

Finally, I want to thank Dr. G. Holst, Director of the Philips' Laboratory, and Prof. R. A. Millikan, Director of the Norman Bridge Laboratory (where the second part of this work was done), for the opportunity of working in these laboratories, Dr. W. de Groot, Dr. F. M. Penning and Prof. K. T. Compton for their interest in this work and many helpful suggestions. I acknowledge also with pleasure the considerable help given in the experimental work by Mr. J. Moubis, (Philips' Laboratory) and Mr. L. F. Green (Norman Bridge Laboratory).

<sup>1</sup> Preliminary abstract presented at the Berkeley Meeting (March 3, 1928) of the American Physical Society, *Phys. Rev.*, **31**, 913, 1928.

<sup>2</sup> Fellow in Physics of the C. R. B. Educational Foundation.

<sup>3</sup> Langmuir and Mott-Smith, *G. E. Rev.*, **27**, 449, etc., 1924.

<sup>4</sup> Those experiments were started in the spring of 1926 in the Physical Laboratory of the Philips' Glowlampworks, Eindhoven (Holland) at the suggestion of Dr. F. M. Penning.

<sup>5</sup> Langmuir, *Science*, **58**, 290, 1923; *G. E. Rev.*, **26**, 721, 1923.

<sup>6</sup> Schottky and von Issendorff, *Zeits. Phys.*, **26**, 85, 1924.

<sup>7</sup> Epstein, *Verh. D. Phys. Ges.*, **21**, 85, 1919; Langmuir, *Phys. Rev.*, **21**, 419, 1923.

<sup>8</sup> Penning, *Proc. Amsterdam Acad.*, **31**, 14, 1927; *Physica*, **8**, 13, 1928.

<sup>9</sup> Webb, *Phys. Rev.*, **24**, 113, 1924.

<sup>10</sup> Messenger, *Ibid.*, **28**, 962, 1926; Coulliette, *Ibid.*, **32**, 635, 1928.

<sup>11</sup> Morse and Uytterhoeven, *Ibid.*, **31**, 827, 1928. We are indebted to Dr. W. de Groot for pointing out an error in this paper in the computation of the average velocity of the ions formed in the sheath. The only effect on the final formulas, however, is a small change in the constants.

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## NOTE ON THE D LINE EXCITATION BY THE GREEN SODIUM BAND AND THE DISSOCIATION POTENTIAL OF SODIUM VAPOR

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Communicated December 12, 1928

The dissociation of molecules into normal and excited atoms by the absorption of light has been shown to occur in a wide variety of cases by many observers, and fluorescence and absorption experiments in which this process operates have been used to furnish values for the heats of dissociation of the molecules in question. For example, the existence of a region of continuous absorption on the short wave-length side of the ultra-violet bands of hydrogen,<sup>1</sup> until recently,<sup>a</sup> was taken as evidence for the dissociation of the hydrogen molecule into a normal and an excited atom, and the heat of dissociation calculated from this assumption was in agreement with the value obtained from an analysis of the Lyman-

Witmer<sup>2</sup> bands by the method of Birge and Sponer.<sup>3</sup> The appearance of the *D* lines in the fluorescent radiation, emitted when the vapor of sodium iodide is illuminated with wave-lengths shorter than 2500 Å, has been attributed by Terenin<sup>4</sup> to the optical dissociation of the molecule into a normal iodine atom, and a sodium atom in the  $2P$  state. A third, and perhaps best known, example of such a process is the optical dissociation of iodine into a normal and metastable atom.<sup>5</sup> This note is a discussion of the evidence for the occurrence of such a process in the fluorescent phenomena of sodium vapor.

Years ago Wood<sup>6</sup> noticed, during his classical researches on sodium vapor, that the *D* lines were stimulated when the vapor was illuminated with light in which wave-lengths known to be absorbable by the atom were absent, and, in the last year, the experimental conditions under which the phenomenon occurred were described by Professor Wood and the author.<sup>7</sup> Recently the experiments have been repeated more carefully by the author, and, where before figures were only qualitative, they are now given quantitatively to within the error of measurement. A short account and discussion of the results of the work appeared in *Nature*,<sup>8</sup> while the method was fully described in the earlier paper.

