[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

Line Spectrum of Samarium Ion in Crystals and its Variation with the Temperature

BY SIMON FREED AND J. G. HARWELL

The magnetic behavior of Sm^{+++}[1] and the absorption spectra[2] showed that there was an equilibrium distribution of the ions between different electronic configurations. The present work was instituted with the view of obtaining quantitative data concerning the differences in energy between the various configurations. These differences may be looked upon as originating through the action of the electric fields about Sm^{+++} in the lattice. They are a measure of their symmetry and intensity. Recently, Miss Amelia Frank[3] obtained rough agreement with the magnetic susceptibility at higher temperatures by taking into account the presence of the activated state $^6H_{7/2}$, presumably about 1000 cm.$^{-1}$ higher in energy than the basic state $^6H_{5/2}$. The agreement is rather surprising since both the basic state, $^6H_{5/2}$ and active state, $^6H_{7/2}$ are largely decomposed into sublevels of wide separation by the electric fields of the lattice. The specific heat of Sm^{+++}[4] at low temperature has given a measure of the separations between the basic electronic levels. It appeared that energy of about 160 cm.$^{-1}$ (450 cal./mole) had to be supplied to activate a mole of Sm^{+++} in the sulfate. Even greater intervals may have resulted in the decomposition of the $^6H_{5/2}$ term, but they must be so great that relatively few ions exist in the upper level.

The present work is mainly concerned with the effect of the electric fields upon the state $^6H_{5/2}$, that is, with levels which are sufficiently occupied at ordinary temperatures to have their presence recorded in the absorption spectrum. They are identified by the change in the relative intensity of the lines as the temperature changes, more especially by those instances when a line increases in intensity apparently at the expense of a neighboring line. When this line is of higher frequency than the one whose intensity is decreasing, there is considerable probability that the lines arise at two levels slightly different in energy and end in a common energy level. And the recurrence of the same interval in different regions of the spectrum practically establishes the existence and separation of the lower energy levels.

The experimental method has been described[5] in another connection. A hydrogen discharge tube served as the source of the continuous radiation

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[1] Freed, THIS JOURNAL, **52**, 2702 (1930).

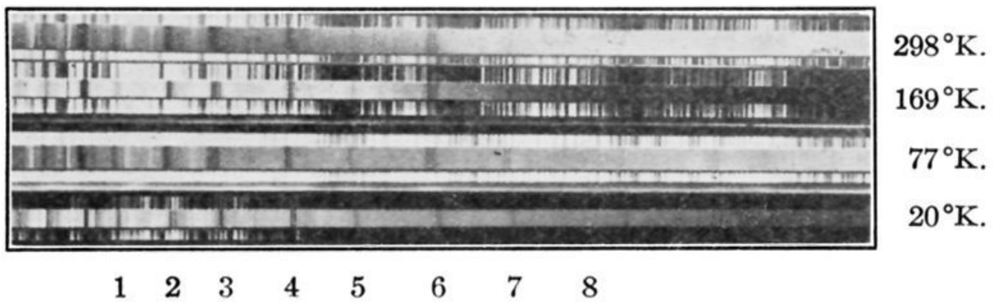
[2] Freed and Spedding, *Nature*, **123**, 525 (1929).

[3] Amelia Frank, *Phys. Rev.*, **39**, 119 (1932).

[4] Ahlberg and Freed, *ibid.*, **39**, 540 (1932).

[5] Freed, *ibid.*, **38**, 2122 (1931).

and the spectra extended from 4200 to about 2200 Å. A Hilger spectrograph of the type E2 was employed. The radiation was passed parallel to the optic axis of the hexagonal crystal[6] $Sm(C_2H_5SO_4)_3 \cdot 9H_2O$ which was about 0.5 mm. thick. For the purpose of lowering the temperature of the crystal, liquid hydrogen (20°K.), liquid nitrogen (77°K.), and liquid ethylene (169°K.) were used, all boiling at atmospheric pressure. The average absolute error in the measurement of the lines is about 5 cm.$^{-1}$. Some of the lines were faint or diffuse and there has been listed next to each line in the table the number of times it was measured and the reproducibility of the measurement. The recorded intensities are visual estimates and should be trusted only as a measure of relative intensity within a restricted region of the spectrum and in spectra originating at the same temperature.



Absorption spectrum of Sm^{+++} in $Sm(C_2H_5SO_4)_3 \cdot 9H_2O$.

