THE SPECTRAL STRUCTURE OF THE LUMINESCENCE EXCITED BY THE HYDROGEN FLAME.

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Synopsis.

Luminescence Spectra Excited by the Hydrogen Flames.—Calcium oxide and the Lenard and Klatt phosphorescent sulphides Nos. 3 and 13 were studied by the aid of a spectrophotometer. The broad-banded spectra were found to consist of the same components, individually overlapping and forming overlapping series of constant frequency intervals. Series and individual components were identified with those entering into the spectral structure of these substances when excited to fluorescence by light, but the relative intensities of the bands were found to differ with the mode of excitation.

THE discovery of the luminescence of many substances when partially bathed in the hydrogen flame but at a temperature below red heat has very recently been reported by Dr. E. L. Nichols.[1] Since the hydrogen flame luminescence was found to be very brilliant when air-slaked lime was presented to the outer layer of the flame this substance was first studied by the author. The specimen was found to fatigue or disintegrate under the flame hence a fine brass gauze was filled with the lime and slowly rotated at a constant speed before the flame. The size of the flame was kept as constant as possible by the use of a reducing valve and a gas regulator. The impossibility of maintaining the flame sufficiently constant necessitated the use of the statistical method and each spectrophotometric curve represents an average of many trials, properly weighted. Fig. 1 represents the distribution of brightness in the visible spectrum of the air-slaked lime. The luminescence before dispersion was of an orange-yellow color and the distribution of color between wave-lengths of .61 μ and 53 μ is indicated in the curve, the maximum lying near .56 μ. The subsidiary crests and shoulders, marked by short vertical lines, although of widely varying intensities and forms are not without a systematic arrangement. When the reciprocals of the wave-lengths of the crests are studied they are readily found to lie in two series of a constant interval of 42 units, designated as the "*A*" or "*B*" series. These wave-lengths and reciprocals are given in Table I. together with the wave-lengths obtained from the luminescence by excitation with the iron spark of natural calcite. The spectral analysis

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[1] E. L. Nichols, 1920.

by the iron spark excitation was done by Nichols, Howes and Wilber with the aid of an elaborate photometric control.[1] The positions of the bands are the same under the two different modes of excitation and the structure of the calcite and air-slaked lime must contain the same luminescing system. Because of the nature of the crests it is not considered possible to locate the positions of the bands within ten Ångström units of the proper places hence the agreement found in Table I. is conclusive. The more interesting fact is that although the general form of the spectral envelope is quite different from that obtained by the iron spark excitation yet the partially resolved crests are in no way shifted by change in mode of excitation. The form of the envelope indicated in Fig. 1 corresponds

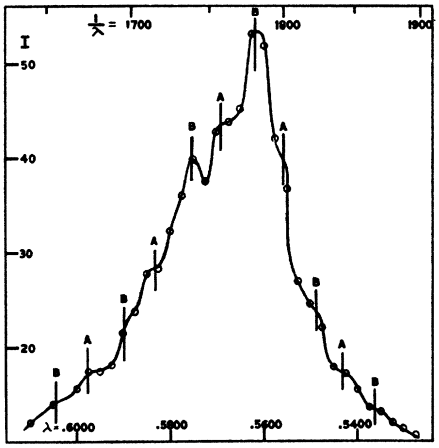

Fig. 1.

TABLE I.

Luminescence of Lime.

Series *A* (Interval = 42).				Series *B* (Interval = 42).			
Band *A*.	Hydrogen Flame, λ.	Iron Spark, λ.	Frequency Unit, 1/λ × 10³.	Band *B*.	Hydrogen Flame, λ.	Iron Spark, λ.	Frequency Unit, 1/λ × 10³.
A_4......	.5975	.5977	1673	B_4.......	.6045	.6046	1654
A_5......	.5833	.5831	1715	B_5.......	.5894	.5896	1696
A_6......	.5689	.5692	1757	B_6.......	.5755	.5754	1738
A_7......	.5563	.5559	1799	B_7.......	.5617	.5618	1780
A_8......	.5432	.5432	1841	B_8.......	.5488	.5488	1822
				B_9.......	.5365	.5365	1864

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[1] Nichols, Howes and Wilber, "The Photo-luminescence and Kathodo-Luminescence of Calcite," PHYSICAL REVIEW (2), Vol. 12, p. 365, Nov., 1918.

more nearly to that for the calcite under the iron spark excitation at 200° C. than at 20° C. See Fig. 13, page 364; Nichols, Howes & Wilber (loc. cit.). This is naturally so, since the hydrogen flame warmed the specimen to a temperature of approximately 350° C. Temperature changes the relative intensities of the crests but the "*A*" and "*B*" series are independent of both temperature and mode of excitation for their frequencies.

