

Chemiluminescent Spectra of YbF and YbCl

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We have obtained the chemiluminescent spectra of YbF and YbCl from the reactions of ytterbium with fluorine and ytterbium with chlorine dioxide under beam-gas conditions and in a high-pressure (3 Torr) flow system. Much more extensive band systems are observed than hitherto reported, and a vibrational reanalysis of the ground and low-lying states is made. Although the $A-X$ and $B-X$ systems appear regular in YbCl, the $A\ ^2\Pi_1-X\ ^2\Sigma^+$ and $B-X$ systems in YbF exhibit extensive vibrational perturbations. The interaction between molecular states arising from the separated atoms $\text{Yb}(5d) + X(np)$ as well as $\text{Yb}(6p) + X(np)$ is believed to cause these perturbations. An unassigned red-band system is observed in emission for both YbF and YbCl, suggesting that the lowest-lying excited state is not the A state.

I. INTRODUCTION

Recently, the electronic transitions of a considerable number of the lanthanide monohalides have been observed in absorption (1-3). Although the chemiluminescent spectra generated from the highly exothermic reactions of these elements with the halogens are generally quite complex because of the large number of excited states populated (4, 5), an exception is to be expected in ytterbium. With a 1S_0 ground state derived from its electronic configuration $[\text{Xe}]4f^{14}6s^2$ and a moderately low ionization potential of 6.2 eV, ytterbium might reasonably resemble a Group IIA element. This fact has been recognized previously by several workers (3, 6).

From the chemiluminescent reactions of ytterbium with fluorine and ytterbium with chlorine dioxide under beam-gas conditions and under higher pressure in a flow of argon, we have observed several extensive band systems of YbF and YbCl. The $\text{Yb} + \text{ClO}_2$ reaction system demonstrates the attack of the central Cl atom, analogous to studies of $M + \text{ClO}_2$, $M = \text{Ca}, \text{Sr}, \text{and Ba}$ (7). However, for $\text{Yb} + \text{ClO}_2$, no YbO^* is observed. The spectral features of YbX resemble those of the alkaline-earth halides, with the strongest transitions being the $\Delta v = 0, \pm 1$ sequences. In this paper molecular constants are derived for a number of these systems.

Analysis of the YbF spectrum has confirmed the observation of Barrow and Chojnicki (3) that extensive vibrational perturbations occur in the upper states, which probably arise from interactions with several other states derived from the low-lying $5d$ level of ytterbium. The origin of an unassigned red-band system that appears in both the YbF and YbCl chemiluminescent spectra may also be connected with the presence of these perturbing states.

II. EXPERIMENTAL DETAILS

The technique for studying beam-gas chemiluminescent reactions used here has been described previously (8, 9). Briefly, a collimated beam of the metal emanating from a differentially pumped source chamber traverses a scattering chamber where it intersects a tenuous oxidizing gas. The ytterbium metal, with a stated purity of 99.99% (Alpha-Ventron Corp.), sits inside a graphite oven, which is resistively heated by a cylindrical graphite tube. The resulting chemiluminescence taken with oxidizer gas pressures in the 10^{-4} Torr range is viewed through a 5 cm diameter port on the side of the scattering chamber and is focused by a quartz lens onto the entrance slits of a 1 m Interactive Technology scanning spectrometer. A cooled (-30°C) Centronics S-20 photomultiplier tube with extended red response is attached to the exit slits of the spectrometer.

Flame spectra of YbF and YbCl are obtained from the reactions of Yb with F_2 and ClO_2 in about 3 Torr of argon. The beam machine has been modified to permit these high-pressure flow reactions (10). Here, a small graphite oven containing ytterbium powder is heated inside a 25 cm graphite tube. A flow of argon through this tube carries the ytterbium vapor into the reaction region, where mixing with F_2 or ClO_2 occurs. The partial pressures of the metal, the oxidizer, and the carrier gas are typically 0.1, 0.05, and 3.0 Torr.

