THE INFRA-RED ABSORPTION SPECTRUM OF NAPHTHALENE AND OF SOME OF ITS MONO-DERIVATIVES IN SOLUTION.

By A. H. Stang.

Introduction.

Although much experimental work has already been done on finding the infra-red absorption spectrum of different substances, there remains a very large number of substances whose spectrum is unknown. The results of the infra-red investigations have been very fruitful in solving problems of molecular structure and in testing the energy quantum theory, especially as applied to the theory of specific heats. Thus Bjerrum[1] from a knowledge of the infra-red absorption bands of CO_2 has proposed a solution for the problem of the arrangement of the atoms in the CO_2 molecule, while Nernst and Lindemann[2] have deduced formulas for the variation of the specific heat with temperature that agree closely with experimental data and are based on the location of infra-red absorption bands of the substances in question.

Still more recently Baly,[3] of the University of Liverpool, has proposed a theory which unites the absorption of an organic substance in the infra-red to that in the visible and ultra-violet regions of the spectrum and to the fluorescence and phosphorescence which a body may emit. He has, in particular, predicted from theoretical considerations at what wave-lengths the infra-red absorption maxima of several substances should occur. Among these substances was naphthalene, $C_{10}H_8$.

The object of this paper is then to investigate the absorption of naphthalene as well as that of several of its mono-derivatives and especially to obtain the positions of maxima absorption. Since these substances are solids at ordinary temperatures, it was determined to obtain their absorption curves when in solutions of carbon disulphide and carbon tetrachloride. These solvents were chosen because they are relatively transparent in the infra-red. From these absorption curves the effect of the solvent and of isomerism will be noted. The agreement of these

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[1] Bjerrum, Verh. der deut. Phys. Gesell., 16, p. 737, 1914.

[2] Zeit. fur Electro-chemie, 17, p. 867, 1911.

[3] Baly, Astro-phys. Journal, 42, p. 4, 1915. Phil. Mag., Vol. 27, p. 632, 1914; vol. 29, p. 223, 1915; vol. 30, p. 510, 1915; vol. 31, p. 417.

absorption maxima with Baly's theory of absorption will also be tested and some conclusions as to the validity of that theory drawn.

APPARATUS.

A fixed arm spectrometer, provided with the Wadsworth[1] constant minimum deviation attachment was used for the work. Fig. 1 gives a diagram of the apparatus. *A* is an adjustable slit. *B* and *E* are 9 cm. diam. 50 cm. focal length spherical mirrors, silvered on the outside. *C* is a rock salt prism, 8 cm. along each face and 8 cm. high, with a refracting angle of 59° 58′.75, obtained from Brashear. The prism was protected from moisture by having a small dish of anhydrous calcium chloride placed upon it and several others on the spectrometer, which was enclosed in a blackened case. When not in use, the prism was covered with a bristol board box painted inside with paraffine which fitted closely to the spectrometer table. The small weight of this box made it preferable to a heavy glass bell-jar. *D* is the Wadsworth plane mirror, while *F* is a plane 10 × 10 cm. mirror used to change the direction of the convergent light from *E* so that the filar microscope *J* could be used for reading the 35 cm. diam. circle *K*. *C* is a Rubens thermopile, made up of iron constantin junctions with a fixed slit width of 0.03 cm. A Leeds and Northrup sensitive galvanometer was used on closed circuit in series with the thermopile. The source of radiation *L* was a 220-volt Nernst glower. A spherical mirror *M* focused the light on the slit.

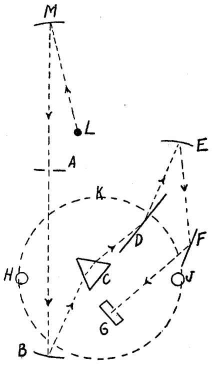

Fig. 1.

The cells used to hold the solutions were made of two plates of polished rock salt about 2 × 4 × .4 cm., between which a clean copper wire bent in U shape was placed. After the plates had been finally polished on an optical grinder with rouge and absolute alcohol, the wire was placed between them and cemented to the plates with SiO_2. The solvents used did not attack any of the materials in the cell. After filling the cell, a glass plate was cemented over the top to prevent evaporation.