The Lenard and Klatt sulphide known as No. 3 is a calcium compound containing both bismuth and fluorine as active elements. Since the spectral structure of this preparation had previously[1] been studied under the excitation of the zinc spark it was thought that an interesting comparison could be based on the resemblance between the zinc spark and hydrogen flame excitation. The spectrum had been known to exhibit a strong band in the blue and a broader but much dimmer band in the orange. See Fig. 4, p. 265, E. L. Nichols (loc. cit.). Under hydrogen flame excitation at a very moderate temperature the blue band was found in approximately the same location but the orange band was of much greater proportionate intensity. To produce the orange band the mounting was rotated more slowly to allow a more favorable temperature. In some trials the specimen was mounted in the gauze without rotating but in such cases every precaution was taken to maintain the temperature constant but below red heat. A comparison of the location of the crests of the complex orange band under the two different modes of excitation is given in Table II. One new band was found at .6360 μ. The agreement is as good as could be expected and no systematic deviation is evident. The bands are undoubtedly in the same position and

Table II.

Luminescence of Calcium Bismuth Sulphide, No. 3.

Hydrogen Flame, λ.	Zinc Spark, λ.	Frequency Unit, $1/\lambda \times 10^3$.	Frequency Interval, $\Delta(1/\lambda) \times 10^3$.
.6365	——	1575	39
.6208	.6200	1614	39
.6048	.6049	1653	39
.5912	.5910	1692	39
.5785	.5781	1731	39
.5650	.5650	1770	39
.5530	.5528	1809	39
.5415	.5411	1848	39
.5300	.5300	1887	

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[1] E. L. Nichols, "Spectral Structure of the Phosphorescence of Certain Sulphides," Proceedings of the American Philosophical Society, Vol. 55, p. 496, 1916

are spaced by a constant frequency interval of 39 units. Again the spectrophotometric curve is not similar to that obtained by the zinc spark excitation, as can be noted by a comparison of Fig. 4, page 265 of the paper last cited with Fig. 2 of the present paper. Evidently a similar vibrating system has been excited by the new method at a slightly higher temperature since the same bands, having the same constant frequency interval of 39 units, are present.

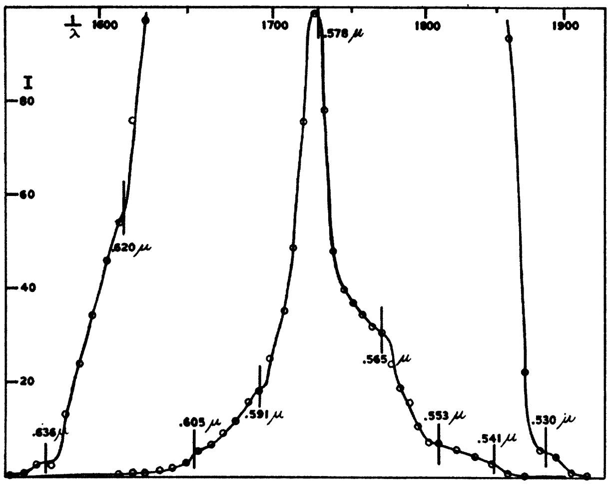

Fig. 2.

To make sure that the identity of band structure was not accidental another sulphide of Lenard and Klatt containing strontium and bismuth was excited by the hydrogen flame. This compound, known as No. 13, had been previously studied by Nichols.[1] The undispersed light was of a delicate blue color and so dim that a considerable study of the method of mounting was necessary before sufficient radiation could be obtained to render spectrophotometric measurements possible. The light from the 4-candle-power tungsten lamp was reduced greatly by interposing three or more sheets of white porcelain between it and the comparison slit. The spectrophotometric field was almost colorless and the time required for eye accommodation about thirty minutes. Since the range of intensities was unusually great, the curve shown in Fig. 3 is broken into five sections to facilitate the location of the partially resolved crests. With the exception of crest .494 μ and .480 μ the presence of partially hidden bands is conclusive. Table III. gives the wave-lengths of these bands together with those of the same specimen excited by the zinc spark.