The experiments were designed to determine the conditions under which it is possible to excite the *D* lines by the blue-green band of the sodium molecule. The familiar long steel tube, closed at each end with glass windows, served to enclose the shorter cylindrical steel retort, placed at its center, which contained the sodium, and in which the fluorescence occurred. An intense beam was focused in the middle of the retort through holes provided in its ends for this purpose. The beam was obtained from a large 50-ampere carbon arc, equipped with carbons impregnated with salts of the rare earths for the purpose of throwing most of the radiation into the visible region, and filtered through a monochromator of high light-gathering power. The fluorescence was observed as before by means of a right-angled prism, placed on one side of the entering beam next the glass window of the tube, whose center was heated electrically, and equipped with a thermocouple, this time, to ensure control and an even distribution of the temperature. Lead tubing coiled around the tube's ends, and carrying a rapid stream of water served to keep the waxed joints at the windows from softening.

Under this very intense illumination, the *D* lines appeared very distinctly in the pure fluorescing vapor, when it was illuminated with various regions in the blue-green, in which the *D* lines themselves were absent. But their intensity varied rather sharply with the wave-length of the exciting light, and with the temperature of the furnace. In the earlier experiments, they failed to appear in pure vapor, and were excited only when the vapor contained small quantities of a foreign gas at a pressure of

a few millimeters. The present experiments showed that a foreign gas was not at all necessary. This pressure effect was anomalous, and is seen now to be due to the way in which the intensity varies with the temperature. As pointed out previously, the atomic lines appeared somewhat below  $400^\circ$ , rose to a sharp maximum around  $410^\circ$ , and disappeared again above  $450^\circ$ , in the pure vapor not mixed with gas. The existence of the maximum near  $410^\circ$  could be detected easily. Now in the previous experiments no adequate temperature control was purposely employed, the tube being heated by bunsen burners, but it was found, in the present work, that the introduction of gas at a few millimeters pressure caused temperature changes of  $10^\circ$  to  $20^\circ$ , the temperature rising on the introduction of the gas. Experiments showed this to be due entirely to the fact that the gas reduced the diffusion of the vapor to the cooler parts of the tube. The rapidly diffusing vapor in the absence of gas keeps the heated section at a lower temperature than it would attain if this diffusion were absent. Although the *D* lines were obtained in this way in the presence of gas they were much less intense, than in the pure vapor, and appeared only in the temperature range indicated above. The existence of a temperature at which the intensity of the atomic lines excited by the green band is a maximum is caused, quite probably, by the simultaneous operation of an increasing intensity of emission, and an increasing intensity of atomic absorption, as both the molecular and atomic densities increase. The long and short wave-length limits of the exciting band, as well as the wave-length of the band which produced the maximum intensity, were measured to within 50 Å. or 0.03 volts. The following is a list of the measurements made.

1. Wave-length producing maximum *D* line fluorescence  
2.55 volts; 4856 Å.
2. Long wave-length limit of excitation of the *D* lines  
2.36 volts; 5240 Å.
3. Short wave-length limit of excitation of *D* lines  
2.76 volts; 4470 Å.
4. Wave-length producing maximum blue-green fluorescence  
2.51 volts; 4930 Å.
5. Short wave-length limit of blue-green fluorescence  
2.75 volts; 4485 Å.

It is easily seen that no such interpretation of the phenomenon, as proposed either for the case of iodine or sodium iodide, is in agreement with the energy values given above. The case analogous to iodine, for example, would be one where band fluorescence is absent on the short wave side of the long wave-length limit of the exciting light for the *D* lines. In such a case fluorescence would cease at the point where the energy was

sufficient to dissociate the molecule into a normal and 2.1-volt atom, and the atomic line would become visible. Instead, here, the band and line fluorescence exist together throughout the entire range of their excitation, and the short wave limit of excitation for both band and *D* line fluorescence correspond to within the error of measurement.

This correspondence between the intensity variation of the *D* lines and the blue-green bands is exactly what one would expect if atoms were excited to the *2P* levels by collisions of the second kind with excited molecules. It is fairly certain now that this is the process occurring and that the excited atoms cannot arise as a result of the dissociation of the molecules. Sufficient energy for dissociation is not available. Loomis<sup>9</sup> gives the heat of dissociation as  $1.0 \pm 0.1$  volt, which he obtained by extrapolating the  $\omega_n$  curve for the normal level of the blue-green system by the method of Birge and Sponer. Extrapolation of the  $\omega_n$  curve for the upper level gives a total energy of 3.07 volts, and assuming the products of dissociation to be a normal and 2.1 volt excited atom, the heat of dissociation, *D*, becomes 0.97 volts. This is a much shorter extrapolation than the first, and hence should give the more accurate value. Professor Birge, in a letter to the writer, pointed out that this gives a possible maximum value, and on replotting the  $\omega_n$  curve for the upper level and giving it the negative curvature that is generally found, he finds  $D = 0.84$  volts, as a possible minimum value. Very recently Polanyi and Schay<sup>10</sup> have determined *D* by what amounts to a chemical method and find it to lie between 0.71 and 0.87 volt. The extrapolated lower limit from Loomis' data as calculated by Professor Birge lies in this range so that better agreement of these values could not be expected. The value of *D* can be taken then as  $0.85 \pm 0.02$  volt.