Fluorine gas is obtained from Matheson. Chlorine dioxide is prepared from the reaction of KClO_3 with $\text{H}_2\text{C}_2\text{O}_4$ and trapped at dry-ice temperatures (11). Immediately prior to a run, the cold trap is briefly opened to the pumps to remove excess Cl_2 and CO_2 .

III. RESULTS AND DISCUSSION

The chemiluminescent spectra of YbF and YbCl in the low-pressure (10^{-4} Torr) regime are presented in Fig. 1. At a pressure of 3 Torr of argon, the flame spectra extend

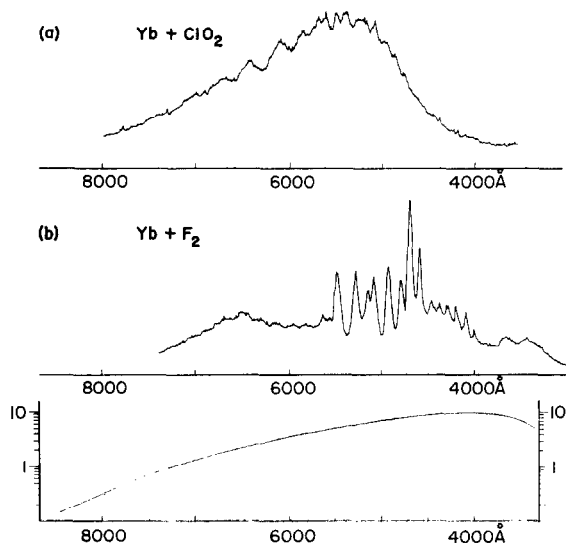


FIG. 1. The chemiluminescence spectra of the reactions (a) $\text{Yb} + \text{ClO}_2 \rightarrow \text{YbCl}^* + \text{O}_2$ and (b) $\text{Yb} + \text{F}_2 \rightarrow \text{YbF}^* + \text{F}$, taken at a scan speed of $500 \text{ \AA}/\text{min}$ with a resolution of 5 \AA . The detector response curve is indicated on the bottom of this figure.

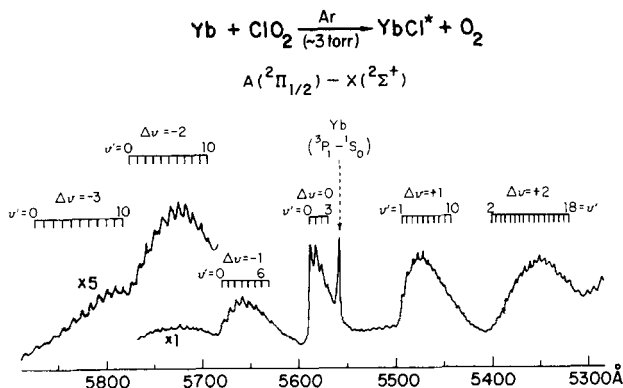


FIG. 2. A portion of the YbCl flame spectrum taken with a resolution of 0.25 Å (scan speed: 50 Å/min) from the reaction of Yb with ClO₂ in a 3 Torr flow of argon.

to about 3000 Å. Between 4500 and 5800 Å one observes the prominent A-X and B-X blue-green systems previously assigned in YbF by Barrow and Chojnicki (3) and in YbCl by Gatterer *et al.* (12). The spectral features above 5800 Å suggest the presence of at least one other system (hereafter denoted the red system), previously observed only in YbF by Yokozeki and Menzinger (13), but so far unassigned.

A. Analysis of the YbCl Spectrum

Figures 2 and 3 show the YbCl flame spectrum under higher resolution obtained from the reaction Yb + ClO₂ at pressures of 3 Torr argon. The bandheads are much clearer than in Fig. 1a, suggesting rotational relaxation in the presence of argon. The analysis of Gatterer *et al.* of the A-X and B-X systems was based on the first few (≤4) vibrational levels of each state. In this study we have observed excited-state vibrational

