

THE SPECTRUM OF FLUORINE

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ABSTRACT

The line spectrum of fluorine from λ 7800 to λ 3400 has been photographed with a 21-foot concave grating, and the wave-lengths measured. Spectra have been taken from a spark between gold electrodes in fluorine at atmospheric pressure and from vacuum tubes at reduced pressures.

The band spectrum of fluorine has been photographed, and the approximate wave-lengths of the heads of ten bands between λ 7000 and λ 5100 have been measured.

Moisson¹ was the first to isolate pure fluorine in considerable quantities. He passed sparks between gold or platinum electrodes in an atmosphere of fluorine at atmospheric pressure, and studied the red lines visually with a three-prism spectroscope. Porlezza² used SiF_4 in vacuum tubes, and compared its spectrum with that of $SiCl_4$ and Si . He studied the violet end of the spectrum chiefly, photographing the spectrum with a concave grating having 10,000 lines to the inch and a focal length of 3.048 meters. Smythe,³ at the Ryerson Physical Laboratory in 1921, photographed the spectrum of fluorine with a quartz spectrograph and with a small concave grating, and measured the lines at the red end of the spectrum. One of the plates, taken with an electrodeless discharge at a reduced pressure, showed bands degraded toward the red, and believed by him to be due to CF_4 . Most of the spectra were photographed from a spark between gold electrodes in a bulb filled with fluorine at atmospheric pressure.

Ten other investigations have been made since 1862. All, except that of Exner and Haschek⁴ in 1912, are cited in Kayser's *Handbuch der Spectroscopie*, Volume V. These have not added materially to our knowledge of the wave-lengths in the fluorine spectrum.

The method used by Smythe for generating the fluorine, and described in his paper, was essentially that developed during the

¹ *Comptes Rendus*, **109**, 937, 1889, and *Annales de Chimie et de Physique* (6), **24**, 224, 1891.

² *Gazetta Chimica Italiana*, **42b**, 42, 1912.

³ *Astrophysical Journal*, **54**, 133, 1921.

⁴ *Die Spectrum der Elemente bei Normalen Druck*, **3**, 85.

war by the Chemical Warfare Service. Dry KHF_2 is melted in a copper vessel, and kept at about 245°C . The liquid is electrolyzed by passing a current of a few amperes between the copper vessel, which serves as a cathode, and a rod of pure, hard graphite, the anode. Fluorine has been generated for the present experiment with Smythe's original apparatus, which has been modified in no essential particulars. Gas from the generator is first passed through a tube of fused NaF to remove the HF which may be present, then through a trap immersed in frozen alcohol at about -100°C .