A thin wooden block that ran in vertical ways between stops was provided with two openings somewhat smaller than the cells. The cell containing the solution to be investigated was placed over the upper opening. Over the lower opening a duplicate cell, having the same absorption when empty, was placed filled with the pure solvent. The

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[1] Wadsworth, Phil. Mag. (5), 38, p. 346, 1894.

elevator was so placed that the cells could be brought in succession exactly to the same position in front of and close to the slit. Between the elevator and mirror M interposed a metal screen which could be operated by the observer.

The naphthalene used was recrystallized from alcohol. The beta naphthylamine was obtained from Merck and Co. The alpha and beta naphthol, the nitronaphthalene and the alpha naphthylamine were very kindly furnished by Professor M. Gomberg of the chemistry department. The solvents were obtained from stock in the laboratory. They were listed as c.p. but since the absorption of the solvents does not enter into the final result, absolute purity is not necessary.

PROCEDURE.

A calibration curve for the rock salt prism was made from values given by Paschen.[1] Since the observation room was always kept at 25° C. the values of the refractive index were corrected for temperature by his correction formula.

Before each set of observations, the instrument was calibrated with an optical setting on the .546 μ Hg line and then tested with the Bunsen flame emission maximum which has been accurately located[2] at 4.40 μ. From the calibration curve, this maximum was always found at a wavelength smaller than 4.4 μ by about 0.4 minute of arc. This discrepancy has been noticed by several investigators[3] who attribute it variously to curvature of the image of the slit and to a real difference between a bolometric and an optical setting of the standard line on the slit. Correction was made by assuming that the Bunsen maximum was at 4.400 μ and displacing the calibration curve by the required amount. It may be noted that the .03 cm. width of slit for a 50 cm. focal length mirror amounts to 2.03 minutes of arc.

After the cells had been placed on the elevator and the zero galvanometer reading taken, the metal screen was raised so that light could pass through the cell which contained the solution. When the maximum deflection had been noted, the elevator was raised until the cell containing the solvent came in front of the slit. The deflection now increased and finally came to rest at a value larger than the first. With a linear thermopile such as was used the percentage of energy transmitted was computed by finding the ratio of the deflection through the solution to that through the solvent.

In general, readings were taken one minute apart on the spectrometer

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[1] Paschen, Ann. der Physik, 26, p. 120.

[2] Paschen, Wied. Ann., 52, p. 209, 1894; 53, p. 337, 1894; 60, p. 714, 1897.

[3] Coblenz, Carnegie Inst. Publ., No. 35, p. 20. Paschen, Wied. Ann., 52, p. 209, 1894.

circle but in the neighborhood of an absorption band they were taken closer together so as to accurately locate the minimum of transmission. Table I. is a sample taken at random from observations through one absorption band. It shows the variation of the intensity of the light caused by the absorption of the solute and of the solvent and by the Nernst glower.

Table I.

Infra-red Absorption Data. α Nitronaphthalene in CS_2.

1.	2.	3.	4.	5.
Angle from $\lambda = .546\mu$.	Wave-length.	Solution Deflection, Cm.	Solvent Deflection, Cm.	Per Cent. Transmitted.
37.00	7.070μ	1.49	2.01	74.0
38.00	7.160	1.79	3.19	56.1
39.00	7.250	1.42	4.12	33.4
40.00	7.334	1.04	4.58	22.7
40.32	7.360	.93	4.83	19.2
40.62	7.384	.87	4.97	17.5
41.00	7.415	.79	4.93	16.0
41.33	7.440	.84	5.03	16.7
41.61	7.463	.89	5.04	17.7
42.00	7.493	1.00	5.00	20.0
43.00	7.571	1.76	4.95	35.6

The minimum of transmission was always determined from a plot made on a large scale of several values near the minimum. The point where the two lines (Fig. 2) meet was taken as the position of maximum absorption. No correction has been made for finite slit width and impurity of the spectrum. Several bands were plotted to an enlarged scale and the correction method proposed by Runge[1] applied. The corrected absorption curve was indeed deeper but there was no shift of the position of the maximum comparable to the experimental error.

