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On the Silicon Oxide Bands

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Pankhurst has described a band spectrum believed by him to belong to an oxide of silicon, possibly SiO_2. A better excitation of the same bands has been obtained from a similar source (a high voltage uncondensed discharge through a constriction in a quartz tube), but in helium gas instead of hydrogen. These bands have been photographed on the 30-foot, 30,000 lines per inch Chicago grating spectrograph. A band near λ3840 has been resolved in the first and second orders and found to be a (0,0) transition, overlapped by a weak (1,1) transition, of the type $^2\Sigma\rightarrow{}^2\Sigma$, having the constants

$$\begin{array}{ll} \nu(0,0)=26{,}015.05\text{ cm}^{-1}, & \nu(1,1)=25{,}991.44\text{ cm}^{-1}, \\ B_0'=0.7180\text{ cm}^{-1}, & B_1'=0.704\text{ cm}^{-1}, \\ B_0''=0.7253\text{ cm}^{-1}, & B_1''=0.712\text{ cm}^{-1}. \end{array}$$

The coefficients of the spin doubling for the two states are $\gamma_0'=+0.012$ cm^{-1}, $\gamma_0''=+0.002$ or $\gamma_0''=+0.022$ cm^{-1}, the value of γ_0'' not certainly fixed as between these two alternatives. The doublet structure and the B values prove that the emitter is SiO^+. Other bands at λ4270 have been resolved with weak intensity and tentatively ascribed to SiO_2.

INTRODUCTION

IN 1940, R. C. Pankhurst[1] described a system of bands lying in the violet region of the spectrum, obtained from a quartz capillary in a hydrogen discharge tube through which passed a heavy current. Part of the system, the region 4400A to 4600A, had been previously described by Cameron[2] and attributed by him to an oxide of silicon. Pankhurst's published photographs show the spectrum to be a series of more or less diffuse regions, the most intense of which had the wave-lengths 4340A, 4270A, and 3840A. He concluded from the general complexity of the spectrum that it was emitted by the triatomic molecule SiO_2.

The general interest in polyatomic molecules stimulated the present investigation of the bands, in particular because until now the spectra of very few polyatomic molecules have been obtained in emission. The large dispersion and high resolving power of the 30-foot Chicago grating have made it possible to resolve the rotational structure of these bands and to find their true emitters. Unfortunately, however, this investigation is incomplete. A band at 3840A was excited with great intensity in helium, and has been analyzed and positively assigned to SiO^+; other bands at 4270A have been resolved with weak intensity and tentatively ascribed to SiO_2; and still others appeared too faintly to allow examination. It was planned to continue these experiments with an atmosphere of hydrogen, in which the 4270A region is excited with greater intensity than is the 3840A region,[1] and to try the effect of other methods of excitation in order to obtain better photographs of the weaker bands, but these plans have necessarily been indefinitely postponed.

EXPERIMENTAL

The general design of the apparatus was like that used by Pankhurst, but with modified electrodes. The bands were obtained by passing an alternating current of 2 amperes at 4000 volts through a discharge tube. Water-cooled steel electrodes were fitted into the glass discharge tube against glass flanges and sealed with Picein. A quartz tube about 1 cm diameter at each end but constricted in the middle of its length to a 2-mm capillary was placed between the electrodes. Concentric with the axis of the quartz capillary, there was a hole through each electrode to permit the light from the capillary to pass to the window of the tube. The quartz tube, itself, was held in position along the axis by two flat doughnut shaped steel disks, on the outer edge of which was a sleeve fitting snugly against the

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[1] R. C. Pankhurst, Proc. Phys. Soc. **52**, 707 (1940).
[2] W. H. B. Cameron, Phil. Mag. **3**, 110 (1927).

inside of the glass discharge tube. Likewise the inside circumference of each ring extended in a sleeve slightly smaller in diameter than the quartz tube, which reached into the tube and held it firmly. These snugly fitting steel sleeves, devised to prevent the discharge from leaking around the quartz tube, forced the current to pass through the capillary and heat it. The whole discharge tube was cooled by immersion in a water tank.

Although Pankhurst excited the spectra in an atmosphere of hydrogen, the present experiments were made in helium so that if the same spectrum were found it would be more certain that its carrier was in some way related to quartz. Also helium gives fewer atomic lines than hydrogen in the visible region, and interferes less with the silicon oxide bands. The tube was run for a long time with frequent charges of fresh helium to clean it, for these bands do not appear as long as many impurities are present. Even after many hours of operation, the tube had to be flushed with helium about every twenty minutes during an exposure. Hydrogen and water were the most persistent impurities.