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[1] E. L. Nichols, loc. cit.

There is again evidence of an identical underlying system of component bands under the two different modes of excitation. The distribution of intensities is again different and two new bands were discovered which fortunately fit the series intervals. The new bands are .5414 μ and .5080 μ.

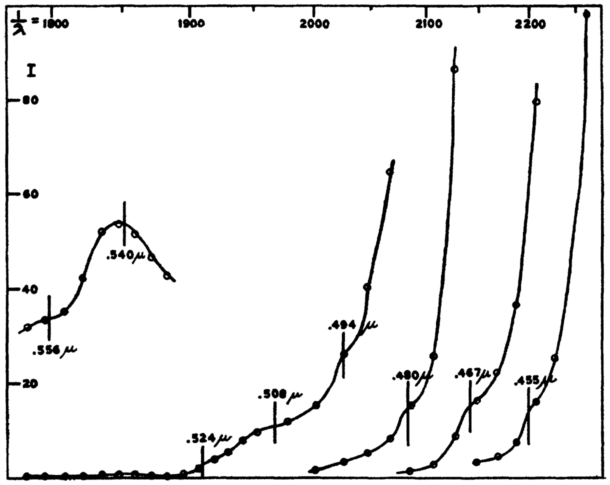

Fig. 3.

As a digression from the field of comparison of the hydrogen flame excitation with that of the metallic spark an attempt was made to compare two Lenard and Klatt preparations which have the same solid solvents and active metals but a different flux under the same hydrogen flame. The formula given for the Lenard and Klatt sulphide No. 13 is $SrSBiNa_2SO_4$ and the series has been given in Table III. The formula given for the Lenard and Klatt Sulphide No. 9 is SrSBiK Phosphate;

Table III.

Luminescence of Strontium Bismuth Sulphide, No. 13.

Hydrogen Flame, λ.	Zinc Spark, λ.	Frequency Unit, $1/\lambda \times 10^3$.	Frequency Interval, $\Delta\ 1/\lambda \times 10^3$.
.5565	.5562	1793	58
.5414	——	1851	58
.5235	.5238	1909	58
.5080	——	1967	58
.4938	.4938	2025	58
.4800	.4801	2083	58
.4668	.4670	2141	
.4546	.4547	2199	

that is, both contain strontium sulphide with bismuth for the element active in luminescence but the flux is a sodium sulphate in the first preparation and a potassium phosphate in the second preparation. The problem was to ascertain the effect of change of flux on the band series. It was thought that the flux might produce little or no effect on the location of the bands. The hydrogen flame was applied to preparation No. 9 and a beautiful dull blue glow appeared. The spectrophotometric curve, not presented in this paper, was obtained with some difficulty from six independent explorations and found to be somewhat similar to that obtained for specimen No. 13. Table IV. gives the wave-lengths and frequency units for comparison with Table III. The interval for No. 9. is 51 frequency units while that for No. 13 is 58 frequency units and it is observed that none of the bands occupy the same positions in both spectra. Band .5235 μ of No. 13 and .5230 μ of No. 9 are the most nearly together. The nature of the flux, then, determines in part the disposition of the bands, although the presence of the same base is the predominant factor.

TABLE IV.

Luminescence of Strontium Bismuth Sulphide with Potassium Phosphate Flux, No. 9.

λ	$1/\lambda \times 10^3$.	$\Delta(1/\lambda) \times 10^3$.
.5525	1810	51
.5373	1861	51
.5230	1912	51
.5094	1963	51
.4965	2014	51
.4843	2065	51
.4726	2116	

A somewhat parallel phenomenon is observed when the luminescence series of lime (Table I.) is studied in comparison with the series obtained from the Lenard and Klatt sulphide No. 3. (Table II.) Both contain calcium as a base; the active element in the lime is unknown while that in the Lenard and Klatt sulphide is bismuth together with fluorine. The frequency interval in both series found in the spectrum of the lime is of 42 units and that of the calcium bismuth preparation is 39 units. It is evident that the strontium or the calcium when used as the base of the compound largely determines the frequency interval.