

VIBRATIONAL ANALYSIS OF THE BLUE AND RED SYSTEM OF
YO¹⁶ AND YO¹⁸. (+)

KEY WORDS: Spectroscopy- Diatomics - Vibrational Analysis - Rare Earths Spectra .

Juan P. Esperon^{*} , Jorge Reyna Almandos^{**} and Carlos B. Suárez^{***} , Departamento de Física, Universidad Nacional de La Plata, C.C. 67, La Plata, Argentina.

ABSTRACT: We have analysed vibrationally the electronic spectrum of Yttrium Monoxide in the blue and red

* Fellow of CONICET.

**Fellow of CCUNLP.

*** Member of Carrera del Investigador, CONICET.

(+) Work partially supported by grants from Consejo Nacional de Investigaciones Cientificas y Técnicas of Argentina (CONICET) and Comisión Científica of the University of La Plata (CCUNLP).

region. For the YO^{18} specie we report the constants for the first time, and for the YO^{16} we report revised values.-

INTRODUCTION

Out of about 1000 leading diatomic compounds only about one half have been produced and spectroscopically analysed (1). One important serie in the periodical table is the one that includes the rare-earths . Among them, ScO, YO, and LaO are very interesting. For them low lying levels have been predicted (2) and for LaO the case has already been established (3).

As soon as new bands are produced it would be interesting to decide whether they are really part of new systems or merely unseen members of old systems. One way of checking would be using the best constants available to predict or check band head positions.

In this paper we present a vibrational analysis of the Yttrium Monoxide spectrum in the blue and red regions. This analysis includes consideration of both YO^{16} and YO^{18} species. Previous study of this molecule are reported by Meggera and Wheeler (4), Johnson and Johnson (5), and Uhler and Åkerlind (6) . According to them the red system corresponds to a ${}^2\Pi - {}^2\Sigma$ transition, and the blue system to a ${}^2\Sigma - {}^2\Sigma$ transition. Both systems have the ${}^2\Sigma$ state as common ground level.

EXPERIMENTAL PART

We photographed the spectrum by means of an Ebert mounted plane grating spectrograph with a ruled area of 56x128 mm² and 600 g/mm. This instrument provided a dispersion of around 4.8 Å/mm that was ideal for the vibrational analysis. As a source of light we used a low pressure arc chamber exciting 99.9 % pure Yttrium electrodes with 7000 volts in an atmosphere of oxygen 18 at about 250 Torr, and of oxygen 16 at 760 Torr. Before filling the chamber with these gases we pumped it out to below 10⁻⁵ Torr. With current of under one ampere the exposure time required to obtain the spectra varied from 1 to 15 minutes on Kodak 103a-F plates. Measurements were done by means of a Grant comparator and the data reduction and processing with an IBM 360/50 computer. As a standard of comparison we used Thorium lines compiled by Giacchetti et al. (7).

DESCRIPTION OF SPECTRA

The red system is located between 5700 and 6700 Å. The 0-0 band of the ${}^2\Pi_{3/2} - {}^2\Sigma$ is centered at 5972 Å and the 0-0 of the ${}^2\Pi_{1/2} - {}^2\Sigma$ subsystem is at 6132 Å for the YO¹⁶ specie. For YO¹⁸ they are at 5770.6 Å and at 5842 Å, respectively. In each band the stronger features are represented by the R branch in the first

case, and by the Q_1 branch in the second case. In this electronic transition of YO the intensity is concentrated on the three leading sequences, namely, those with $\Delta v = 0, +1$, and -1 . The sequence $\Delta v = -1$ of the $3/2$ subsystem overlaps the sequence with $\Delta v = +1$ of the $1/2$ subsystem.

The blue system is located between 5300 and 4500 Å with the 0-0 band at about 4818 Å for the YO^{16} specie and at 4817 for YO^{18} . In both cases the doublet splitting corresponding to the $^2\Sigma - ^2\Sigma$ transition is clearly resolved. Also in this transition the three leading sequences are the strongest ones and the only seen on our plates. The overall intensity of this system is very much weaker than that of the red system. In fact, the intensity of the 3-3, 4-3, and 3-4 bands were so weak that we could not measure them with accuracy and for that reason they are not reported here.