When the tube was clean, the capillary glowed brilliantly yellow in the helium atmosphere and remained red hot for several seconds after the current was shut off. The capillary of a quartz tube which had been used for a long time became coated with sputtered electrode metal, easily removable with acid, and with a glassy brown material which resisted HCL, H_2SO_4, and mechanical scraping. Even aqueous HF did not act on it rapidly. It disappeared, however, if the capillary was heated in an oxygen flame, and the capillary became clear quartz again. This brownish material is thought to be SiO, an hypothesis supported by the disappearance of the brown color inside the capillary when the outside was heated to high temperatures. The identity of the substance was suggested by a review in *Chemical Abstracts* of an article[3] which could not be obtained in this country. The authors, Zintl and others, report that a bright brown powder, whose composition had the formula SiO, was condensed from vapor sublimed from a mechanical mixture of SiO_2 and Si under conditions such that the components themselves were not volatile. Slow condensation of the vapor on a hot surface, conditions which obtained in the discharge tube used here, produced a "brown-black brittle glass or shellac like membrane" also of the composition represented by the formula SiO. The authors further report that both the powder and the glassy material acted like a compound in that each had physical and chemical properties different from those of the parent substances or of the mixture SiO_2+Si.

The same review mentions the reaction of SiO at room temperature with atmospheric oxygen, to form SiO_2, a pyrophoric reaction if the SiO is powdered. This information indicates that the free energy of the reaction $SiO+\frac{1}{2}O_2\rightarrow SiO_2$ is much greater than that of the reaction $CO+\frac{1}{2}O_2\rightarrow CO_2$; that is SiO_2 is much more stable against dissociation into SiO than is CO_2 against dissociation into CO. That SiO_2 is more stable than CO_2 against dissociation into the elements is indicated by the heats of formation. Since the spectrum of CO_2 is readily excited in discharges at low currents, it is quite logical that the spectrum of SiO_2 could be excited under the same conditions. The great difficulty in exciting spectra of polyatomic molecules in discharges, namely that the high energy electrons break the molecules less stable than CO_2 into diatomic fragments, might be no difficulty in this case.

After exposures varying from 1 to 30 seconds, on a Hilger E-1 spectrograph, showed the spectrum to be clean and the band at 3840A to be very intense, an exposure of five hours was made on Process plates in the first and second orders of the 30-foot, 30,000 lines per inch, grating spectrograph. The 3840A band was of sufficient intensity to analyze, but the rotational structure of the several bands at 4270A was barely discernible. In hydrogen gas Pankhurst observed the 4270A region to be more intense than the 3840A region by a ratio 5:3. Since the excitation potential of helium is higher than that of hydrogen, electrons in a helium discharge have greater energy than in a hydrogen discharge. That the 4270A bands become less intense in helium than the 3840A band of SiO^+ then indicates that these bands are not emitted by an ionized molecule. The spacing of the rotational structure in these bands is com-

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[3] Zintl, Bräuning, Grube, Krings, and Morawietz, Zeits. f. anorg. allgem. Chemie **245**, 1–7 (1940); Chem. Abs. **35**, 1719 (1941).

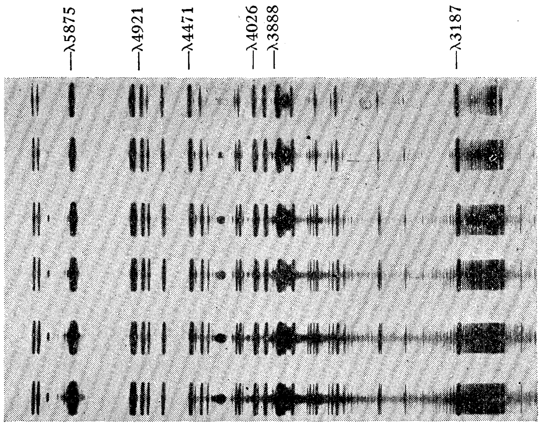

FIG. 1. Photograph from Hilger E-1 spectrograph showing spectrum of helium and some impurities, chiefly water. The small inner spectrum is that of the excited molecules in the quartz capillary. The $^2\Sigma\rightarrow{}^2\Sigma$ band of SiO at λ3840 in helium is much more intense than the group of bands at λ4270.

parable to or less than the spacing of the R branch in the 3840A band of SiO^+ where it is approaching a head. While it is possible that the 4270A bands belong to neutral SiO, it is the belief of the present author, based on the foregoing evidence and supported by the pyrophoric formation of SiO_2 from SiO, that they are emitted by the triatomic molecule SiO_2.