The group of lines assigned to energy levels have undergone such changes in intensity that the increase or decrease in intensity of one line with respect to another could be told at a glance on an enlargement of the spectrogram.

ABSORPTION LINES OBTAINED AT 20°K.

Intensity	Wave number	Measured	Intensity	Wave number	Measured
2 D	42,940 ± ?	1	2 D	28,241 ± 1	2
2 D	42,915 ± 1	2	1 S	28,184 ± ?	1
3 S	42,867 ± 2	4	3 D	28,149 ± 0	2
3 B	42,834 ± 1	4	2 D	28,138 ± 3.5	2
5 S	42,542 ± 3	3	7 D	27,639 ± 1	2
5 S	42,513 ± 3	3	10 B	27,629 ± 1	2
5 B	42,457 ± 1	4	7 B	27,597 ± 0	2
5 B	42,321 ± 1	4	5 B	27,585 ± 3.5	2
1 S	42,260 ± 2	4	5 B	27,537 ± 0	2
2 S	42,025 ± 1	4	2 D	27,469 ± 1	2
Faint	42,002 ± ?	1	Faint	27,403 ± ?	1
3 B	41,949 ± 1	4	Faint	26,934 ± ?	1
Faint	38,381 ± ?	1	Faint	26,885 ± ?	1
2 S	37,508 ± 1	2	3 D	26,735 ± 2	3
Faint	37,486 ± ?	1	1 S	26,708 ± ?	1
2 S	37,474 ± 2	2	5 B	26,670 ± 1.5	4

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[6] Jaeger, *Rec. trav. chim.*, **33**, 362 (1914).

ABSORPTION LINES OBTAINED AT 20°K. *(Concluded)*

Intensity	Wave number	Measured	Intensity	Wave number	Measured
Faint	36,540 ± ?	1	4 B	26,650 ± 0	2
Faint	36,523 ± ?	1	4 S	26,621 ± 0	2
3 S	35,857 ± 1	2	10 B	26,597 ± 2	2
3 B	35,834 ± 2	4	Faint	26,566 ± ?	1
3 D	34,464 ± 6	4	Faint	26,514 ± ?	1
Faint	33,800 ± ?	1	Faint	26,487 ± ?	1
2 S	33,656 ± 1	2	Faint	26,449 ± ?	1
2 D	33,641 ± 1	2	Faint	26,408 ± ?	1
Faint	33,569 ± 1	2	Faint	26,372 ± ?	1
Faint	33,515 ± ?	1	2 D	26,296 ± ?	1
Faint	33,490 ± 2	2	2 S	26,261 ± ?	1
1 S	33,103 ± ?	1	2 S	26,230 ± ?	1
1 S	33,074 ± ?	1	2 S	25,943 ± ?	1
3 S	32,721 ± 0	2	2 S	25,915 ± ?	1
4 B	32,708 ± 1	2	2 S	25,793 ± ?	1
2 S	32,691 ± 1	2	2 S	25,775 ± 1	2
Faint	32,632 ± ?	1	2 S	25,739 ± 4	3
3 D	31,530 ± 1	2	2 S	25,714 ± ?	1
2 B	31,511 ± 1	2	Faint	25,614 ± ?	1
5 S	31,463 ± 0	2	5 B	25,586 ± 3	4
4 B	31,448 ± ?	1	5 B	25,543 ± 1.5	2
2 D	31,401 ± 1	3	5 S	25,536 ± 2	2
1 D	31,353 ± 4	4	1 S	25,485 ± 5	2
Faint	30,218 ± ?	1	2 D	25,186 ± 0	2
2 S	30,211 ± 1.5	2	1 S	25,151 ± ?	1
2 S	30,133 ± ?	1	4 D	25,107 ± 0	2
3 D	30,115 ± 1.5	2	2 S	25,083 ± 3	2
Faint	30,106 ± 1.5	2	1 S	24,987 ± ?	1
1 D	30,071 ± 1.5	2	1 S	24,965 ± ?	1
2 D	30,058 ± 1	2	10 B	24,919 ± 0	3
Faint	29,970 ± 0	2	10 B	24,869 ± 4	4
2 S	29,953 ± 2.5	2	1 S	24,730 ± 4	3
Faint	30,000 ± ?	1	1 S	24,681 ± ?	1
1 D	29,937 ± ?	1	1 S	24,669 ± 1.5	2
1 D	29,255 ± 0.50	2	5 B	24,522 ± 1	2
1 D	29,173 ± 0	2	1 S	24,487 ± ?	1
Faint	29,084 ± ?	1	1 S	24,466 ± 3	2
5 B	29,008 ± 0	2	1 S	24,451 ± ?	1
7 S	28,996 ± 3	2	3 D	24,417 ± 4	3
4 S	28,964 ± 1.5	2	2 S	24,376 ± 2	3
4 D	28,949 ± 1	2	2 D	24,334 ± 2	2
5 S	28,936 ± 1	2	1 S	24,082 ± 5	2
5 D	28,924 ± 1	2	1 S	24,054 ± ?	1
Faint	28,251 ± 2	2	7 S	24,016 ± 0	4

