

Rotational Analysis of the ${}^2\Phi\text{-}{}^2\Delta$ and ${}^2\Delta\text{-}{}^2\Delta$ Systems of Titanium Monofluoride

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The absorption spectrum of TiF has been studied. The rotational analysis of the ${}^2\Phi\text{-}{}^2\Delta$ and ${}^2\Delta\text{-}{}^2\Delta$ systems with a common lower state has been carried out. Previously the 0-0 bands of these systems were considered as the 0-0 and 1-0 bands of the ${}^4\Pi\text{-}X^4\Sigma$ transition. For the lower ${}^2\Delta$ state the following molecular constants (in cm^{-1}) have been derived: $B_0 = 0.3691$, $D_0 = 4.4 \cdot 10^{-7}$, and $\Delta G_{1/2} = 674.4$. © 1985 Academic Press, Inc.

INTRODUCTION

The electronic spectrum of TiF was obtained by Diebner and Kay (1) in absorption and by Deschamps and Pannetier (2) in emission. The spectrum was not rotationally analyzed. The interpretations of the most prominent group of bands in the 4070-Å region given in Refs. (1, 2) were based on the strong similarity between the appearance of the TiCl and TiF spectra and on the JANAF estimates of vibrational constants.

According to a simple theoretical calculation on TiF (3) there are two close-lying, low-energy states, ${}^4\Sigma^-(\sigma\delta^2)$ and ${}^2\Delta(\sigma^2\delta)$; either of them can be expected to be the ground state of the molecule.

The JANAF estimates for the ground $X^4\Sigma^-$ state of TiF ($\omega_e = 590.0$, $\omega_e x_e = 6.6 \text{ cm}^{-1}$, and $r_e = 1.95 \text{ Å}$) are not quite convincing now. The linear extrapolation of the ground state vibrational levels using the constants recommended yields an unreasonably low value for the dissociation energy as compared to mass spectrometric expectations (5). The internuclear distance seems to be too large as compared to the Ti-F bond length in titanium tetrafluoride (6).

This paper deals with the rotational analysis of two systems with a common ${}^2\Delta$ lower state. The 0-0 bands of these systems were previously interpreted as the 0-0 and 1-0 bands of the ${}^4\Pi\text{-}X^4\Sigma$ transition (1, 2).

EXPERIMENTAL DETAILS

The absorption spectrum of TiF was obtained when a mixture of CaF_2 and Ti powders were heated in a vacuum furnace with a tantalum heater in the temperature range of 1500-1800°C. The cylindrical heater made of 0.15-mm-thick tantalum foil was about 150 mm long and 10 mm in diameter. The mixture was placed directly into the heater, and the furnace was filled with argon at a pressure of 20 mm Hg. A xenon lamp, DKSSh-1001, served as a light source for absorption continuum.

The initial experiments utilized the PGS-2 spectrograph with different gratings to photograph the spectrum in the region 3000–7000 Å with a dispersion of 1.25–7.4 Å/mm. The rotational structure of the bands was photographed in the experimental SEM-1 spectrograph equipped with a large grating (200 mm long) having 300 lines/mm and a blaze angle corresponding to a wavelength of 60 000 Å. A predisperser was employed to isolate the region of interest. An iron cathode lamp provided a reference spectrum; wavelengths of iron lines were taken from the tables given in Ref. (7) and measurements were carried out using an IZA-2 comparator.

The absorption spectrum contains the CaF bands (8) and the bands ascribed to the TiF molecule (1, 2). There are no CaF bands in the region of the TiF spectrum (8). The TiF spectrum consists of seven groups of bands with close-lying bandheads located in the regions 4026–4088, 3955–3968, 3890–3906, 3840–3861, 3730–3748, 3678–3714, and 3640–3660 Å. The bands of the first and fourth groups are violet-degraded, those of the fifth and sixth groups are red-degraded, and the other groups contain red- and violet-degraded bands.

Not many bands are available for rotational analysis because of strong mutual overlapping of bands. The rotationally analyzed violet-degraded bands (3967, 3964, 3861, and 4076, 4074 Å) are located on the red side of the groups and are less blended than others. The spectrograms were taken in the XV and XVI orders of grating with a dispersion of about 0.25–0.30 Å/mm.