The plates taken on the Hilger E-1 show a possible band at about 6530A of about the same intensity as the 4270A bands, but no attempt has been made yet to photograph it on the big grating. These plates also show, in the region 3650 to 4270A, indications of the several bands reported by Pankhurst, but much less intense than the 4270A bands. It is easy to distinguish between the bands of silicon oxides and the remaining spectrum on the plates from the small spectrograph, because the spectrum from the capillary is distinct from the spectrum of the wider part of the quartz tube. When light from the discharge was focused in a spot on the slit of the Hilger E-1, light from the capillary formed a sharp bright pinpoint of light in the center of the spot. On the photographic plate there were then two spectra: (1) a wide spectrum of helium lines and OH bands through the center of which ran (2) a narrow spectrum of bands of silicon oxides and lines of silicon. See Fig. 1. The group of silicon lines at about 2510A and the many ultraviolet bands of neutral SiO appeared strongly in the spectrum from the capillary.

ANALYSIS

The band at 3840A is a (0,0) vibrational transition of the type $^2\Sigma\rightarrow{}^2\Sigma$, plus a corresponding (1,1) transition. The spin doublet structure is unresolved at low K values, then increasingly widens in the P branch. See Fig. 2. In the R branch, the doublet structure widens but the rotational structure closes up as it approaches the band head, so the spin components for successive values of K approach each other, overlap, and finally form two separate heads. The origin of the $1\rightarrow1$ band is displaced toward the red from the $0\rightarrow0$ origin. The Condon parabola should be practically a straight line, since as will be seen later the B' and B'' values are nearly equal. No other bands were observed. The wave numbers of lines for the $0\rightarrow0$ and $1\rightarrow1$ vibrational transitions are given in the Tables I and II.

Because the first P and R lines were diffuse or too faint, the location of ν_0 was uncertain. To find its position, the number of missing lines was determined by linear interpolation, and an arbitrary numbering was made. The actual spin doublet splitting, which in terms of the true K'' values (which are to be determined) must be

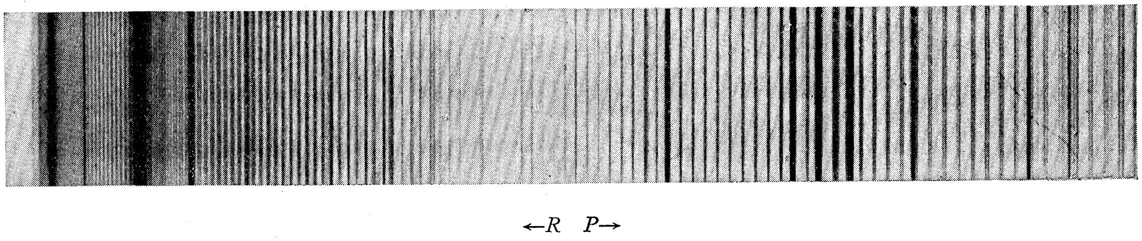

FIG. 2. The $^2\Sigma\rightarrow{}^2\Sigma(0\rightarrow0)$ 3840A transition of SiO^+. The spin doubling and the doublet heads are clearly visible. At the band origin the spin doublets of the $(1\rightarrow1)$ transition can be observed but are of much weaker intensity.

Table I. The system $^2\Sigma\rightarrow{}^2\Sigma$ of SiO$^+$ (cm^{-1}).