ABSORPTION LINES OBTAINED AT 77°K.

Intensity	Wave number	Measured	Intensity	Wave number	Measured
Faint	42,862 ± 1	2	3 D	30,121 ± 2	2
3 B	42,834 ± 1	4	1 B	30,067 ± 1	4
2 S	42,538 ± 1	2	5 B	29,010 ± 2	4

Absorption Lines Obtained at 77 °K. (*Concluded*)

Intensity	Wave number	Measured	Intensity	Wave number	Measured
2 S	42,513 ± ?	1	5 S	28,996 ± ?	1
3 B	42,457 ± 3	4	Faint	28,978 ± ?	1
3 B	42,430 ± 1	2	5 B	28,945 ± 3	4
3 D	42,423 ± 1	2	3 S	28,936 ± ?	1
2 S	42,374 ± ?	1	Faint	28,251 ± ?	1
2 S	42,351 ± ?	1	5 B	27,647 ± 1	4
3 B	42,319 ± 1	4	2 D	27,595 ± 2	4
2 S	42,283 ± ?	1	5 B	27,540 ± 1	4
2 B	42,251 ± 1	4	5 B	27,478 ± 1	4
Faint	42,023 ± 2	2	1 S	26,737 ± 1	3
1 S	41,976 ± ?	1	1 S	26,708 ± 1	4
3 B	41,949 ± 1	4	5 S	26,664 ± 2	3
1 S	37,579 ± ?	1	5 S	26,643 ± 2	3
1 S	37,564 ± ?	1	5 S	26,623 ± 2	3
1 S	37,536 ± 3	2	10 B	26,604 ± 1	3
1 S	37,508 ± 4	2	5 S	26,581 ± 1	2
1 S	37,481 ± ?	1	Faint	26,432 ± ?	1
2 D	37,450 ± 1	4	Faint	26,378 ± ?	1
Faint	37,404 ± ?	1	1 S	26,257 ± 0	2
Faint	37,306 ± ?	1	Faint	25,976 ± 2	2
Faint	37,287 ± ?	1	Faint	25,931 ± 1	2
Faint	37,275 ± ?	1	1 S	25,786 ± 1	2
1 S	37,000 ± 1	2	1 S	25,746 ± 1	2
2 D	35,846 ± 2	4	1 S	25,664 ± ?	1
2 D	35,833 ± 0	2	2 S	25,588 ± 2.5	4
2 D	35,777 ± 3	4	1 S	25,544 ± ?	1
Faint	34,714 ± ?	1	2 S	25,532 ± 1	3
Faint	34,628 ± ?	1	1 S	25,503 ± 1	2
2 D	34,467 ± 2	4	2 D	25,186 ± 5	3
1 S	34,415 ± 0	2	1 S	25,153 ± 0	3
1 S	34,409 ± 1	3	2 D	25,108 ± 2	3
1 S	34,384 ± ?	1	2 B	25,077 ± 0	2
1 S	34,370 ± ?	1	1 S	25,008 ± 2	2
1 S	34,351 ± 2	4	1 S	24,981 ± 3	3
3 B	32,723 ± 1	4	1 S	24,959 ± ?	1
1 S	32,686 ± 2	4	1 S	24,935 ± 0	2
2 D	32,655 ± 2	4	1 S	24,910 ± 2	3
2 D	31,533 ± 1	2	10 B	24,888 ± 2	2
3 D	31,511 ± ?	1	10 B	24,794 ± 1	4
2 D	31,502 ± 1	3	2 S	24,725 ± ?	1
3 D	31,497 ± ?	1	5 B	24,532 ± 1	2
3 D	31,461 ± 1	4	5 B	24,493 ± 1	2
2 D	31,408 ± 2	4	2 S	24,136 ± ?	1
3 D	31,364 ± 1	4	Faint	24,047 ± ?	1
			7 S	24,016 ± 0	4

Absorption Lines Obtained at 169 °K.