ROTATIONAL ANALYSIS AND DISCUSSION

The wavenumbers of rotational lines are given in Tables I and II. The lines overlapped by other identified band lines or atomic lines are marked with asterisks. Heavily blended lines are indicated by two asterisks. The lines which form the bandhead are indicated by "H".

The 3861-, 3964-, and 3967-Å bands consist of single *R* and *P* branches. The *P*-branch is slightly stronger than the *R* branch. The *Q* branch was not detected. The relative numbering has been established by finding agreement between the combination differences $\Delta_2 F''(J) = R(J - 1) - P(J + 1)$ of the 3861- and 3967-Å bands, and $\Delta_2 F'(J) = R(J) - P(J)$ of the 3861- and 3964-Å bands. The absolute numbering has been found by the requirements that $\Delta_2 F(J) = 4B(J + 1/2)$ plotted as a function of *J* should go through zero at $J = -1/2$. The numbering was checked by least-squares fitting the experimental $\Delta_2 F$ values to the combination difference formula. The minimum value of the standard deviation of fit was obtained at the half-integral numbering given in Table I.

The 4074- and 4076-Å bands consist of single *R*, *Q*, and *P* branches with intensity distribution $I(Q) > I(R) > I(P)$. Because of the small difference, $B' - B''$, the bands show only one strong *Q* head. *P* lines stretch far toward the red from the *Q*-heads until they fade out before head formation. An independent analysis was carried out for each band. The relative numbering was determined by comparing the combination differences: $\Delta_1 F'(J) = R(J) - Q(J) = Q(J + 1) - P(J + 1)$ for the upper state and $\Delta_1 F''(J) = R(J) - Q(J + 1) = Q(J) - P(J + 1)$ for the lower state. The absolute numbering in the 4076-Å band was established by finding an agreement between combination differences $\Delta_2 F''(J)$ and those of the lower state of the 3967- and 3861-

TABLE I
Rotational Lines of ${}^2\Delta_{3/2}-{}^2\Delta_{3/2}$ Subbands

J	0 - 0		1 - 0		1 - 1	
	R	P	R	P	R	P
3.5			25908.26	25902.24		
4.5			09.23	01.56		
5.5			10.02			
6.5			10.97			
7.5			11.94	25899.80		
8.5			13.09	99.29		
9.5	25215.29		14.12	98.85		
10.5	16.42		15.16	98.46		
11.5	17.66	25199.22		97.99		
12.5	19.01**	98.87*	17.46	97.64		
13.5	25220.03	25198.58*	25918.70	25897.34		
14.5	21.42*	98.35*	19.85	97.02		
15.5	22.74	98.17*	21.02	96.75*		
16.5	24.13	98.04*	22.33	96.51*		
17.5	25.60	98.04*	23.76	96.29*		
18.5	27.07	97.91H	25.03	96.10*		
19.5	28.56	97.91H	26.31	95.95*		
20.5	30.13	97.91H	27.79	95.80*		
21.5	31.69	98.04*	29.18	95.68H		
22.5	33.31	98.04*	30.64	95.68H	25256.31	25221.35H
23.5	25234.94	25198.17*	25932.10	25895.68H	25257.79	25221.35H
24.5	36.65	98.35*	33.76**	95.68H	59.47	21.42*
25.5	38.44	98.58*	35.15	95.68H	61.03	21.58
26.5	40.20	98.87*	36.73	95.68H	62.59	21.58
27.5	42.03	99.09	38.32	95.80*	64.32	21.80
28.5	43.82	99.43	39.94	95.95*	65.97	22.03
29.5	45.76	99.79	41.60	96.10*	68.03	22.34
30.5	47.62	25200.21	43.32	96.29*	69.59	22.61
31.5	49.62	00.65	45.01	96.51*	71.58	23.05
32.5	51.58	01.11	46.80	96.75*	73.61	23.49
33.5	25253.65	25201.59	25948.59	25897.02	25275.46	25223.93
34.5	55.75	02.15	50.34	97.34	77.44	24.29
35.5	57.80	02.71	52.21	97.64	79.45	25.06
36.5	59.96	03.33P	54.02	97.99	81.40	25.37
37.5	62.10	04.01	56.02	98.46	83.52	25.95
38.5	64.33	04.69	57.96	98.85	85.78	26.37
39.5	66.57	05.43	59.90	99.29	88.05	27.34
40.5	68.85**	06.18	61.90	99.80	90.19	28.01
41.5	71.17	06.98	63.89	25900.26	92.42	28.89
42.5	73.45P	07.81	65.93	00.81	94.69	29.57
43.5	25275.91	25208.67	25968.07	25901.39	25297.00	25230.38
44.5	78.55	09.55P	70.14	02.01	99.33	31.24
45.5	80.99	10.61	72.32	02.65	25301.77	32.16
46.5	83.52	11.69	74.39	03.33	04.21	33.12
47.5	85.93	12.70	76.39	03.96	06.67	34.11
48.5	88.70	13.81	78.73	04.72	09.22	35.24
49.5	91.35P	14.92	81.04	05.49	11.83	36.28
50.5	93.92	16.09	83.38	06.26	14.41	37.41
51.5	96.55	17.35P	85.66	07.05	17.06	38.54
52.5	99.33	18.61**	88.02	07.93	19.73	39.78
53.5	25302.04	25219.78	25990.36	25908.79	25322.47	25241.01
54.5	04.82	21.03	92.72	09.71	25.22	42.33
55.5	07.65	22.34	95.15	10.61		43.65
56.5	10.50	23.74	97.53	11.58		44.98
57.5	13.37	25.06	26000.03	12.58		46.42
58.5	16.33	26.57	02.50	13.54		47.89
59.5	19.36	28.01	04.99	14.57		49.45
60.5	22.35	29.57	07.58	15.79**		50.95
61.5	25.40	31.12	10.22	16.81		
62.5	28.42**	32.70	12.72	17.92		
63.5	25331.65	25234.33		25919.18		
64.5	34.74	36.04		20.23		
65.5	37.94	37.71		21.57		
66.5	41.17	39.46		22.81		
67.5	44.40	41.20		24.03		
68.5	47.79	43.03		25.35		
69.5	51.04	44.87		26.67		
70.5	54.42	46.75				
71.5		48.70				