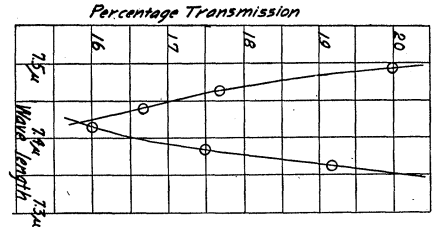

Fig. 2.

α Nitronaphthalene Absorption Band in CS_2 at 7.42 μ.

In the tables giving the positions of maximum absorption are given

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[1] Runge, Zeit. für Math. und Phys., 42, p. 205, 1897.

the estimated limits of error in location after account has been taken of errors that may arise in percentage transmission, plot, calibration curve, adjustment test, and change in temperature.

CHEMICAL STRUCTURE OF NAPHTHALENE AND OF ITS DERIVATIVES.

Naphthalene, $C_{10}H_8$[1] consists of two benzene nuclei which have in common two carbon atoms. The accepted formula is given in Fig. 3. The replacement of an H atom in naphthalene gives rise to two isometric mono-derivatives. They are called either α or β derivatives according as the substituent is adjacent to the complex of Fig. 4, common to both groups, or separated from it by a CH group.

α naphthol, $C_{10}H_7(OH) + H_2O$ is represented by the formula of Fig. 5 while β naphthol is shown in Fig. 6. The α and β naphthylamine $C_{10}H_7(NH_2) + CO_2 + H_2O$ correspond to Figs. 7 and 8 respectively and α nitronaphthalene $C_{10}H_7(NO_2)$ has the formula of Fig. 9.

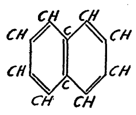

Fig. 3.

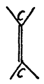

Fig. 4.

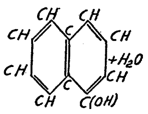

Fig. 5.

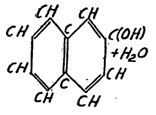

Fig. 6.

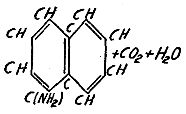

Fig. 7.

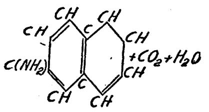

Fig. 8.

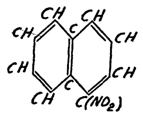

Fig. 9.

Fig. 3. Naphthalene.
Fig. 5. α Naphthol.
Fig. 6. β Naphthol.
Fig. 7. α Naphthylamine.
Fig. 8. β Naphthylamine.
Fig. 9. α Nitronaphthalene.

DISCUSSION OF THE RESULTS.

In Fig. 10 are given the transmission curves for naphthalene in CS_2 and in CCl_4 respectively. Table II. gives the location of the absorption maxima. The CS_2 solution gives more bands but except for the band at 3.30 μ the location of the common bands agrees within experimental error. Coblenz[2] has investigated the absorption of naphthalene in CCl_4 in this region and found a band at 3.25 μ. The CS_2 band was however located at 3.30 μ in several solutions, the observations having been taken more than two months apart. This shift from 3.25 μ to 3.30 μ must be due to the effect of the solvent itself.

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[1] Richter-Smith, Organic Chemistry, vol. 2, p. 390, 1900.

[2] Coblenz, *loc. cit.*

Since naphthalene consists of two benzene nuclei, it will be of interest to note that Coblenz has found absorption maxima of benzene at 2.7 μ, 3.25 μ, 4.4 μ, 4.9 μ, 5.5 μ, 6.2 μ, 6.75 μ, 7.25 μ, 7.8 μ, 8.67 μ, and 9.78 μ.

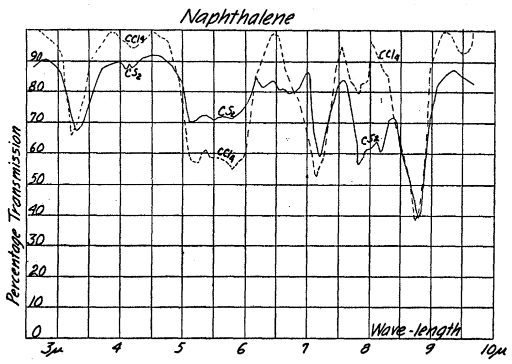

Fig. 10.