Intensity	Wave number	Measured	Intensity	Wave number	Measured
Faint	37,514 ± ?	1	5 B	27,549 ± 0	2
2 D	37,457 ± 1	2	5 B	27,491 ± 0	2

ABSORPTION LINES OBTAINED AT 160°K. *(Concluded)*

Intensity	Wave number	Measured
Faint	35,838 ± 0	2
Faint	35,777 ± 0	2
Faint	34,680 ± ?	1
Faint	34,533 ± ?	1
Faint	34,467 ± 1	2
Faint	34,418 ± 0	2
Faint	34,360 ± 1	2
3 D	32,728 ± 1	2
3 D	32,666 ± 1	2
1 D	31,903 ± ?	1
1 D	31,883 ± ?	1
Faint	31,540 ± ?	1
3 B	31,510 ± ?	1
Faint	31,505 ± ?	1
Faint	31,494 ± ?	1
2 D	31,458 ± 1.5	2
2 D	31,416 ± 1	2
3 D	31,371 ± 1	2
2 D	31,295 ± ?	1
1 D	31,259 ± ?	1
1 S	30,169 ± ?	1
Faint	30,158 ± ?	1
1 S	30,118 ± 1	2
2 D	30,072 ± 2	2
5 B	29,015 ± 2.5	2
7 B	28,955 ± 0	2
1 S	28,673 ± ?	1
1 S	28,642 ± ?	1
5 B	27,639 ± 0	2
1 S	27,591 ± 1	2
1 S	27,439 ± ?	1
1 S	27,405 ± ?	1
1 S	27,349 ± ?	1
1 S	27,307 ± ?	1
Faint	26,850 ± ?	1
Faint	26,800 ± ?	1
1 S	26,762 ± ?	1
1 S	26,736 ± 0	2
5 S	26,654 ± 1.5	2
5 B	26,609 ± 2.5	2
2 S	25,596 ± 2	2
1 D	25,550 ± 0	2
1 S	25,200 ± 0	2
1 D	25,119 ± 1.5	2
1 S	24,936 ± 1	2
1 S	24,919 ± 2	2
10 B	24,895 ± 2	2
10 B	24,814 ± 0	2
1 S	24,742 ± ?	1
1 S	24,669 ± 1	2
1 S	24,627 ± 3	2
3 D	24,567 ± ?	1
5 B	24,529 ± 3	2
5 B	24,511 ± ?	1
1 S	24,535 ± 1	2
1 S	24,350 ± 0	2
5 S	24,037 ± 1	2
3 S	23,986 ± 1.5	2
3 D	23,941 ± 1	2

For convenience, the groups have been numbered on the reproductions of the spectra. Below each diagram is given a list of the frequencies derived from the energy levels and these are compared with the observed frequencies for each group of lines. All the deviations are well within the errors of measurement. Groups *4*, *7*, *8* and *10* under low dispersion appear as doublets having the same energy difference at each temperature. Under higher dispersion, each line is found to be doubled and with the data in hand it is impossible to prove rigorously whether the "fine-structure" energy level belongs to the basic term system or not. More data, we are informed, will be available soon in a more extensive paper by Spedding and Bear from Berkeley.[7] If the "fine-structure" level is assigned to the basic multiplet, it becomes possible to include the quartet *5* and also the sextets *3* and *6*. This arrangement of levels has a considerable degree of probability and by its aid all the multiplets in which marked intensity changes occur can be interrelated.

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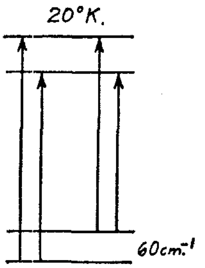
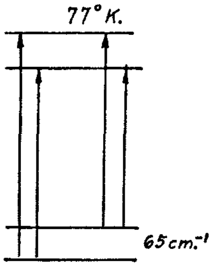
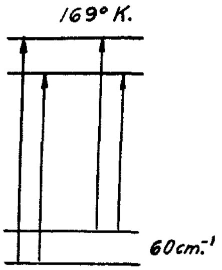
[7] Spedding and Bear, *Phys. Rev.*, in press.

Below is a typical example of an energy level pattern which the quartets *4*, *7*, *8* and *10* accord with and also the basic separations which are valid for all of them. The intensities too agree with these assignments.