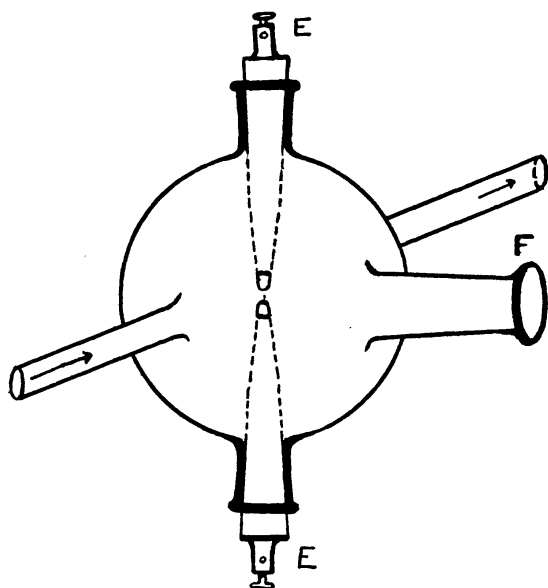
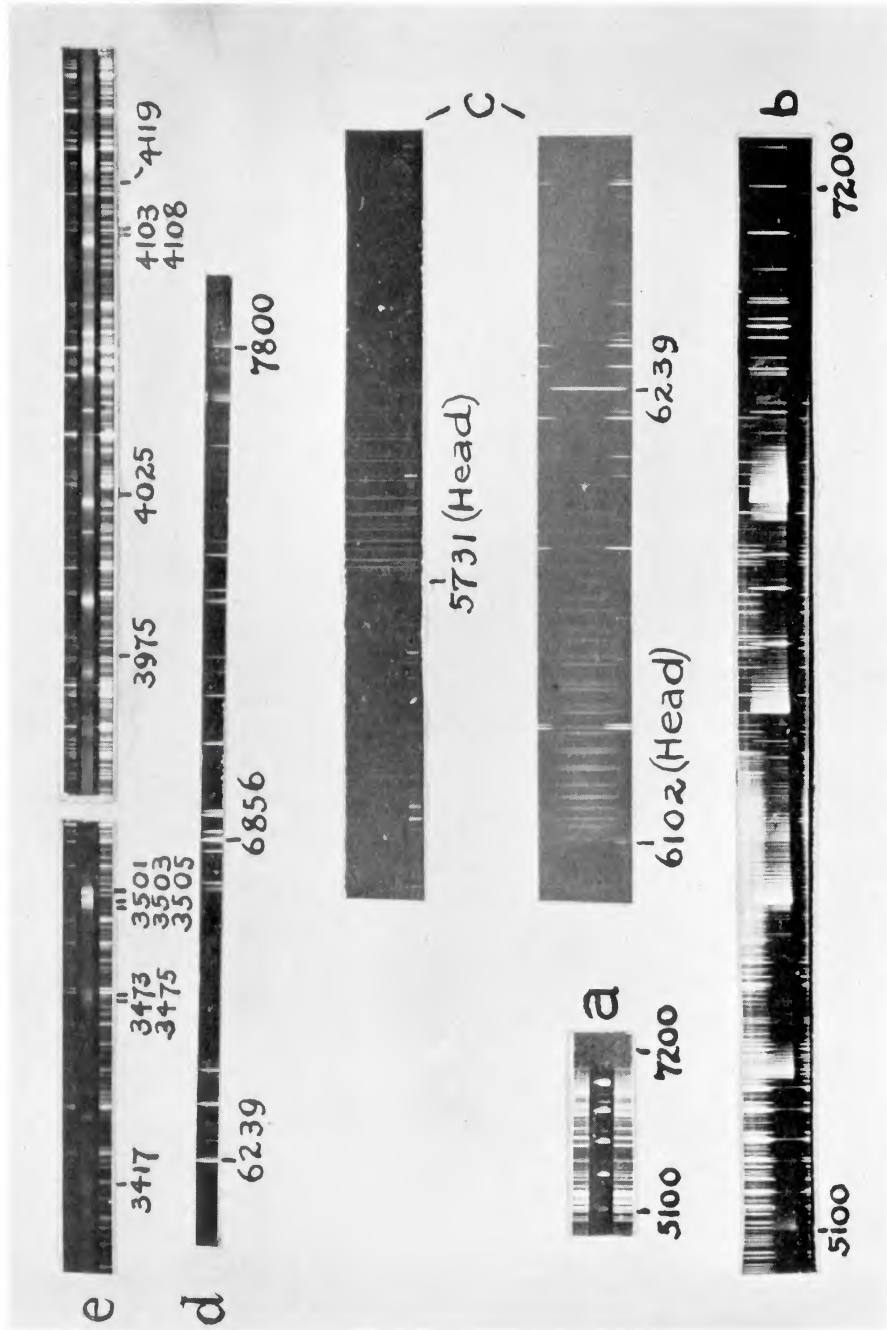


FIG. 1.—*EE*, electrodes; *F*, fluorite window

Since HF liquifies at 19.44°C . at atmospheric pressure, any remaining traces of it were condensed and frozen in the alcohol trap, collecting as a white, powdery deposit. To obtain the spark spectrum, a steady flow of purified fluorine was passed through a bulb about 2 inches in diameter, fitted with heavy copper electrodes tipped with gold, as outlined in Figure 1. The spark gap was opposite a fluorite window. Pure, cold fluorine does not attack clean, dry glass readily, but the interior of the bulb became gradually coated and opaque after a few days' use. The fluorite window, however, remained clean and perfectly transparent indefinitely. The spark was operated by an induction coil giving a 6-inch spark, used with a condenser in parallel with the spark gap, on a 15-volt storage-battery circuit. The spectra are shown in Plate IV, *d* and *e*. When, after several hours' flow, the gas in the discharge chamber consisted almost entirely of pure fluorine, it became very difficult to operate the spark. For several exposures the storage battery e.m.f. was increased to 25 volts, and