TABLE II
 Rotational Lines of ${}^2\Phi-{}^2\Delta(0-0)$ Bands

${}^2\Phi_{5/2} - {}^2\Delta_{3/2}$				${}^2\Phi_{7/2} - {}^2\Delta_{5/2}$		
J	R	Q	P	R	Q	P
5.5	24531.67					
6.5	32.65					
7.5			24521.48			
8.5	33.85		20.71*			
9.5			20.01			
10.5	35.56		19.34			
11.5	36.22		18.61			
12.5	36.98		18.04			
13.5	37.84		17.26*			
14.5	38.58		16.59*			
15.5	24539.37		24515.94			
16.5	40.19		15.26			
17.5	40.97		14.70			
18.5	41.79		13.98*			
19.5	42.61*		13.33			
20.5	43.34*		12.64			
21.5	44.24*					
22.5	45.05*		11.38*			
23.5	45.91*		10.78*			
24.5	46.75*		10.09			
25.5	24547.60*		24509.50			
26.5	48.34*		08.86			
27.5	49.22	24528.35	08.26		24542.61*	
28.5	50.11	28.48	07.62	24564.79	42.73*	24521.57
29.5	50.92*	28.62	07.05		42.88	20.71*
30.5	51.83	28.70	06.42*	66.66	43.04*	20.18
31.5	52.69	28.86	05.82	67.52	43.19	19.56
32.5	53.55	28.97	05.25	68.47	43.34*	18.94
33.5	54.39	29.14	04.64*	69.41	43.51*	18.35
34.5	55.28	29.26	04.06	70.40	43.70	17.80
35.5	24556.05	24529.44	24503.46	24571.29	24543.86*	24517.26*
36.5	57.03	29.58	02.88*	72.13	44.04	16.59*
37.5	57.90	29.76	02.33	73.10	44.24*	16.17
38.5	58.74	29.89	01.76	74.00	44.43	15.57
39.5	59.66	30.05	01.17	74.88	44.61*	15.04
40.5	60.59	30.23	00.62	75.85	44.82	14.48
41.5	61.46	30.33	00.06	76.76	45.05*	13.98*
42.5	62.34	30.55	24499.49	77.67	45.22	
43.5	63.23	30.75	98.97	78.62	45.45	12.93
44.5	64.13	30.90	98.43	79.64	45.66	
45.5	24565.05	24531.10	24497.87	24580.67	24545.91*	
46.5	65.91	31.29	97.33	81.48	46.12	24511.58*
47.5	66.83	31.47	96.84	82.55	46.30	10.78*
48.5	67.81	31.67	96.29	83.53	46.49	10.26
49.5	68.74	31.88	95.79	84.54	46.75*	09.73
50.5	69.65	32.08	95.25	85.50	47.07	09.29
51.5	70.57	32.28	94.76	86.47	47.32	08.86
52.5	71.47	32.45	94.23	87.43	47.60*	08.46
53.5	72.38	32.71	93.71	88.38	47.84	07.82
54.5	73.34	32.93	93.25	89.52	48.08	07.28
55.5	24574.29	24533.16	24492.73	24590.48	24548.34*	24506.89
56.5	75.21	33.36	92.26	91.43	48.63	06.42*
57.5	76.15	33.61	91.78	92.49	48.86	06.00
58.5	77.12	33.85	91.30	93.40	49.09	05.57
59.5	78.04	34.07	90.81		49.37	05.07
60.5	79.07	34.32	90.34	95.30	49.61	04.64*
61.5	80.00	34.58	89.85	96.46	49.86	04.21
62.5	81.01	34.81	89.42	97.59	50.26	03.69
63.5	81.97	35.10	88.97		50.62	03.30
64.5	82.80	35.33	88.48		50.92*	02.88*