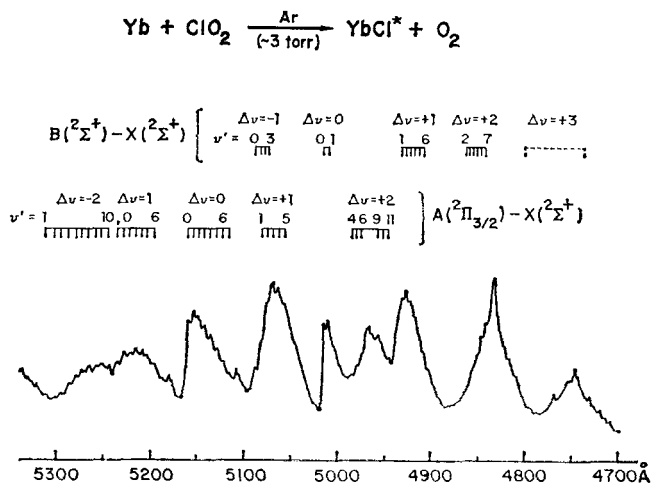


FIG. 3. A portion of the YbCl flame spectrum taken with a resolution of 0.25 Å (scan speed: 50 Å/min) from the reaction of Yb with ClO₂ in a 3 Torr flow of argon.

TABLE I
 Measured Bandhead Positions and Vibrational Assignments of
 YbCl A ($^2F_{3/2}$) - X ($^2F_{7/2}$) Bands.

bandhead assignment (v', v'')	bandhead position (cm ⁻¹)	obs.-calc. (cm ⁻¹)	relative intensity	remarks
17,15	18770.6	0.7	4	b
16,14	18754.0	2.1	5	b
15,13	18734.4	0.2	5	
14,12	18715.4	-0.9	6	
13,11	18696.9	-1.8	6	
12,10	18680.4	-0.7	6	
11,9	18663.7	0.1	6	
10,8	18643.9	-2.4	7	
9,7	18626.5	-2.4	7	
8,6	18609.5	-2.2	7	
7,5	18593.6	-1.0	6	
6,4	18577.0	-0.6	5	
5,3	18562.2	1.6	4	
4,2	18547.0	3.3	3	a
3,1	18528.1	1.1	2	a
2,0	18511.7	1.3	2	a, b
10,9	18374.9	3.9	4	
9,8	18351.9	0.2	5	
8,7	18334.4	1.7	6	
7,6	18313.1	-0.4	7	
6,5	18294.9	0.1	7	
5,4	18277.5	1.5	8	
4,3	18258.1	0.9	8	
3,2	18239.8	1.2	7	a
2,1	18221.5	1.5	6	a
1,0	18202.9	1.4	4	a
3,3	17951.6	-0.4	5	b
2,2	17931.6	0.1	7	a
1,1	17911.7	0.5	9	a
0,0	17892.4	1.5	9	a
8,9	17780.7	0.4	3	b
7,8	17757.1	-0.4	3	
6,7	17733.8	-1.1	4	
5,6	17711.4	-0.8	4	
4,5	17689.5	-0.2	4	
3,4	17666.1	-1.2	4	
2,3	17644.9	-0.1	4	a
1,2	17622.5	-0.2	3	a
0,1	17600.1	-0.4	2	a
10,12	17557.5	0.9	2	b
9,11	17531.3	-0.4	2	
8,10	17508.3	1.3	2	
7,9	17481.3	-0.9	2	
6,8	17457.8	0.2	2	
5,7	17431.3	-1.8	2	
4,6	17406.2	-2.6	2	
3,5	17383.5	-1.0	2	
2,4	17359.9	-0.3	1	a
1,3	17334.9	-1.2	1	a
0,2	17310.0	-2.1	1	a
0,3	17004.4		1	b
1,4	17034.0		1	b
2,5	17065.4		1	b
3,6	17095.1		1	b
4,7	17125.3		1	b
5,8	17153.2		1	b
6,9	17183.3		1	b
7,10	17209.9		1	b
8,11	17235.7		1	b
9,12	17258.3		1	b
10,13	17286.4		1	b

a Observed and assigned by Gatterer, *et al.* (12).

b Position less certain due to low intensity.

levels up through as high as $v' = 17$ in the $A\ ^2\Pi_{3/2}$ state, $v' = 18$ in the $A\ ^2\Pi_{1/2}$ state, and $v' = 7$ in the $B\ ^2\Sigma^+$ state. These bandheads are listed in Tables I-III. Molecular constants presented in Table IV have been derived numerically by standard means. Essentially, all the calculated positions agree to within 5 cm^{-1} of the observed values.