	(0→0) vibrational transition			
K''	P_a	P_b	R_a	R_b
3	26010.75			
4	26009.20		26022.25	
5	26007.79		26023.59	
6	26006.29		26024.98	
7	26004.77		26026.32	
8	26003.20		26027.64	
9	26001.68		26028.90	
10	26000.03		26030.19	
11	25998.29		26031.43	
12	25996.83		26032.69	
13	25995.12		26031.95	26033.82
14	25993.51		35.18	35.11
15	25991.83		36.41	36.28
16	25990.29	25990.16	—	37.56
17	88.57	88.40	38.78	38.68
18	86.90	86.74	39.98	39.88
19	85.22	85.04	41.14	41.00
20	83.51	83.34	42.23	42.13
21	81.75	81.58	43.39	43.19
22	79.82	79.80	44.50	44.34
23	78.24	78.05	45.57	45.41
24	76.46	76.24	46.71	46.47
25	74.59	74.39	47.72	47.49
26	72.84	72.58	48.70	48.48
27	71.10	70.75	49.78	49.52
28	69.27	68.90	50.82	50.47
29	67.37	67.08	51.85	51.54
30	65.46	65.15	52.78	52.51
31	63.60	63.14	53.76	53.45
32	61.66	61.37	54.71	54.41
33	59.77	59.43	55.65	55.26
34	57.88	57.48	56.50	56.21
35	55.94	55.56	57.49	57.07
36	53.98	53.53	58.30	57.90
37	51.96	51.56	59.17	58.79
38	49.94	49.60	59.98	59.66
39	48.02	47.58	60.82	60.43
40	46.02	45.61	61.64	61.25
41	44.02	43.56	62.45	62.01
42	41.98	41.52	63.26	62.86
43	39.90	39.43	64.01	63.59
44	37.77	36.78	64.78	64.34
45	35.72	35.25	65.55	65.03
46	33.66	33.14	66.24	65.80
47	31.49	31.08	66.96	66.48
48	29.38	28.83	67.79	67.09
49	27.12	26.78	68.34	67.78
50	25.04	24.64	68.99	68.44
51	22.88	22.44	69.66	69.08
52			70.26	69.66
53			70.85	70.26
54			71.41	70.85

	(1→1) vibrational transition			
K''	P_a	P_b	R_a	R_b
11	26007.15			
12	26008.32			
13	26009.58			
14	26010.86			
15	26012.00			
16	26012.99	26013.30		
17	26014.14	26014.50		
18	26015.19	26015.63		
19	26016.34	26016.72		
20	26017.46	26017.90	25960.06	25960.51
21	26018.54	26018.95	—	25958.40
22	26019.52	26019.95	25956.28	25956.72
23	26020.55	—	25954.55	25954.99
24	26021.69	26022.16	25952.80	—
25	26022.73	26023.14	25951.02	—
26			—	—
27			—	—
28			—	25946.09
29			25943.77	25944.35
30			—	25942.54
31			25940.06	25940.69

represented by the equations[4]

$$\Delta\nu_{12}(R)=(\gamma'-\gamma'')K+\tfrac{1}{2}(3\gamma'-\gamma'')\qquad K=0,\ 1,\ 2\cdots\ \text{in } R,$$

$$\Delta\nu_{12}(P)=(\gamma'-\gamma'')K-\tfrac{1}{2}(\gamma'+\gamma'')\qquad K=1,\ 2,\ 3\cdots\ \text{in } P,$$

was then plotted. The two lines obtained by plotting $\Delta\nu_{12}(P)$ against $m=K$ and $-\Delta\nu_{12}(R)$ against $m=-(K+1)$, form a continuous curve whose value at $m=0$ is $-\frac{1}{2}(\gamma'+\gamma'')$ and whose value at $m=-1$ is $-\frac{1}{2}(3\gamma'-\gamma'')$. The intercept of the curve with the m axis determined the true K numbering of the lines. This gave ν_0 with a small uncertainty. The slope of the curve gave

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[4] G. Herzberg, *Molecular Spectra and Molecular Structure* (1939), p. 274.

TABLE II. Constants of the 3840A ($^2\Sigma-{}^2\Sigma$) band of SiO$^+$ (cm^{-1}).

v'	v''	B'	B''	D'	D''	$\nu(v', v'')$
0	0	0.7180	0.7253	2.25×10^{-6}	2.11×10^{-6}	$26{,}015.05=\nu_{(0,0)}$
1	1	0.704	0.712			$25{,}991.44=\nu_{(1,1)}$