TABLE II—Continued

J	${}^2\Phi_{5/2} - {}^2\Delta_{3/2}$			${}^2\Phi_{7/2} - {}^2\Delta_{5/2}$		
	R	Q	P	R	Q	P
65.5	24583.92	24555.56	24488.16		24551.30	
66.5	84.93	35.88	87.58			
67.5	85.90	36.14	87.15			
68.5	86.86	36.41	86.71			
69.5	87.78	36.67	86.28			
70.5	88.87	36.98	85.85			
71.5	89.76	37.23	85.42			
72.5	90.71	37.57	85.00			
73.5	91.76	37.84	84.61			
74.5	92.77	38.14	84.21			
75.5	24595.68	24538.42	24485.80			
76.5	94.86	38.76	83.41			
77.5	95.84	39.04	83.00			
78.5		39.37	82.61			
79.5	97.89	39.72	82.23			
80.5	98.75	40.01	81.85			
81.5	99.78	40.34	81.47			
82.5	24600.91	40.63	81.10			
83.5	01.93	40.97	80.74			
84.5	02.92	41.34	80.39			
85.5	24604.03	24541.70	24480.03			
86.5	05.09	42.04	79.67			
87.5	06.03	42.37	79.32			
88.5		42.73*	78.97			
89.5		43.04*	78.64			
90.5		43.51*	78.32			
91.5		43.86*	78.04			
92.5		44.24*	77.75			
93.5		44.61*	77.58			
94.5		45.05*	77.06			

Å bands. The absolute numbering in the 4074-Å band was determined from the condition: $\Delta_1 F(J) = 2B(J+1) - 4D(J+1)^3 = 0$ at $J = -1$, and was checked by the above fitting procedure.

Since the TiF molecule has an odd number of electrons the half-integral numbering is the J numbering, thereby implying that none of the states under consideration is a Σ state.

The structure of the 3967-, 3964-, and 3863-Å bands corresponds to the transition with $\Delta\Lambda = 0$. Based on the good agreement of the combination differences the bands were assigned as the 0-0, 1-1, and 1-0 bands of the same subsystem.

The number of branches and the intensity distribution show that the 4076- and 4074-Å bands belong to the transition with $\Delta\Lambda = +1$, $\Lambda \neq 0$. By comparing the B values of both bands in the upper and lower states it was concluded that they are different subbands of the same multiplet transition. Vibrational assignment as the 0-0 band is evident from the high intensity of band with very small difference $B' - B''$ as well as from the agreement of $\Delta_2 F''(J)$ of the 4076-, 3967-, and 3861-Å bands.

Among the low-lying states ${}^4\Sigma^-(\sigma\delta^2)$, ${}^2\Delta(\sigma^2\delta)$, ${}^4\Phi(\sigma\delta\pi)$ and ${}^4\Pi(\sigma\delta\pi)$ predicted by the theoretical calculation on the TiF molecule (3), only the ${}^2\Delta$ state can undoubtedly be considered as the lower state of the bands analyzed. The ${}^4\Sigma^-$ state is eliminated

from consideration by rotational analysis. As far as the other quartet states are concerned it is impossible to find four components in the $\Delta\Lambda = 0$ transition, but all the violet-degraded bands in this region can readily be arranged into the ${}^2\Delta\text{-}{}^2\Delta$ system. The rotational analysis of the other subbands was not undertaken because of the very strong overlapping.