VIBRATIONAL ANALYSIS

To analyse both spectra we completed the Deslandres tables for the blue system and for each subsystem of the red transition. Almost unnecessary though, we used the isotopic shift properties for such a task confirming previous vibrational assignment of YO^{16} .

In order to obtain the vibrational constants we used the following formula: (8)

$$G(v) = \omega_e (v + \frac{1}{2}) - X_e \omega_e (v + \frac{1}{2})^2$$

$$\Delta G_{v+\frac{1}{2}} = \omega_e - 2\omega_e x_e - 2\omega_e x_e v$$

and $\Delta^2 G_{v+\frac{1}{2}} = -2\omega_e x_e$

for the vibrational term, and the first and second differences, respectively. ω_e and $\omega_e x_e$ are the vibrational constants.

In Table I we report the band head measurements for the red system of both species. In Table II the figures are given for the blue system. Table III shows the vibrational constants for YO¹⁶. Table IV is for YO¹⁸.

Recalculated position of any band shows that the maximum deviation is always under 3 cm⁻¹, and in most cases is under 1 cm⁻¹, using the constants given.

As a final check of the correctness of our determination we calculated the ratio between related constants of each specie and found satisfactory results, as shown in Table V. It is seen that the agreement between theoretical and calculated ρ value is excellent. For ρ^2 the agreement is only fairly good because the accuracy of the smaller vibrational constants involved should be improved, but only by the means of complete rotational analysis where all the band origins can be determined.

Table I

Bandheads, in cm^{-1} , of YO^{16} and YO^{18} . Red system (${}^2\Pi_{3/2}$ ${}^2\Sigma$)

Band	YO^{16}	YO^{18}	Band	YO^{16}	YO^{18}
1-0	17545.70	17506.96	5-5	16513.99	16525.40
2-1	17496.42	17460.61	6-6		16479.26
3-2	17446.92	17413.37	7-7	16417.40	16434.19
4-3	17395.63	17365.34	8-8	16365.70	16390.60
5-4	17343.56	17316.31	9-9	16315.58	16345.10
6-5	17290.89	17265.85	10-10		16295.30
7-6	17236.62	17216.01	11-11		16252.46
8-7	17181.52	17164.62	12-12		16204.40
9-8	17124.22	17110.96	0-1		15931.39
10-9		17056.52	2-3		15855.04
11-10	1700.16		4-5	15737.75	
0-0	16740.18	16739.64	5-6	15694.57	
1-1	16696.44	16697.88	6-7	15652.40	
2-2	16652.18	16655.97	7-8	15606.90	
3-3	16607.02	16613.34	8-9	15561.94	
4-4	16561.05	16569.58	9-10	15512.46	

Table II

Bandheads, in cm⁻¹, of YO¹⁶ and YO¹⁸. Red system (²Π_{1/2} - ²Σ)

Band	YO ¹⁶	YO ¹⁸	Band	YO ¹⁶	YO ¹⁸
1-0	17112.90	17073.06	6-6	16029.42	16044.18
2-1	17063.50	17027.71	7-7		15995.26
3-2	17013.23	16980.23	8-8	15931.66	15951.23
4-3	16691.91	16931.94	9-9	15880.10	15905.16
5-4	16909.48	16882.61	10-10	15827.69	15855.04
6-5	16855.49	16832.08	11-11	15773.12	15802.52
7-6	16801.99	16779.24	0-1	15455.91	15493.50
8-7	16748.69	16731.42	2-3	15377.40	15421.32
0-0	16303.02	16303.21	3-4	15337.10	15382.84
1-1	16259.98	16262.12	4-5	15295.98	15343.87
2-2	16215.90	16220.35	5-6	15253.93	15303.81
3-3	16170.84	16177.68	6-7	15210.52	
4-4	16124.94	16134.24	7-8	15167.05	
5-5	16077.96	16089.77	8-9		15176.19

Table III

Bandheads, in cm^{-1} , of YO^{16} and YO^{18} . Blue system (${}^2\Sigma - {}^2\Sigma$)