the value $|\gamma_0'-\gamma_0''|=0.011$ cm^{-1}. From the sum of the intercepts with the two ordinate axes, the value $\gamma_0'=\pm0.012$ cm^{-1} was obtained, and the other possible K numbering gave the value $\gamma_0'=-0.0005$ cm^{-1}. Consideration of the signs of the intercepts and their relation to the signs of the γ's leads to the conclusion that if $\gamma_0'=-0.0005$, then $\gamma_0''=-0.011$, a possibility which was discarded on the grounds that the spin splitting coefficients of the $^2\Sigma$ levels of the analogous molecule CO$^+$ are positive.[5] If one assumes that SiO$^+$ and CO$^+$ are in this respect similar, that is, that $\gamma_0''>0$, then one finds that the conditions $|\gamma_0'-\gamma_0''|=0.010$ and $|\gamma_0'|=0.012$ require $\gamma_0'>0$. It follows that $\gamma_0'=+0.012$ cm^{-1}, and $\gamma_0''=+0.002$ cm^{-1} or $\gamma_0''=+0.022$ cm^{-1}. Further information is needed to fix the value. The determination of γ from combination differences, namely $\gamma=\frac{1}{2}\{\Delta_2T_1(K+\frac{1}{2})-\Delta_2T_2(K-\frac{1}{2})\}$ was found inadequate because of the smallness of the γ's compared with experimental errors.

The quantities

$$[R_1(K+\tfrac{1}{2})-P_1(K+\tfrac{1}{2})]/(4K+2),$$
$$[R_2(K-\tfrac{1}{2})-P_2(K-\tfrac{1}{2})]/(4K+2),$$
$$[R_1(K-1+\tfrac{1}{2})-P_1(K+1+\tfrac{1}{2})]/(4K+2),$$

and

$$[R_2(K-1-\tfrac{1}{2})-P_2(K+1-\tfrac{1}{2})]/(4K+2)$$

were plotted against $K(K+1)$. From the slopes of the lines D' and D'' were determined, and from the intercepts at $K=0$, B' and B'' were determined.[6] The very approximate values $\omega_0'=811$ cm^{-1} and $\omega_0''=851$ cm^{-1} were calculated from the relation $\omega^2=4B^3/D$. Although this relation is an exact one, the values of D are not accurate enough to give good values of ω.

This same procedure was followed to determine the constants of the 1→1 transition (Table II). However, not enough lines could be measured to determine the D values because the transition is severely overlapped by the 0→0 band. The quantity $\nu_{0,0}-\nu_{1,1}=23.61$ cm^{-1} agrees with the calculated difference of the values of ω in order of magnitude.

The B values and the doublet structure of the lines show that the band at 3840A is emitted by the ionized molecule SiO$^+$.

If the SiO$-$SiO$^+$ energy level diagrams are roughly analogous to those of CO$-$CO$^+$ the existence of a $^2\Pi\rightarrow{}^2\Sigma$ band of SiO$^+$ lying in the infra-red can be expected, probably lying at wave-lengths greater than 8000A.

The writer is very grateful to Dr. S. Mrozowski who suggested this problem, for his kindness, pertinent suggestions, and frequent help, and to Professor R. S. Mulliken for his unfailing interest and valuable advice.

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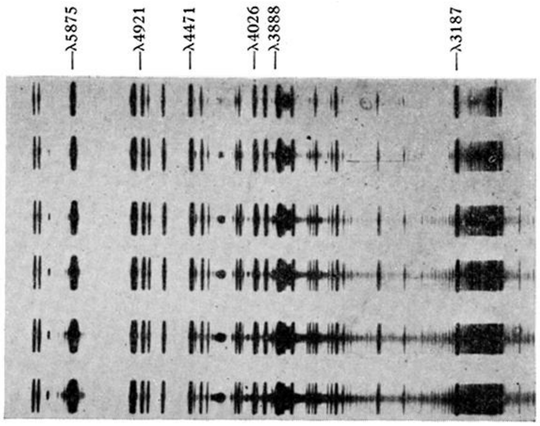
[5] L. H. Woods, Phys. Rev. **63**, 431 (1943).

[6] See reference 4, p. 199.



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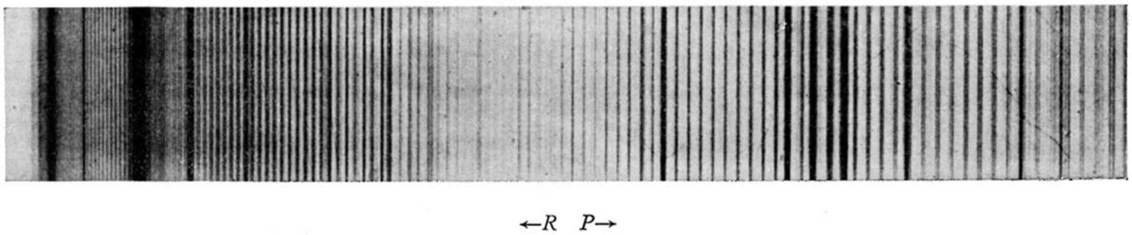

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