TABLE II.

Naphthalene Absorption Maxima.

No.	In CS_2.	In CCl_4.	Wave No.
1	3.30μ ± .03μ	3.25μ ± .03μ	308
2	4.2 .10	4.22 .04	237
3	5.15 .10		194
4		5.27 .03	190
5	5.5 .10		182
6	5.8 .10	5.80 .02	172
7	6.31 .02		159
8	6.75 .10		148
9	7.20 .03	7.18 .03	139
10	7.84 .02	7.84 .03	127
11	8.18 .02		122
12	8.79 .02	8.78 .02	114
13	9.81 .03		102

It is to be noticed that many naphthalene bands occur at the same wave-lengths. These must be due to the vibration of the benzene ring, still present in the naphthalene and are not characteristic of the naphthalene itself.

Baly[1] in his theory has arrived at the conclusion that the wave numbers of the absorption band in the visible or ultra-violet region of the spectrum should be equal to the product of the wave numbers of several infra-red bands by whole numbers. Such a test would serve as a criterion of the worth of his theory. For example, Russel and Lapraik[2] found three

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[1] Baly, *loc. cit.*

[2] Chem. Soc. of Lon. Trans., 39, p. 171, 1881.

naphthalene absorption bands, the maximum absorption occurring from .714 μ to .707 μ, from .636 μ to .634 μ, and from .619 μ to .611 μ while the mean wave numbers for these bands are 1407, 1571, and 1626 respectively. The wave numbers of the infra-red bands giving closest agreement are for 1407, 139 × 10 = 1390, 127 × 11 = 1397, 238 × 6 = 1428; for 1571 there are no close values; for 1626, 102 × 16 = 1632, and 148 × 11 = 1628.

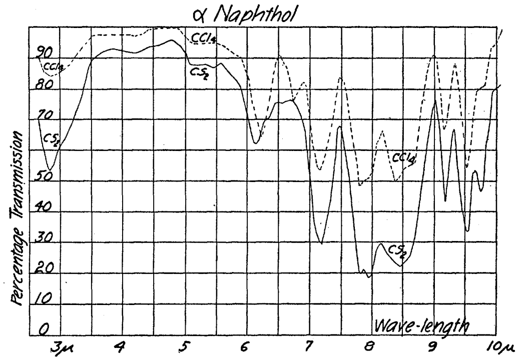

Fig. 11.

TABLE III.

Infra-red Absorption Maxima. Alpha Naphthol.

1.	2.	3.	4.	5.	6.	7.
No.	In CS_2.		In CCl_4.		Wave No.	
1	2.85μ	±.03μ	2.87μ	±.04μ	286	
2	6.15	.02			162	D
3			6.24	.03	160	
4			6.76	.03	148	ND
5	7.19	.03	7.19	.03	139	ND
6	7.84	.03	7.82	.03	127	ND
7	7.97	.03			125	
8	8.44	.04	8.40	.03	119	D
9	9.17	.02	9.17	.02	109	
10	9.54	.03	9.54	.02	105	
11	9.73	.03			103	D

Purvis at 3068 (2, 5, 6, 9, 11); at 3324 (5, 6, 8).

The wave numbers of the other bands found by various investigators in the visible region are given below. The numbers in parenthesis after each wave number refer to the infra-red bands listed in Table II. which are very nearly integral factors of this visible wave number.

By Hartley[1] at 3504 (4, 7); at 3670 (4, 7, 11, 13); at 3801 (3, 6, 7, 11); and at 3922 (2, 11).

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[1] Chem. Soc. of Lon. Trans., 47, p. 685, 1885.

By Baly and Tuck[1] at 3125 (4, 8); at 3222 (9); at 3700 (1, 4, 8, 10).

By Guthrie[2] at 3102 (4, 5, 6, 8); at 3167 (7, 11, 13); at 3207 (9, 12); at 3306 (2, 3, 4, 10, 11, 12); at 3488 (4, 7, 9); at 3574 (10, 13); at 3625 (5, 6, 9); and at 3745 (9, 12).