B. Analysis of the YbF Spectrum

Recently, Barrow and Chojnicki (3) reported that the upper states of the YbF blue-green systems are highly perturbed and that the vibrational intervals, ΔG , cannot be satisfactorily generated by a quadratic in $(v' + \frac{1}{2})$. Their analysis, however, was limited to the first four vibrational levels of each state. We have confirmed their observation only for the $A\ ^2\Pi_{3/2}$ and $B\ ^2\Sigma^+$ states. It can be seen in Fig. 4 that the $\Delta v = +1$ sequence of the $A\ ^2\Pi_{3/2}$ - $X\ ^2\Sigma^+$ subsystem is quite regularly spaced up through $v' = 17$, suggesting that the $A\ ^2\Pi_{3/2}$ state is at most only slightly perturbed. Indeed, a least squares fit shows that all calculated positions agree to within 7 cm^{-1} of the observed values. These are listed in Table V. It is interesting that extensive perturbations should occur in the vibrational levels of the $A\ ^2\Pi_{3/2}$ and $B\ ^2\Sigma^+$ states in YbF, while similar states in YbCl are known to be regular. (We have no simple explanation for this observation.) The derived spectroscopic constants of the $A\ ^2\Pi_{3/2}$ - $X\ ^2\Sigma^+$ system, together with their standard errors, are presented in Table VI.

TABLE II
Measured Bandhead Positions and Vibrational Assignments of
YbCl A ($^2\Pi_{3/2}$) - X ($^2\Sigma^+$) Bands.

bandhead assignment (v', v'')	bandhead position (cm^{-1})	obs.-calc. (cm^{-1})	relative intensity	remarks
8,6	20115.1	-1.8	6	
7,5	20092.9	-5.0	7	
6,4	20072.7	-6.3	8	b
5,3	20054.6	-5.6	9	b
3,2	19732.9	-0.4	8	b
2,1	19706.7	-7.2	6	b
7,7	19550.6	12.7	6	b
6,6	19523.9	8.6	7	b
5,5	19499.2	6.5	8	
4,4	19470.7	0.5	9	
3,3	19447.2	-0.5	10	
2,2	19423.4	-2.0	10	a,b
1,1	19403.0	-0.1	10	a
0,0	19381.2	0.2	10	a
6,7	19236.5	0.3	7	b
5,6	19215.4	3.7	8	
4,5	19191.5	4.1	8	
3,4	19167.5	4.5	9	
2,3	19140.8	1.9	8	a
1,2	19118.8	4.1	8	a
0,1	19088.9	-1.8	7	a
8,10	19002.5	-9.6	7	b
7,9	18984.5	-1.1	8	b
6,8	18956.7	-2.3	7	
5,7	18934.1	1.4	7	
4,6	18907.2	0.8	6	
3,5	18878.7	-1.5	6	
2,4	18851.2	-0.4	7	
1,3	18824.3	-3.8	4	

a Observed and assigned by Gatterer, *et al.* (12).

b Position less certain due to low intensity or overlapping bands.

TABLE III
Measured Bandhead Positions and Vibrational Assignments of
YbCl² B (²Σ) - X (²Σ⁺) Bands.

bandhead assignment (v', v'')	bandhead position (cm ⁻¹)	obs.-calc. (cm ⁻¹)	relative intensity	remarks
7,5	20663.9	-0.8	9	
6,4	20644.7	0.5	9	
5,3	20623.4	-0.3	8	
4,2	20602.2	-0.9	8	
3,1	20581.0	-1.5	7	
2,0	20560.7	-1.2	6	
5,4	20342.3	1.5	5	b
4,3	20319.5	1.0	7	
3,2	20296.8	0.6	9	
2,1	20275.4	1.5	10	
1,0	20251.6	0.0	9	a
1,1	19963.7	2.3	10	
0,0	19939.7	0.9	10	a
3,4	19728.9	0.1	5	b
2,3	19700.9	-2.3	6	
1,2	19677.2	-0.3	7	a
0,1	19650.5	-1.3	8	a

a Observed and assigned by Gatterer, *et al.* (12).

b Position less certain due to low intensity.