Band	YO^{16}	YO^{18}
1-0	21503.56	21467.05
	21498.30	21464.34
2-1	21380.55	21350.97
	21378.04	21348.10
3-2	21249.73	21222.41
	21246.66	21218.99
0-0	20752.09	20753.25
	20748.64	20750.17
1-1	20646.76	20653.45
	20643.34	20650.40
2-2	20531.36	20542.20
	20258.57	20538.80
0-1	19897.61	19939.77
	19893.97	19936.34
1-2	19797.58	19844.61
	19794.18	19841.43
2-3	19687.76	19739.22
	19684.64	19735.44

Table IV

Vibrational constants for YO¹⁶ and YO¹⁸. In cm⁻¹.

State (from transition)	YO ¹⁶		YO ¹⁸	
	w _e	w _e x _e	w _e	w _e x _e
B (² Σ ⁻ - ² Σ)	765.78	7.92	730.96	8.43
A (² Π _{1/2} - ² Σ)	814.47	3.15	775.29	2.85
(² Π _{3/2} - ² Σ)	812.29	3.02	772.29	2.55
X (² Π _{1/2} - ² Σ)	855.21	2.50	814.90	2.34
(² Π _{3/2} - ² Σ)	854.50	2.52	813.62	2.28
(² Σ ⁻ - ² Σ)	860.88	2.87	819.16	2.64
<hr/>				
System				
origins: ² Σ ⁻ - ² Σ	20797.64		20795.95	
² Π _{1/2} - ² Σ	16323.78		16323.57	
² Π _{3/2} - ² Σ	16761.21		16760.03	

Table V

Relationship between vibrational constants ($\rho = w^i/w$ and $\rho^2 = wx^i/wx$)

	B $^2\Sigma$	$^2\Pi_{3/2}$	$^2\Pi_{1/2}$	X $^2\Sigma$
$\rho_{\text{OBS.}}$	0.95	0.95	0.95	0.95
$\rho^2_{\text{OBS.}}$	1.06	0.84	0.90	0.92
$\rho_{\text{THEOR.}}$	= 0.95		$\rho^2_{\text{THEOR.}}$ = 0.905	

CONCLUSIONS

We have obtained the spectra of YO^{16} and YO^{18} with a resolution of around 60,000, and measured 66 band-heads in YO^{16} , and 61 in YO^{18} , at a dispersion of 4.8 Å/mm. We estimate that the accuracy of our measurements is about 0.1 cm^{-1} , taking into account the uncertainty produced by band edges not well defined,

overlappings, and in many cases undesirable features like strong atomic lines.

The vibrational constants should agree, within experimental errors, when a common level from which they are derived is shared. This is the case if we look at those figures produced by the analysis of the lower level of both red sub-systems in either species. However, a discrepancy is shown when they are compared with those obtained from the analysis of the blue system, for the same common lower level. We attribute this discrepancy to the fact that the variation in the band-head to band-origin distance is different for both transitions.

Finally, we found that the constants for YO¹⁶ agree with those reported by Johnson and Johnson. Some bands that these investigator list could not be found by us.

REFERENCES:

- 1- C.B.Suarez, OPTICA PURA Y APLICADA, 1974, 7, 133-140
- 2- K.D.Carlson, E.Ludena, and G.Moser, J.CHEM. PHYS. 1965, 43, 2408.
- 3- D.W.Green, J.MOL.SPECTRY., 1971, 38, 155.
- 4- W.F.Meggers, J.A.Wheelers, NAT.B.STAND.J.RES., 1931, 6, 239.

- 5- L.W.Johnson, and R.C.Johnson, PROC.ROY.SOC.LONDON A, 1931, 133, 207.
- 6- U.Uhler, and L.Akerlind, ARK.F.FYSIK, 1961, 19, 61.
- 7- A.Giacchetti, R.W.Stanley, and R. Zalubas, J.O.S.A., 1970, 60, 474.
- 8- G.Herzberg, 1950, "Molecular Spectroscopy and Molecular Structure", D.Van Nostrand Co. Inc., 2nd ed.

Received 2-20-78

Accepted 3-15-78