PLATE IV



THE SPECTRA OF FLUORINE

a, band spectrum with quartz spectrograph; b, vacuum tube spectrum with 1.5 m concave grating; c, bands with 21-ft. concave grating; d, lines in red with 1.5 m concave grating; e, lines in violet with 21-ft. concave grating.

two induction coils were used, the primaries and secondaries of which were in series separately. Frequently, however, the duration of an exposure was limited by the complete failure of the spark. In the later exposures, one of the spark terminals was made adjustable, so that the length of the spark gap could be altered. Even with this improvement, the length of exposure was limited, as reshaping of the terminals became necessary after three or four hours.

Several times, after the apparatus had been subjected to a heavy flow of fluorine for two or three days, the spectrum of silicon showed in the photographs. These lines were easily identified. It was very difficult to identify the fluorine lines in the blue and violet, where the spectrum of air persisted, no matter how long the fluorine was flowed through the discharge chamber. To determine the fluorine lines, a series of spectrograms was usually taken, the first while the fluorine was displacing the air in the bulb, and a second with the bulb filled with fluorine as pure as possible; then the generator was disconnected and a stream of air blown through the bulb, and another spectrogram was taken when there was no fluorine present.

Photographs were obtained of the spark spectrum in the first order of a 1.5 meter concave grating, and the first order of a 21-foot concave grating. Several times the gas was led first through a discharge tube or spark chamber located in front of the 21-foot instrument, and from there through a second chamber in front of the 1.5 meter spectrograph in the room above. Two photographs were thus obtained simultaneously. If clean when installed, the long length of tubing thus required was not attacked by fluorine, except to a very slight degree after several weeks' use. The spectra obtained by the same form of discharge at different parts of the apparatus were identical, thus indicating that the lines identified as fluorine were probably not due to impurities caused by the action of the fluorine on the glass.

Vacuum-tube spectrum.—Vacuum-tube spectrograms show a series of bands degraded toward the red, between λ 4800 and λ 6550, in addition to the red lines. These bands are shown in Plate IV, *a*, *b*, and *c*. Attempts were first made to obtain the vacuum-tube spectrum photographically by collecting in traps, surrounded by

liquid air, a large amount of condensed fluorine, a clear liquid of a golden hue. To obtain as much as 25 cc of this liquid required continuous operation of the generator for ten or fifteen hours. The trap was then sealed off from the generator. The irrevocable nature of this step and the deterioration of the tubing about the seal caused it to be abandoned. Stopcocks of special design were then employed, but the fluorine attacked the stopcock grease so vigorously that no stopcock could be made to remain tight and not stick, even if it withstood the heat generated. Sufficient fluorine could be collected in this way for a visual examination of the spectrum, but not enough for a prolonged exposure. Finally, a constant flow was obtained, at a pressure of about 5 mm in the discharge tube, by the insertion of a finely drawn capillary between the generator and the discharge tube. Additional regulation of the flow was obtained by means of a large stopcock on the low-pressure side of the capillary. Traps surrounded by frozen alcohol were at first placed on each side of the discharge tube, although later this was found to be unnecessary. A Hyvac oil pump was used to obtain the low pressure. The arrangement is shown in Figure 2.

Smythe first obtained this band spectrum with a discharge tube of the electrodeless type, but attributed the bands to CF_4 due to the backing up of this gas from a carbon tube in front of the pump. In order to determine the origin of the bands, electrodeless tubes and tubes with electrodes of aluminum, iron, copper, and tungsten were used, and the position of the tube in the apparatus was varied. In all cases the bands were the same. The same bands were observed to be very brilliant when a trap full of liquid fluorine was allowed to evaporate quickly into the discharge tube, and they died away as soon as the last of the clear, golden liquid evaporated and was pumped off. In the bottom of such a trap there was usually a white, powdery deposit, which was evidently principally hydrofluoric acid in the solid state. HF has a melting-point of $-92.3^\circ C.$, and a boiling-point of $19.44^\circ C.$, which indicates that these bands are probably not due to HF , as they disappeared before the white deposit began to evaporate. In order to check this point further, a generator was built for the production of HF , and the spectrum observed visually with discharge tubes of the same dimensions as

those used with fluorine, and with the electrical conditions the same. The spectrum observed was the same as seen in the fluorine apparatus after the golden liquid had all disappeared and the white deposit began to evaporate. Attempts to photograph this spectrum were unsuccessful because of the breakdown of the apparatus in a short time under the attacks of the HF on the glass. Since the main object had been attained, i.e., identification of the HF spectrum as that obtained from the white deposit, and the removal of any possibility that the bands were due to HF , nothing further was done along this line.