C. Unidentified Band Systems

In both the YbF and YbCl spectra, we have also observed what appear to be the C ²Π-X ²Σ⁺ band systems between 4000 and 4600 Å, based on the analogy with the ordering of electronic states in BaF (12). The vibrational analysis of these bands has proved puzzling because of extensive perturbations in the upper states. The spectral fea-

TABLE IV
Spectroscopic Constants for YbCl² (units in cm⁻¹)

State	T _e	A _e	A _e X _e	T _{0c}	Remarks	Ref.
A ² Π _{1/2}	18625.4 ± 5.8	313.35 ± 0.29	0.898 ± 0.001	19381.2 (² Π _{3/2}) 17892.4 (² Π _{1/2})	a	This work
A ² Π _{3/2}	19369.3	314.62	1.376	19381.2		(12)
A ² Π _{1/2}	17882.0	314.37	1.124	17892.4		(12)
B ² Σ	19927.7 ± 3.3	313.60 ± 0.28	0.844 ± 0.005	19940.6	b	This work
B ² Σ	19928.0	315.0	2.0	19940.6		(12)
X ² Σ ⁺	0.0	292.24 ± 0.42	0.944 ± 0.002		c	This work
X ² Σ ⁺	0.0	294.1	1.12		d	(12)
		293.1	1.34		e	(12)
		293.0	2.4		f	(12)

a The bandhead wavenumber of the (v', v'') band in the A ²Π_{1/2} - X ²Σ⁺ subsystem is given in reference (14). $\nu = T_e' + [A_e' + a_e'(v'+\frac{1}{2})]B\Sigma + x_e'(v'+\frac{1}{2}) - x_e'x_e''(v'+\frac{1}{2})^2 - x_e''(v''+\frac{1}{2}) + x_e'x_e''(v''+\frac{1}{2})^2$

where A_e'=1489.16 ± 2.71 and a_e'=1.885 ± 0.096 cm⁻¹.

b. The bandhead wavenumber of the (v', v'') band is given by $\nu = T_e' + A_e'(v'+\frac{1}{2}) - x_e'x_e''(v'+\frac{1}{2})^2 - x_e''(v''+\frac{1}{2}) + x_e'x_e''(v''+\frac{1}{2})^2$.

c From a least squares fit of the A ²Π_{1/2} - X ²Σ⁺ band systems.

d From analysis of the A ²Π_{3/2} - X ²Σ⁺ band system.

e From analysis of the A ²Π_{1/2} - X ²Σ⁺ band system.

f From analysis of the B ²Σ - X ²Σ⁺ band system.