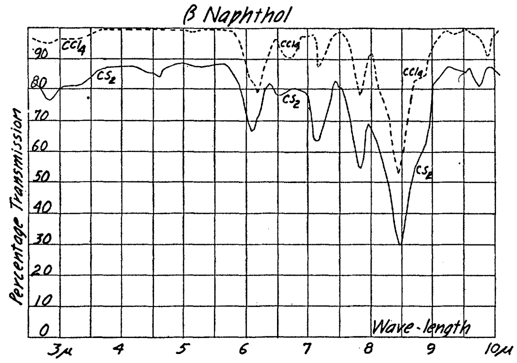

Fig. 12.

TABLE IV.

Infra-red Absorption Maxima. Beta Naphthol.

1.	2.	3.	4.	5.	6.	7.
No.	In CS_2.		In CCl_4.		Wave No.	
1			2.77μ	±.10μ	361	
2	2.87μ	±.04μ			350	
3	6.12	.03	6.18	.03	163	D
4	6.5	.10			154	
5			6.75	.03	148	ND
6	7.18	.03	7.21	.02	139	ND
7	7.84	.02	7.85	.03	128	ND
8	8.47	.02	8.47	.02	118	D
9	9.72	.02			103	D
10			9.90	.06	101	

Purvis at 2996 (8) at 3712 (4, 5, 7, 9).

[1] Purvis, Chem. Soc. of Lon. Trans., 101, p. 1315, 1912.

From these results it is seen that nearly all of the absorption maxima in the visible and ultra-violet have wave numbers which are integral multiples of several infra-red absorption wave numbers.

The constant frequency difference between bands in the visible or in the infra-red which one might expect from Baly's theory have not been found. This detailed discussion of the results has been undertaken to see if the theory does account for the position of the visible absorption

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[1] Chem. Soc. of Lon. Trans., 93, p. 1902, 1908.

[2] Baly, Astrophys. Jour., 42, p. 44.

bands. The proof may be sufficient. It would however be going too far to say that the results are as conclusive as might be desired. From his theory of fluorescence, Baly has predicted that bands would be found at 3.27 μ, 3.86 μ, 4.72 μ, 6.06 μ, and at 8.48 μ. Only the 3.27 μ band has been found, and this band had already been located by Coblenz.

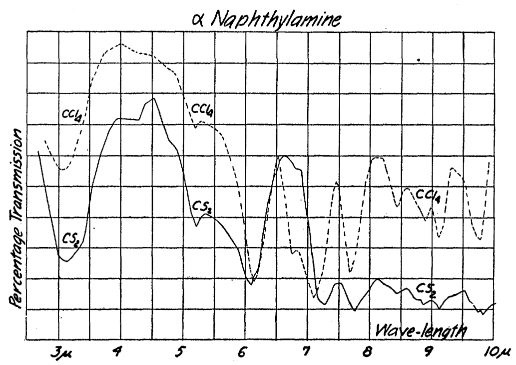

Fig. 13.

TABLE V.

Infra-red Absorption Maxima. Alpha Naphthylamine.

1.	2.	3.	4.	5.	6.	7.
No.	In CS_2.		In CCl_4.		Wave No.	
1	3.09μ	±.04μ			323	
2			3.18μ	±.04μ	314	
3	5.19	.03	5.20	.03	194	N
4	6.10	.03	6.18	.02	163	D
5			6.80	.04	147	
6			7.11	.03	141	
7	7.27	.03			138	ND
8	7.76	.03	7.71	.03	129	D
9	8.44	.03	8.47	.02	118	D
10	8.87	.05	8.92	.03	112	
11	9.11	.02	9.12	.03	110	
12	9.80	.04	9.75	.06	103	ND

Purvis at 3174 (9, 11, 12).

The tables given below for the various isomers list the absorption maxima wave-lengths as found with the two solutions and also show the corresponding wave numbers. In column 7, a band is marked N if it is a naphthalene band, and D if the band is found in both the alpha and the beta derivative. At the bottom of each table is given a list of the wave numbers of the known visible absorption bands and following each wave number, as before in parenthesis, are the numbers of the infra-red bands which are integral factors of the visible wave numbers. The absorption curves for these compounds are given in Figs. 11 to 15.