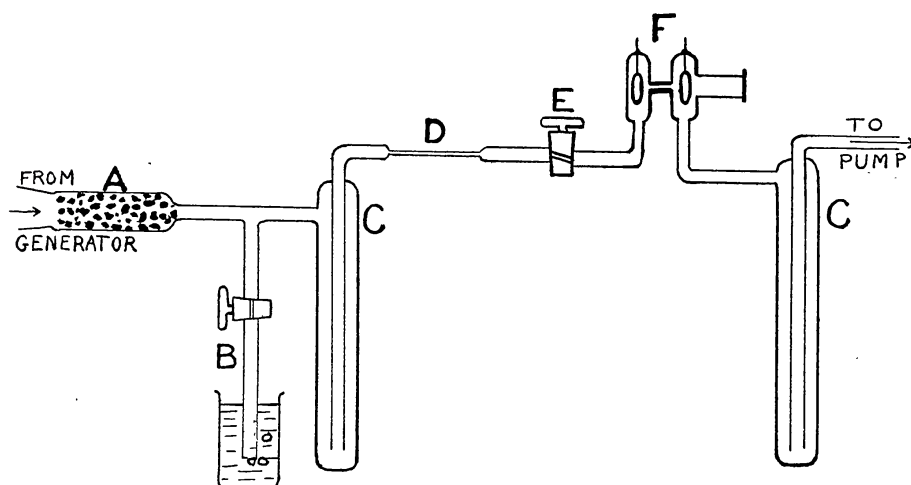


FIG. 2.—*A*, NaF tube; *B*, pressure indicator; *CC*, traps in frozen alcohol; *D*, capillary to control flow; *E*, stopcock to control flow; *F*, discharge tube.

It may also be mentioned that it was easy to collect the golden liquid in traps immersed in fresh liquid air (temperature $-192^{\circ}C.$), and difficult with old, standing liquid air from which most of the nitrogen (temperature $-195^{\circ}C.$) had escaped, leaving a preponderance of oxygen ($-182.5^{\circ}C.$). The boiling-point of fluorine is $-187^{\circ}C.$

The bands in question are not due to SiF_4 . The bands due to this compound were photographed by Mr. Durbin, and formed a beautiful group at entirely different positions in the spectrum. Attempts to secure the spectrum of CF_4 by Mr. Porter and Mr. Blackburn have so far been unsuccessful. Certain new bands have been observed visually by Mr. Blackburn, but they do not coincide with the bands in question.

Line spectra of fluorine.—The lines of the fluorine spectrum fall under two heads. The sharp lines are listed in Table I. These occur both in the spark discharge at atmospheric pressure and the vacuum-tube discharge at low pressures. They are sharper at reduced pressures than at atmospheric pressure, but no changes in their positions or relative intensities have been observed. It will be seen that all the lines of this group are in the orange and red.

TABLE I
LINES OF FLUORINE
(Obtained in Discharge Tube at Pressure of 3 mm Mercury)

Wave-Length	Int.	Wave-Length	Int.	Wave-Length	Int.
5659.02.....	00	6239.63*.....	30	6856.01*.....	40
5667.48.....	0	6254.68.....	2	6870.21*.....	18
5671.62.....	1	6348.46*.....	28	6902.46*.....	30
5700.72.....	2	6356.87.....	1	6909.79*.....	20
5707.23.....	3	6405.15.....	3	6966.33*.....	4
5967.30.....	0	6413.61*.....	23	7037.48*.....	50
5996.76.....	1	6416.30.....	3	7202.34*.....	15
6014.08.....	0	6502.04.....	1	7311.40†.....	15
6015.90.....	1	6522.67.....	1	7332.25†.....	18
6017.90.....	2	6569.66*.....	10	7398.96†.....	20
6024.02.....	0	6580.36.....	4	7426.2†.....	12
6038.04.....	1	6650.40.....	3	7482.95†.....	5
6047.55.....	4	6690.48*.....	5	7552.20†.....	5
6049.66.....	0	6762.91.....	6	7573.32†.....	5
6039.02.....	0	6766.98.....	3	7754.8†.....	5
6080.13.....	1	6773.96*.....	20	7800.5†.....	2
6149.77.....	2	6795.47.....	3		
6210.85.....	3	6834.25*.....	18		

* Lines measured also in spark at atmospheric pressure.