Group	Temp., °K.	Separation of upper level, cm.⁻¹	Calcd. line, cm.⁻¹	Observed line, cm.⁻¹	Deviation, cm.⁻¹
4	20	12		29,008 (accepted)	
			28,996	28,996 ± 3	0
			28,948	28,949 ± 1	1
			28,936	28,936 ± 1	0
	77	12		29,010 (accepted)	
			28,998	28,996 ± ?	2
			28,945	28,945 ± 3	0
			28,933	28,936 ± ?	3
	169			29,016 (accepted)	
			28,956	28,955 ± 0	1
7	20	12		32,721 (accepted)	
			32,708 too faint		
	77			32,723 ± 1 (accepted)	
			32,658	32,655 ± 2	3
	169			32,728 ± 1 (accepted)	
			32,668	32,666 ± 1	2
8	20	23		35,857 (accepted)	
			35,834	35,834	
	77	12		35,846 ± 2 (accepted)	
			35,834	35,833 ± 0	1
			35,781	35,777 ± 3	4
	169			35,838 ± 0	
			35,778	35,777 ± 0	1
10	20			42,321 ± (accepted)	
			42,261	42,260 ± 2	1
	77			42,319 ± 1 (accepted)	
			42,254	42,251 ± 1	3

Some of the lines which one would normally expect from these levels were too faint to be measured. At higher temperatures, some of the lines were so diffuse that the average between two unresolved lines is given.

There can be no doubt concerning the existence of an interval of 60 cm.$^{-1}$ (at 20°K., 65 cm.$^{-1}$ at 77°K. and 60 cm.$^{-1}$ at 169°K.) between two energy levels in the basic multiplet. Also, there is little doubt but that this interval can be related to the influence of the electric fields of the lattice upon $^6H_{5/2}$. It may be predicted at this point that a close study of the specific heat measurements at low temperatures will confirm the existence of this interval.

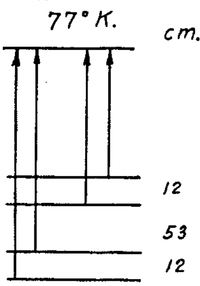
Based upon the same pattern of levels as those given above, the quartet *5* will have the following basic intervals: 60 cm.$^{-1}$ at 20°K., 54 cm.$^{-1}$ at 77°K. and 43 cm.$^{-1}$ at 169°K.

Group	Temp., °K.	Calcd. line, cm.$^{-1}$	Obs. line, cm.$^{-1}$	Deviation
5	20		30,115 ± 2 (accepted)	
		30,130	30,133 ± ?	3
		30,070	30,071 ± 2	1
		30,055	30,058 ± 1	3
	77		30,121 ± 2 (accepted)	0
		30,067	30,067 ± 1	
	169		30,118 ± 1	
		30,075	30,072 ± 2	3

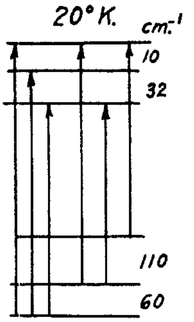
Now it is clear that if the 12 cm.$^{-1}$ interval (the "fine-structure" interval) is inserted in the basic multiplet of *4, 7, 8, 10,* the group *5* fits into the same scheme as groups *4, 7, 8, 10* and we shall see later the sextets *3* and *6* will also be associated with the same levels. As an example we shall give the energy levels of group *4* and *5* at 77°K., employing the same basic multiplet for both.

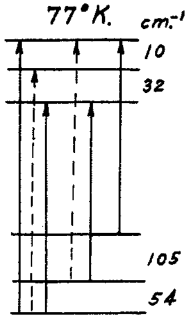
The fact that the "fine structure" interval is of the same magnitude in all groups (with the possible exception of *8*) is evidence for including it in the basic multiplet. Its inclusion results naturally in any attempt to superpose the levels of the groups for the purpose of obtaining all the components into which $^6H_{5/2}$ has been split. It must be stated again that more data are necessary for this purpose, especially spectra at the temperature of liquid helium.

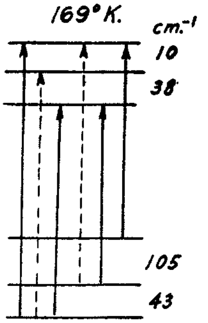
Quartets *4* and *5*



Since the spectrum of Sm^{+++} consists of rather isolated groups, one would expect the lines to originate and end at neighboring levels. The intensities justify this point of view as the components of greater frequency always become more intense as the temperature is reduced. The sextets *3* and *6* contain the same energy interval as the quartet *5* and the intensities of corresponding lines behave in the same way with regard to temperature. We shall therefore associate *3* and *6* with the same basic states as *5*. Below is the energy level pattern of *3* based upon that of *5*.