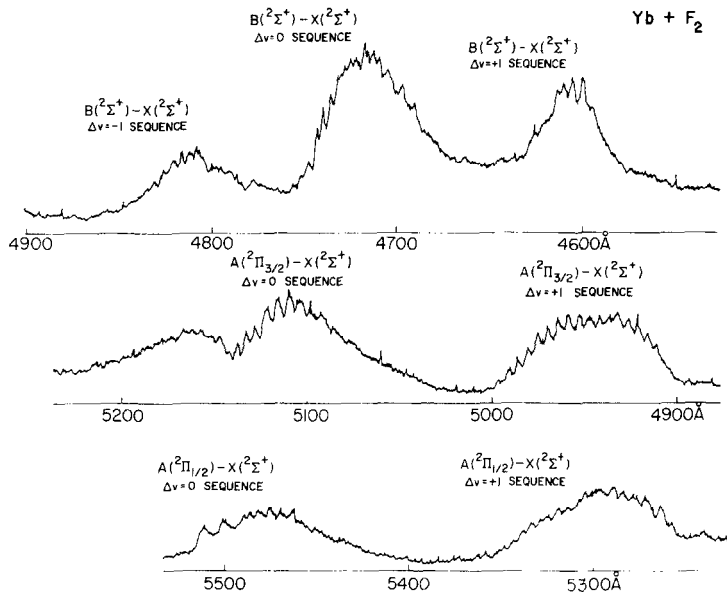


FIG. 4. The chemiluminescence spectrum from the beam-gas reaction $\text{Yb} + \text{F}_2 \rightarrow \text{YbF}^* + \text{F}$ at 10^{-4} Torr, taken with a resolution of 1 \AA at a scan speed of $100 \text{ \AA}/\text{min}$. The prominent sequences are labeled according to the assignments of Barrow and Chojnicki (3).

tures at still lower wavelengths, between 3600 and 4000 \AA , probably belong to the $D^2\Sigma^+ - X^2\Sigma^+$ system, again in analogy with the BaF states. These bandheads are extremely well defined in the YbF flame spectrum, a portion of which is shown in Fig. 5. A tentative vibrational assignment is presented in Table VII.

Emission bands appear in the red for both YbF and YbCl. In the case of YbF, these bands are rather well structured under single-collision conditions (see Fig. 6). Unfortunately, it was not possible to recognize ground-state intervals in this spectrum. However, we can reject the possibility that this band system terminates on the A state (or higher states), since this would place the bond energy of YbF at an unacceptably high value (15).¹ Accordingly, we suggest that the A state is not the lowest-lying excited state of YbF. This is contrary to the known ordering of the excited states of the Group IIA monohalides. It is tempting to speculate that this band system may involve the transition from a molecular state formed from $\text{Yb}(5d) + \text{F}(2p)$ to the YbF ground state (see next section).

D. Comments on the Nature of the YbX Excited States

The mysterious red bands of YbX and the observation of extensive vibrational perturbations in the A and B states of YbX cause us to consider the possible low-lying electronic states of the ytterbium monohalides. The ground state of YbX should be

¹ Upper bounds for the dissociation energies of YbF and YbCl were determined to be 5.0 and 3.2 eV , respectively, based on the short-wavelength cutoff of the YbF* and YbCl* chemiluminescence spectra under single-collision conditions.

TABLE V
Measured Bandhead Positions and Vibrational Assignments of
YbF A $^2\Pi$ - X $^2\Sigma^+$ Bands.

bandhead assignment (v', v'')	bandhead position (cm $^{-1}$)	obs.-calc. (cm $^{-1}$)	remarks
15,13	20725.6		
14,12	20706.3		
13,11	20687.0		
12,10	20668.2		
11,9	20651.1		
10,8	20634.1		a
9,7	20614.9		a
8,6	20604.3		
7,5	20578.9		
6,4	20566.2		a
5,3	20549		a
4,2	20528.1		a
3,1	20510.0		a
2,0	20490.3		a
20,19	20403.5	1.2	
19,18	20378.8	-1.4	
18,17	20356.8	-1.4	
17,16	20335.2	-0.9	
16,15	20313.3	-0.8	
15,14	20290.7	-1.4	
14,13	20272.2	2.0	
13,12	20253.7	5.5	
12,11	20229.1	2.9	
11,10	20204.6	0.3	
10,9	20185.4	3.0	
9,8	20160.5	0.2	
8,7	20138.2	-0.2	
7,6	20116.1	-0.4	
6,5	20093.9	-0.7	
5,4	20072.3	-0.3	
4,3	20051.1	0.5	b
3,2	20029.7	1.1	b
2,1	20008.2	1.6	b
1,0	19985.1	0.4	b
10,10	19719.9	-1.8	
9,9	19690.8	-5.5	
8,8	19665.2	-5.4	
7,7	19639.7	-5.1	
6,6	19613.5	-5.2	
5,5	19589.7	-2.9	
4,4	19565.6	-0.6	
3,3	19543.3	3.7	b
2,2	19516.9	4.1	b
1,1	19489.2	3.4	b
0,0	19451.8	-6.9	b
11,12	19296.7	3.7	
10,11	19266.2	1.6	
9,10	19235.0	-0.7	
8,9	19206.0	-0.5	
7,8	19177.1	0.1	
6,7	19147.2	0.1	
5,6	19117.9	1.1	
4,5	19087.8	1.6	
3,4	19057.9	2.7	b
2,3	19027.8	4.0	b
1,2	18995.6	3.6	b
0,1	18953.5	-6.4	b