† Lines measured only in spark at atmospheric pressure, but of the same general character as other lines in table.

In Table II are listed the broad, hazy lines. These have been observed only in the spark discharge at atmospheric pressure. Unsuccessful attempts were made to obtain them with a vacuum tube of the usual form having a capillary of about 1 millimeter diameter. The tube was operated by an induction coil with a Wehnelt interrupter, carrying about 65 volts on the primary, and with a condenser in parallel with the discharge tube. While the color of the tube operated with an ordinary induction coil and no capacity in the secondary was a brilliant orange, due to the presence of the bands, the tube with the more powerful discharge was

greenish white in the capillary, where no bands were observed, but remained brilliant orange in the wider portions of the tube where the bands persisted. On account of the violent discharge, the glass in the capillary was more strongly attacked, and the silicon lines appeared as soon as the tube was operated.

TABLE II
LINES OF FLUORINE
(Obtained with Spark Discharge at Atmospheric Pressure. Lines not Observed in Discharge Tube)

Wave-Length	Int.	Wave-Length	Int.	Wave-Length	Int.
3417.85.....	I	3601.70.....	I	4024.83 	2
3473.53.....	I	3603.32.....	I	4025.09?.....	I
3475.24.....	I	3704.75.....	I	4103.41.....	2
3501.68.....	I	3847.05.....	4	4109.10.....	I
3503.32.....	2	3849.97.....	3	4116.50¶.....	I
3505.85.....	3	3851.73.....	3	4119.35.....	I
3541.85?.....	I	3898.80.....	2	4246.41.....	4
3590.49*.....	I	3902.00.....	2	4299.03.....	2
3598.16?.....	O	3905.67?†.....	I	4361.35.....	2
3598.98.....	I	3974.80‡§.....	I	6762.13.....	4

Also possible lines at 4368.36, 4398.4, 4400.6; and at 3641.3, 3642.3, 3642.9.

* Si 3590.77.

† Si 3905.37; O 3907.5.

‡ O 3973.5.

§ On one plate measured as double: 3972.75, 3976.24.

|| On one plate measured as double: 4024.80, 4025.65.

¶ Si 4116.15.

Doubtful if Si lines have any effect, as stronger lines of Si did not appear on many of these plates.

Band spectrum of fluorine.—The bands attributed to fluorine for the reasons already mentioned are of fairly equal intensity visually, although the bands of longer wave-length are perhaps stronger. The approximate wave-lengths of the heads of the bands

TABLE III

1.....	6977.0	6.....	5851.3
2.....	6927.2	7.....	5731.4
3.....	6518.6	8.....	5515.5
4.....	6488.7	9.....	5393.9
5.....	6102.6	10.....	5102.2

are given in Table III. The original of Plate IV, *b*, is on a panchromatic plate, the weakness of which in the green makes the bands of that wave-length seem to be unduly faint. An inspection of the

large-dispersion photographs of the bands, Plate IV, *c*, suggests at once that many of their lines lie on the well-known parabolic curves into which band spectra can be analyzed. Preliminary calculations show that four of these bands yield such branches for about twenty terms, which plot on smooth curves, presumably parabolas since the second differences of the frequencies are approximately constant. The most obvious characteristics of these bands are:

1. They are degraded toward the red.
2. The sharpness of their lines is greatest in the band at the violet end of the spectrum. Each succeeding band toward the red has broader lines, suggesting that the component lines are complex.
3. Each band is composed of a large number of branches. There are two branches of nearly equal intensity dominating each band. In the reddest band photographed with large dispersion, the first two components of these strong branches are double lines.

While they possess many easily recognizable characteristics, such as have been mentioned, these bands are not simple. The work of making a more complete analysis and explanation of their structure is in progress, and will be published later.

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