Temp., °K.	Calcd. line, cm.$^{-1}$	Obs. line, cm.$^{-1}$	Deviation, cm.$^{-1}$
20		27,639 ± 1 (accepted)	
	27,629	27,629 ± 1	0
	27,597	27,597 ± 0	0
	27,579	27,585 ± 6	6
	27,537	27,537 ± 0	0
	27,469	27,469 ± 1	0
77		27,637 ± 1 (accepted)	
	27,595	27,595 ± 2	0
	27,541	27,540 ± 1	1
	27,478	27,478 ± 1	0
169		27,639 ± 0	
	27,591	27,591 ± 1	0
	27,548	27,549 ± 0	0
	27,491	27,491 ± 0	0

The sextet *6* follows a similar pattern, its first interval being identical at each temperature with that of *3* but the over-all separation of the basic multiplet is slightly different. This difference can probably be ascribed to another "fine structure" interval in the basic term system.

The lines which have been studied here because of the variation in their intensities constitute about one-half the prominent lines of the spectrum.

A part of this experimental work was done by one of us (S. F.) during his stay in the laboratory of Professor de Haas, Leyden, Holland, while he was a fellow of the John Simon Guggenheim Memorial Foundation.

Summary

The absorption spectra of Sm^{+++} in the hexagonal crystal $Sm(C_2H_5SO_4)_3\cdot 9H_2O$ were taken parallel to the optic axis at 20, 77 and 169°K. Absorption lines are listed in the region of the spectrum between 4200 Å. and 2200 Å.

This paper is principally concerned with the various electronic configurations in the basic multiplet, especially as they result from the interaction of Sm^{+++} and the electric fields of the lattice. In consequence, all the lines

whose relative intensities vary with the temperature have been studied in terms of energy level diagrams.

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Photodissociation of Hydrogen Peroxide in the Presence of Hydrogen and Carbon Monoxide and the Recombination of OH Radicals

BY GUENTHER VON ELBE[1]

The ultraviolet absorption spectrum of hydrogen peroxide in the gas phase has been determined by Urey, Dawsey and Rice.[2] The authors conclude that for every absorbed light quantum two hydroxyl radicals are formed according to the equation

$$H_2O_2 + h\nu = 2OH \qquad (1)$$

Hydroxyl radicals are also involved in Bonhoeffer and Haber's scheme of the hydrogen and carbon monoxide combustion[3]

$$\begin{aligned} H + O_2 + H_2 &= H_2O + OH &(2)\\ OH + H_2 &= H_2O + H &(3)\\ \text{or } OH + CO &= CO_2 + H &(4) \end{aligned}$$

This scheme has been discussed by Frankenburger and Klinkhardt[4] who carried out experiments on the action of photochemically generated hydrogen atoms in hydrogen and oxygen mixtures. They propose that reaction (2) should be followed either by (3) or by

$$OH + OH + M = H_2O_2 + M \qquad (5)$$

and that reaction (3) should require an activation energy of not less than 14,000 cal. An activation energy of that order would keep the rate of (3) sufficiently small until about 400° to make (5) the predominant reaction. The formation of chains would thus be prevented until about that temperature, which is consistent with the observed behavior of hydrogen–oxygen mixtures.

In the present work, mixtures of hydrogen peroxide vapor with hydrogen or carbon monoxide were exposed to the light of a condensed zinc spark. A small but distinct reaction was observed in both cases, suggesting the occurrence of reaction (1) and (3) or (1) and (4). In view of Frankenburger and Klinkhardt's work, most of these experiments were made with hydrogen. If OH was formed, according to (1), these experiments should allow one to test the reaction scheme proposed by these authors. In the

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[1] Research Associate, University of Virginia.

[2] Urey, Dawsey and Rice, THIS JOURNAL, **51**, 1371 (1929).

[3] Bonhoeffer and Haber, *Z. physik. Chem.*, **137A**, 263 (1928).

[4] Frankenburger and Klinkhardt, *Trans. Faraday Soc.*, **123**, 431 (1931); *Z. physik. Chem.*, **15B**, 421 (1932).