. The (5,8) band is now the longest wavelength reported band, at 5606.3Å. The previously named "Blue" system has thus been extended to become a Blue/Visible system. The thermal excitation process in the shock tube readily excites higher vibrational quantum numbers than had previously been achieved. All bands were easily observable.

Precise band identification was done in three steps: *i* – Tentative vibrational quantum numbers were assigned to the bands using the previously reported vibrational constants[10]. *ii* – Accurate wavelength determinations of the heads of these bands were used in two separate processes iteratively to obtain new *effective* vibrational constants. These effective constants were used to derive more precisely the original band positions and to accurately locate new bands. The process was repeated for different combinations of possible new bands. *iii* – Franck-Condon factors $q\left(v',v''\right)$ were calculated at each stage using the effective constants, and band identifications had to be consistent with them.

After the final iteration of step *ii*, our band head positions were corrected for band origins using the B_e' and B_e'' values from reference (10). Revised T_e and vibrational constants based on these were calculated. Franck-Condon factors were also calculated using these values.

The processes for obtaining revised vibrational constants were a least mean squares computer program (which also calculates the electronic term value T_e), and the method of wavenumber differences. Vibrational constants determined by these two methods are very close to each other. Term values and vibrational constants from least squares for band heads and origins are listed in table (2). The large difference in term values from heads to origins is obvious as is the expected slight difference in vibrational constants. The table also displays constants from reference (10). Vibrational constants for

Table 2: Term values and vibrational constants of the Blue/Visible system from least squares method

Term Value, Vibrational Constant (cm^{-1})	Band Heads	Band Origins	Uncertainty	Previously Reported[10]
T_e	21392.20	21386.72	±0.46	21385.3(1)
ω_e'	849.22	849.59	±0.04	850.4(8)
$\omega_e x_e'$	3.23	3.24	±0.00	3.3(7)
ω_e''	988.57	988.91	±0.04	989.0(0)
$\omega_e x_e''$	3.74	3.73	±0.00	3.8(3)

Table 3: Vibrational constants of the Blue/Visible system from wavenumber difference method

Vibrational Constant (cm^{-1})	Band Heads	Band Origins	Uncertainty
ω_e'	849.2	849.6	±5.3 (±4.8 *origins*)
$\omega_e x_e'$	3.3	3.3	±0.9 (±0.8 *origins*)
ω_e''	989.7	990.1	±6.4
$\omega_e x_e''$	3.9	3.9	±0.8

band heads and origins calculated by wavenumber differences are shown in table (3).

The uncertainties in the constants generated by least squares reflect a systematic error of 0.1Å in aligning the comparator with a band head. These were determined by running the program for band head wavenumbers with no error, then once for band head data raised by the desired error and once again for data reduced by the error. Differences between the extreme constants and those with no uncertainty were computed. An assumption is made that all band head wavenumbers are either overestimated or underestimated. This

Table 4: Measured band head wavelengths and wavenumbers of a near infrared transition of NbO

$*$ — Possible low wavelength doublet bands

• — Very faint bands

λ *air* (Å)	ν *vacuum* (cm^{-1})
7952.0	12572.0
7988.7 •	12512.7
7997.6	12500.3
8045.1	12426.5
8092.0	12354.5
8145.4 •	12273.4
8188.4 •	12209.0
8283.9	12068.2
8320.5 •	12015.2
8341.6	11984.9
8387.9	11918.6
8433.4	11854.3

is reasonable since the error in comparator alignment may be considered to be consistent. There is also a random error for band heads and origins of $T_e = 0.19cm^{-1}$, $\omega_e^{'} = 0.05cm^{-1}$, $\omega_e x_e^{'} = 0.01cm^{-1}$, $\omega_e^{''} = 0.04cm^{-1}$ and $\omega_e x_e^{''} = 0.01cm^{-1}$, separate from the systematic error.

The uncertainties in the vibrational constants calculated from wavenumber differences were derived from the same 0.1Å systematic error, using the theory of error propagation.

3.2 Near Infrared Region

There are 12 previously unreported red degraded bands in the wavelength range 7952Å - 8450Å which probably belong to a new system. They appear in two groups; one in the region 7950Å - 8190Å, and the other in the region 8280Å - 8440Å. Bands in this entire wavelength range have not been previously reported, and there is no previous electronic assignment in this region.

After close inspection of these groups, a few possible descriptions of the gross band structure are proposed. These are:

a) two sequences of single headed bands

b) two groups of doublet bands

c) two groups of band progressions

At this stage of the analysis, there is no conclusive evidence for any one of these possibilities, nor a probable electronic assignment. Thus, it is not possible to assign vibrational quantum numbers to the bands.

Table (4) lists the bands. Most of them are distinct, but two of them are faint. These are indicated in the table. The bands which display possible doublet structure are also indicated in the table - one band in the first group and one in the second. The possibility of band progressions is more clearly revealed in the first group of bands, (especially that recorded on the 0.65*m* spectrograph). There appear to be a few lower intensity bands (not listed in the table) between the 7952.0Å band and the next analysed band at 7997.6Å.

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