From the above consideration and from the relationship between the effective rotational constants,

$$B_z = B(1 + 2B\Sigma/A\Lambda), \quad (1)$$

and bearing in mind that the ${}^2\Delta(\sigma^2\delta)$ is a regular state, the 3967-, 3964-, and 3861-Å bands were assigned as the ${}^2\Delta_{3/2}\text{-}{}^2\Delta_{3/2}$ subbands and the 4076- and 4074-Å bands as the ${}^2\Phi_{5/2}\text{-}{}^2\Delta_{3/2}$ and ${}^2\Phi_{7/2}\text{-}{}^2\Delta_{5/2}$ subbands, respectively.

The molecular constants of TiF derived from the rotational analysis are given in Table III. The rotational constants, B and D , and the band origins were calculated by the least-squares method using the following relations:

$$\Delta_2 F(J) = 4B(J + 1/2) - 8D(J + 1/2)^3 \quad (2)$$

$$R(J - 1) + P(J) = 2\nu_0 + 2(B' - B'')J^2 - 2(D' - D'')J^2(J^2 + 1) \quad (3)$$

$$Q(J) = \nu_0 + (B' - B'')J(J + 1) - (D' - D'')J^2(J + 1)^2. \quad (4)$$

The molecular constants listed in Table III were chosen according to Herzberg's recommendations (9). The B_0 and D_0 values for the lower ${}^2\Delta$ state were obtained from extensive data on the ${}^2\Phi\text{-}{}^2\Delta(0\text{-}0)$ band using Eq. (2). The rotational constants for the upper states were calculated from these B'_0 and D'_0 values and from the

TABLE III
Molecular Constants of Titanium Monofluoride (cm^{-1})*

State	v	T_v	B_v	$D_v 10^7$
${}^2\Delta_{3/2}$	1	25904.57(1)	0.38028(5)	5.03(7)
	0	25205.22(2)	0.38386(5)	4.77(6)
${}^2\Phi_{7/2}$	0	24540.62(2) + a	0.37592(18)	4.86(40)
${}^2\Phi_{5/2}$	0	24526.80(4)	0.36678(5)	4.30(5)
${}^2\Delta_{5/2}$	0	a	0.37338(15)	4.59(30)
${}^2\Delta_{3/2}$	1	675.41(4)	0.36316(10)	7.74(15)
	0	0	0.36475(4)	4.25(4)

*The numbers in parentheses are uncertainties in the last digits and represent two standard deviations.

appropriate $B'_v - B''_0$ and $D'_v - D''_0$ values obtained from Eqs. (3) and (4), with an accuracy of about $\pm 1 \times 10^{-5}$ and $\pm 3 \times 10^{-9} \text{ cm}^{-1}$, respectively. The adopted molecular constants describe wavenumbers of unblended lines with an accuracy of $\pm 0.06 \text{ cm}^{-1}$, while those obtained directly from the combination differences give wavenumbers which deviate systematically from observation; for some bands the deviations increase with J and reach 0.4 cm^{-1} at the highest J observed.

The noticeable deviations of the $R(42.5)$, $P(44.5)$, and $R(49.5)$, $P(51.5)$ lines in the ${}^2\Delta_{3/2} - {}^2\Delta_{3/2}(0-0)$ band from the calculation may be due to perturbations at $J = 43.5$ and 50.5 in the upper state. There is another perturbation in this band which results in a distinct weakening of the $P(36.5)$ line. Nothing definite can be said about the appropriate R line because it lies within a red-degraded head structure. Since the $P(36.5)$ line in the ${}^2\Phi_{3/2} - {}^2\Delta_{3/2}(0-0)$ band is not perturbed, it shows that the perturbation occurs at the $J = 35.5$ level of the upper ${}^2\Delta_{3/2}$ state.