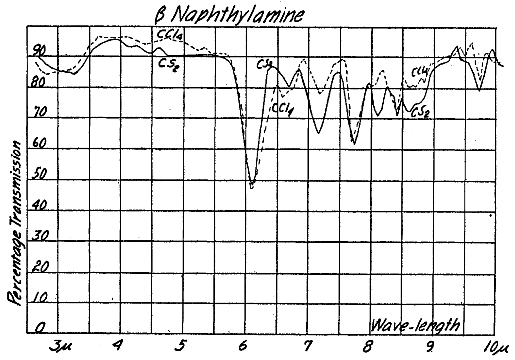

Fig. 14

TABLE VI.

Infra-red Absorption Maxima. Beta Naphthylamine.

1.	2.	3.	4.	5.	6.	7.
No.	In CS_2.		In CCl_4.		Wave No.	
1			2.86μ	±.04μ	350	
2	3.25μ	±.02μ			308	N
3	4.44	.04	4.44	.04	225	
4	6.13	.03	6.13	.02	163	D
5	6.67	.03	6.64	.04	150	
6	7.18	.03	7.20	.02	139	ND
7	7.73	.02	7.74	.03	129	D
8	8.09	.02			124	
9	8.40	.03	8.41	.02	119	D
10	8.59	.03			116	
11	9.74	.03	9.76	.02	103	ND

Purvis at 2922 (3, 4, 6, 10) and 3470 (5, 6, 9).

CONCLUSIONS.

1. The absorption of naphthalene and of several of its derivatives has been investigated from 2.7 μ to 10 μ in solutions of carbon disulphide and carbon tetrachloride.

2. Bands which are present when one of the solvents is used are nearly always present or indicated by breaks in the curve when the other solvent is used.

3. Although the positions of maximum absorption are generally the

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[1] Purvis, Chem. Soc. of Lon. Trans., 101, p. 1315, 1912.

same, in both solutions, the general appearance of the absorption curves may be very different.

4. Naphthalene has several absorption bands which are due to the benzene nucleus.

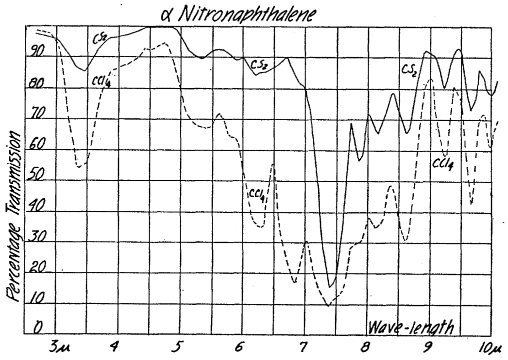

Fig. 15.

Table VII.

Infra-red Absorption Maxima. Alpha Nitronaphthalene.

1.	2.	3.	4.	5.	6.	7.
No.	In CS_2.		In CCl_4.		Wave No.	
1	3.44μ	±.02μ	3.42μ	±.02μ	282	
2	5.29	.04	5.36	.04	188	
3	6.22	.04	6.24	.03	160	
4			6.83	.02	146	N
5	7.42	.02	7.42	.03	135	
6	7.87	.02			127	N
7	8.17	.03	8.20	.04	122	N
8	8.67	.03	8.62	.03	116	
9	9.25	.02	9.23	.03	108	
10	9.67	.02	9.66	.03	103	
11	9.95	.03	9.96	.03	101	

Purvis at 2930 (4, 6, 7, 9, 11).

5. The mono-derivatives of naphthalene have several of the naphthalene absorption bands.

6. There are however many absorption bands present which are characteristic of the derivative itself.

7. Those naphthalene bands occurring in the alpha derivative are generally present in the beta derivative and there are always several other bands common to both derivatives.

8. The infra-red absorption curve of the alpha derivative is however as a whole different from that of the beta derivative in the same solvent.

9. Nearly all wave numbers of absorption bands for these substances in the visible possess, as integral factors, two or more infra-red absorption maxima wave numbers as Baly's theory predicts.

In conclusion, the writer desires to thank Professor H. M. Randall for proposing the subject and also for many valuable suggestions during the progress of the work.

Physical Laboratory,
Ann Arbor, Mich.,
May 2, 1916.