(a) Position less certain due to low intensity or overlapping bands.

(b) Observed and assigned by Barrow and Chojnicki (3).

well described by the molecular orbitals

$$\dots (np\pi_X)^4 (6s\sigma_{Yb})^1, \quad X^2\Sigma^+,$$

corresponding to the ionic description $Yb^+ X^-$. The excited states of YbX are expected to

TABLE VI
Spectroscopic Constants for YbF A ${}^2\Pi_{3/2}$ - X ${}^2\Sigma^+$ Subsystem (units in cm^{-1})

State	T_e	w_e	$w_e x_e$	$w_e y_e$	B_e	α_e	Ref.
A ${}^2\Pi_{3/2}$	19445.0 ± 64.8	531.35 ± 5.03	2.721 ± 0.132	0.0304 ± 0.0003			This work
	19470.99	540.35 ^a			0.24863	0.0016 ^b (3)	
X ${}^2\Sigma^+$	0.0	503.98 ± 5.57	2.620 ± 0.160	0.0300 ± 0.0004		0.00159 ^c	This work
	0.0	506.32	2.0		0.24140	0.0015 (3)	

a Value of $\Delta G_{1/2}$.

b Derived from the Pekeris expression $\alpha_e = 6[(w_e x_e B_e^3)^{1/2} - B_e^2]/w_e$, using our values of r_e and $w_e x_e$.

c Derived from the Pekeris expression for α_e using the value of B_e given by reference (3).

involve promotion of the "metallic" $6s\sigma_{Yb}$ orbital. In the Yb⁺ ion, the $5d$ level and the $6p$ level lie close together at 23 784 and 29 282 cm^{-1} , respectively (16). This is in contrast to the energy levels of Ca⁺, Sr⁺, and Ba⁺ where the $5d$ and $6p$ term values are separated by more than 1 eV. Accordingly, there are a number of low-lying states of the form

$$\begin{aligned} \dots (np\pi_X)^4 (a5d\sigma_{Yb} + b6p\sigma_{Yb})^1, & \quad {}^2\Sigma^+, \\ \dots (np\pi_X)^4 (b5d\sigma_{Yb} - a6p\sigma_{Yb})^1, & \quad {}^2\Sigma^+, \\ \dots (np\pi_X)^4 (a'5d\pi_{Yb} + b'6p\pi_{Yb})^1, & \quad {}^2\Pi, \\ \dots (np\pi_X)^4 (b'5d\pi_{Yb} - a'6p\pi_{Yb})^1, & \quad {}^2\Pi, \end{aligned}$$

and

$$\dots (np\pi_X)^4 (5d\delta_{Yb})^1, \quad {}^2\Delta,$$

where the values of the mixing coefficients a , b and a' , b' are not known. It is likely that the ${}^2\Sigma$ and ${}^2\Pi$ states perturb one another, suggesting that the ${}^2\Pi_{3/2}$ state might be less perturbed than the ${}^2\Pi_{1/2}$ state in case (c) coupling.