The total energy necessary for the molecule to dissociate into a normal and 2.1-volt excited atom is

$$0.85 + 2.1 = 2.95 \text{ volts}$$

and at no point in the entire range of wave-lengths which excite the *D* lines is this amount available. It is true that at  $600^\circ$ , the temperature of the experiments, the average kinetic energy is about 0.1 volt and that there will be a distribution of energy over some of the lower vibrational levels. This quantity would be available for dissociation in addition to the amount added by absorption. But when the excitation energy is 2.55 volts and the *D* lines have their maximum intensity, the initial energy of the molecule must be 0.4 volt to supply sufficient energy for dissociation. The number of molecules in this state will be approximately less than one two-thousandth of those in the normal state, so that the occurrence of such an absorption is highly improbable. On the other hand, it is probable that approximately three out of every ten excited molecules collide with

an atom before they radiate, so that the probability of collisions of the second kind is enormously larger than the probability of absorptions occurring which begin on an initial level of 0.4 volt.

These results emphasize the fact that in mixtures of atoms and molecules, stimulation of atomic lines by radiation which can excite only the molecule (cf. Winans, *Phys. Rev.*, **32**, 427, 1928) cannot be taken as evidence for molecular dissociation. Estimates of heats of dissociation from such experiments can be given small value.

\* The experimental work was carried on while the writer was a NATIONAL RESEARCH FELLOW at Yale University.

<sup>1</sup> Dieke and Hopfield, *Phys. Rev.*, **30**, 400, 1927.

<sup>2</sup> Witmer, *Ibid.*, **28**, 1223, 1928.

<sup>3</sup> Birge and Sponer, *Ibid.*, **28**, 260, 1928.

<sup>4</sup> Terenin, *Zeit. Phys.*, **37**, 98, 1926.

<sup>5</sup> Dymond, *Ibid.*, **34**, 553, 1925.

<sup>6</sup> Wood, *Physical Optics*, p. 574.

<sup>7</sup> Wood and Kinsey, *Phys. Rev.*, **31**, 793, 1928.

<sup>8</sup> Kinsey, *Nature*, **121**, 904, 1928.

<sup>9</sup> F. W. Loomis, *Phys. Rev.*, **31**, 323, 1928.

<sup>10</sup> Polanyi and Schay, *Z. Phys. Chem.*, **1**, 30, 1928.

<sup>a</sup> Professor Birge has pointed out to the writer that recent plates, obtained by Professor Hopfield of the ultra-violet absorption of hydrogen, show that the region which was thought to be one of continuous absorption, turns out, under lower pressures, to consist of bands.

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## ON THE SUMMABILITY OF FOURIER SERIES. SECOND NOTE

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Communicated December 10, 1928

1. Shortly after our first note on the summability of Fourier series (these PROCEEDINGS, **12**, 915-918, 1928) was communicated to the Academy, we succeeded in carrying the discussion of the Hausdorff case considerably further. The present note gives a short account of the results which we have obtained in this direction. We refer to our first note for the formulation of the problem and for the notation employed.

The function  $q(u)$  associated with the method  $(H, q)$  is supposed to be of bounded variation in  $(0, 1)$ ,  $q(0) = 0$  and  $q(1) = 1$ ; further  $q(u)$  must be continuous at  $u = 0$  and  $u = 1$  to define a regular method of summation. Let  $q(u)$  be continued outside of the interval  $(0, 1)$  by setting  $q(u) = 0$  when  $u < 0$  and  $q(u) = 1$  when  $u > 1$ . We introduce the function

$$\Omega(h) = \text{Max}_{0 < a \leq h} \int_{-\infty}^{+\infty} |d[q(u+a) - q(u)]|, \quad h > 0, \quad (1)$$