The $T_1 = \Delta G_{1/2}$, B_1 , and D_1 values for the lower ${}^2\Delta_{3/2}$ state were estimated from the differences of the R and P lines of the 1-0 and 1-1 ${}^2\Delta_{3/2} - {}^2\Delta_{3/2}$ bands, using the following expression:

$$\begin{aligned} {}^{1-0}R(J) - {}^{1-1}R(J) &= {}^{1-0}P(J) - {}^{1-1}P(J) \\ &= \Delta G_{1/2} - (B_0 - B_1)J(J+1) + (D_0 - D_1)J^2(J+1)^2. \end{aligned}$$

The D_1 value obtained is unusually high, but the lines cannot be described within the experimental error using the D_0 value, which coincides with a value of D calculated from the Kratzer relation. Any conclusions from this result would be premature because the measurements of the weak, heavily blended 1-1 band might be insufficiently accurate and the interval of J observed is not sufficiently wide for an accurate determination of the D_1 value.

A very complicated band group whose position in the spectra slightly changes from 4000 to 4500 Å is characteristic of all titanium monohalides. It is prominent in absorption. Previously, this group was assigned as ${}^4\Pi - X^4\Sigma$ transition (10-13) on the basis of the multiplet analysis of bandheads. This work shows that two bands on the red side of this group in the TiF spectrum belong to a ${}^2\Phi - {}^2\Delta$ transition. The same result was obtained by Lanini in analyzing analogous bands in the TiCl spectrum. Unfortunately, his work was not published; some results were cited in Ref. (13) although not quite correctly [the effective B constants for the ${}^2\Delta(\sigma^2\delta)$ state correspond to an inverted state].

Numerous TiF bands in the 4026- to 4088-Å group cannot be arranged in one doublet ${}^2\Phi - {}^2\Delta$ system. The group obviously consists of bands belonging to several electronic transitions. An attempt to interpret the TiCl group as an overlapping of three systems was made by de Vore (13). However, the vibrational analysis presented is not convincing. Most of the bands in this group look like bands connected with transitions between states having close values of r_e . In this case it seems very unlikely to observe developed $\Delta v \neq 0$ groups as was suggested by de Vore.

To conclude, whether or not the lower ${}^2\Delta$ state is the ground state the molecular constants $r_e = 1.832 \text{ Å}$, $\Delta G_{1/2} = 674.41$, and $\omega_e x_e \approx 2 \text{ cm}^{-1}$ (estimated from Pekeris relation) are more reasonable for the TiF ground state than those given in the JANAF table.

REFERENCES

1. R. L. DIEBNER AND J. G. KAY, *J. Chem. Phys.* **51**, 3547-3554 (1969).
2. A. CHATALIC, P. DESCHAMPS, AND C. PANNETIER, *C. R. Acad. Sci. Paris, Ser. C* **270**, 146-149 (1970).
3. R. GAMBI, *Gazz. Chim. Ital.* **105**, 27-35 (1975).
4. D. R. STULL, Ed., "JANAF Thermochemical Table," 2nd ed., NSRD-NBS 37, 1971.
5. K. F. ZMBOV AND J. L. MARGRAVE, *J. Phys. Chem.* **71**, 2893-2894 (1967).
6. V. M. PETROV, G. V. GIRICHEV, N. I. GIRICHEVA, K. S. KRASNOV, AND E. Z. ZASORIN, *Zh. Strukt. Khim.* **20**, 55-59 (1979).
7. H. M. CROSSWHITE, *J. Res. Nat. Bur. Stand. A* **79**, 17-69 (1975).
8. B. ROSEN, Ed., "International Tables of Selected Constants. 17. Spectroscopic Data Relative to Diatomic Molecules," Pergamon, New York, 1970.
9. G. HERZBERG, "Molecular Spectra and Molecular Structure, Vol. 1. Spectra of Diatomic Molecules," 2nd ed., pp. 187-188, Van Nostrand, Princeton, New Jersey, 1950.
10. E. SHENYAVSKAYA, YU. YA. KUSYAKOV, AND V. M. TATEVSKII, *Opt. Spektrosk.* **12**, 359-363 (1962).
11. A. CHATALIC, P. DESCHAMPS, AND G. PANNETIER, *J. Chim. Phys.* **67**, 316-322 (1970).
12. CH. SIVAJI, D. V. K. RAO, AND P. T. RAO, *Curr. Sci. (India)* **39**, 153-154 (1970).
13. T. C. DE VORE, *High Temp. Sci.* **15**, 263-273 (1982).