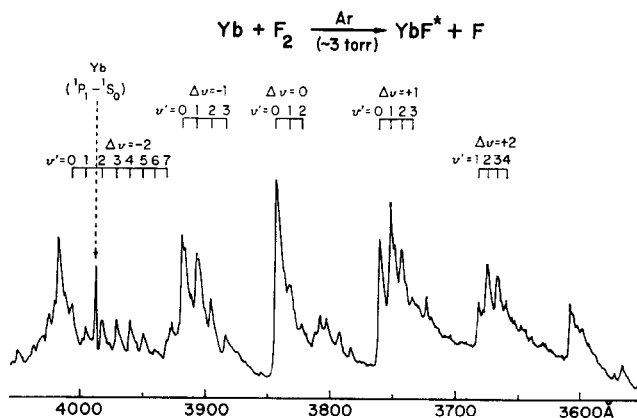


FIG. 5. A portion of the flame spectrum obtained from the reaction of Yb with F₂ in 3 Torr of argon, taken with a resolution of 0.25 Å at a scan speed of 50 Å/min.

TABLE VII
Measured Bandhead Positions and Tentative Vibrational Assignments of a YbF Band System in the Near Ultraviolet.*

bandhead assignment (v', v'')	bandhead position (cm^{-1})	obs.-calc. (cm^{-1})	relative intensity
5,3	27319.1	-1.5	9
4,2	27266.2	3.3	10
3,1	27210.5	5.7	10
2,0	27152.9	6.2	9
3,2	26701.8	-7.3	7
2,1	26641.3	-4.8	8
1,0	26579.7	-2.5	7
2,2	26150.0	-0.4	2
1,1	26077.7	-3.9	3
0,0	26009.2	-2.0	6
2,3	25660.1	1.5	2
1,2	25586.5	0.6	3
0,1	25510.8	0.2	3
6,8	25427.1	1.3	1
5,7	25367.1	-2.0	1
4,6	25306.1	-1.1	1
3,5	25242.2	1.7	1
2,4	25169.1	-0.3	1
1,3	25096.5	2.4	1
0,2	25018.0	3.1	1

*This band system is believed to be the $D^2\Sigma^+ - X^2\Sigma^+$ band system.

Radiative transitions from the excited states to the ground state favor those excited states having large $6p\sigma_{Yb}$ or $6p\pi_{Yb}$ character. The former is associated with the *B* state, the latter with the *A* state. Other states, such as the upper state of the red-band system (assuming that the lower state is the ground state) would be expected to be much weaker in absorption or emission and to have a much longer radiative lifetime.

The behavior of the red-band system is consistent with the hypothesis that it is mostly of *5d* character. First of all, it has been observed that in cases where excited molecules are short-lived the chemiluminescence assumes the shape of the well-collimated metal beam (see, for instance, Ref. (9)). In cases where emitter lifetimes are long (on the order of microseconds, for example), these molecules, on the average,

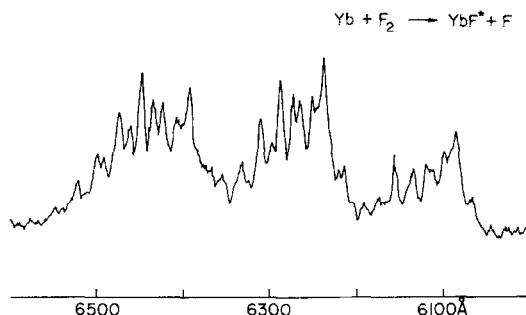


FIG. 6. An unassigned red-band system of YbF obtained from the beam-gas reaction of Yb with F_2 at 10^{-4} Torr regime, taken with a resolution of 1 \AA at a scan speed of $100 \text{ \AA}/\text{min}$.

travel outside the beam path before radiating, thus rendering the chemiluminescence diffuse. Under beam-gas conditions, where oxidizer pressures are 10^{-4} Torr or less, the blue-green emission appears sharp, i.e., localized in space, while the red emission is diffuse. Furthermore, the relative intensities of these band systems are found to be a very sensitive function of the pressure. Thus, while the red emission disappears entirely at a pressure of 3 Torr of argon, the blue-green chemiluminescence is affected only to the extent that the bandheads become more well-defined, as a result of rotational relaxation. That the lifetime of the upper state is relatively long could explain why Barrow and Chojnicki were unable to observe the red system either in absorption or in emission (17).

ACKNOWLEDGMENT

This work was supported by the Army Research Office under grant DAAG29-76-G-0208.

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