

Citation:

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of the nitramine in benzene gave results which were still less favourable.

One of us had noticed previously that among the aromatic amines which generally react on an alcoholic solution of the nitramine quite as readily as on picryl chloride, *p*-toluidine in particular gives a beautifully crystallised *p*-toluylpicramide m. p. 166°¹⁾ whilst the alcoholic solution contains only comparatively few, not very dark coloured byproducts. In an experiment in which 35 grams of the nitramine were heated on the waterbath with an equal weight of *p*-toluidine and 100 c.c. of 96 % alcohol, a fairly violent reaction set in after some time. The heating was continued for 5 hours and, after the picramide derivative had been removed by filtration, the alcohol was distilled off and the residue extracted with dilute sulphuric acid. The liquid filtered off from the toluidine sulphate was shaken with ether. On evaporation of the ether a still yellow coloured liquid product was left which on being inoculated with a crystal of methylnitramine became crystalline and after having stood for some time over sulphuric acid weighed 7 grams. On pressing between filter paper light yellow crystals were obtained which after being sublimed in vacuo (a treatment which methylnitramine stands very well) melted at 38°. On mixing the same with a preparation consisting of pure nitramine the melting point was not affected.

p-Toluidine appears, therefore, to be a suitable means for readily procuring in a short time methylnitramine from *s*-trinitrophenylnitramine.

We are continuing our investigations with different amines and also with other nitrated aromatic nitramines, and will state the results more elaborately in the "Recueil".

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Physics. — "*Wave-lengths of formerly observed emission and absorption bands in the infra-red spectrum.*" By Prof. W. H. JULIUS.

If in the infra-red spectrum, as formed by means of a rock-salt prism, the positions of emission or absorption bands have been carefully determined, the corresponding wave-lengths still are uncertain by an amount which, in a considerable part of the spectrum, is greater than the probable error of those determinations, because the

¹⁾ We now obtained this substance in two modifications, one coloured dark red and the other orange.

dispersion curve of rock-salt is not yet known with sufficient exactness.

Mr. W. J. H. MOLL¹⁾ has lately compared with each other the dispersion curves that have been calculated according to KETTELER's formula with two sets of constants, one given by RUBENS²⁾, the other by LANGLEY³⁾. LANGLEY's results held for a temperature of 20°, the numbers given by RUBENS were corrected by Mr. MOLL so as to apply to the same temperature. While coinciding in the visible spectrum, the two dispersion curves appeared to diverge very sensibly in the entire infra-red region, the wave-lengths corresponding to given indices of refraction being smaller with RUBENS' than with LANGLEY's constants. At $\lambda = 1,5 \mu$ e. g. the difference amounts to $0,028 \mu$, it increases unto $0,062 \mu$ (at $\lambda = 3 \mu$) and then decreases to $0,032 \mu$ (at $\lambda = 8,5 \mu$). If, on the other hand, the indices of refraction, which according to LANGLEY's and according to RUBENS' formula belong to rays of given wave-lengths, be compared with each other, the difference appears to be rather constant between $\lambda = 1 \mu$ and $\lambda = 8,3 \mu$, namely 1,5 units of the 4th decimal of the index, and to increase from 0 to 1.5 similar units in the region between $0,6 \mu$ and 4μ .

The apparatus, nowadays available for the investigation of the infra-red, admit of determining the position of sharp maxima or minima of radiation with an accuracy, going a good deal farther than 1,5 units of the 4th decimal of the index.

When between 1887 and 1891 I investigated several infra-red emission and absorption spectra, our knowledge of the dispersion of rock-salt was restrained to the outcome of LANGLEY's first determinations¹⁾, which extended only as far as $5,3 \mu$. As a great part of my work bore upon longer waves, I published my results in the form given by direct observation, viz, as galvanometer deflections and corresponding angles of minimum deviation, reduced to the temperature 10°. The refracting angle of the prism being also recorded, the indices of refraction of rock-salt for waves, corresponding to the observed maxima, were thus implicitly given.

In order to obtain a rough estimate of the wave-lengths, I had extended LANGLEY's dispersion curve in a straight line, though under strict reservation. The wave-lengths as read on this lengthened

¹⁾ W. J. H. MOLL, Onderzoek van ultra-roode spectra. Dissertation, Utrecht, 1907.

²⁾ H. RUBENS, Wied. Ann. 60, 724; 61, 224; 1897. Cf. also KAYSER, Handbuch der Spectroscopie I, 371, 1900

³⁾ S. P. LANGLEY, Ann. Astroph. Obs of the Smiths. Inst. I. 1900.

⁴⁾ S. P. LANGLEY, Phil. Mag., Aug. 1886.

curve, to which I myself assigned little weight¹⁾, have found their way to some text-books²⁾, where they unfortunately appear as the results of my investigation, with the incidental remark that they are incorrect, as founded on a false extrapolation. It is clear, however, that this incorrectness has nothing to do with the accuracy with which the position of the bands in the prismatic spectrum has been determined. Now I have reason to believe, that the spectrometric and heat-measuring apparatus used in that research were not less valid than those employed by many later observers of infra-red spectra (DONATH, PUCCIANTI, IKLÉ, COBLENTZ, NICHOLS, RUBENS and ASCHKINASS and others), so that the results still retain their value as a first contribution to our knowledge of the examined spectra.

I therefore thought it suitable to republish the principal results obtained at that time³⁾, but now to mention the indices of refraction for the maxima of emission and absorption, as following directly from my observations, and to add the wave-lengths, as derived from the more recent dispersion curves of RUBENS and of LANGLEY.

The positions in the infra-red were determined in my work with respect to the place of the *D*-lines of a BUNSEN flame coloured with chloride of sodium. But the latter were too faint to be observed with the bolometer; and the transition from the visual observation of the *D*-lines to the bolometric observation of infra-red radiations caused an uncertainty in the determination of the relative positions, which was still increased through the necessity of displacing the bolometer along the optical axis of the rock-salt lens according to its different focus for visible and invisible rays. It was chiefly in the part of

¹⁾ Cf. „Bolometrisch onderzoek van absorptie spectra”, *Verhandelingen der Kon. Akad. v. W. te Amsterdam*, Vol I, N^o. 1, p. 8 (1892), or the German translation in: *Verhandl. des Vereins zur Beförderung des Gewerbflusses*, 1893, p. 235, where I have clearly stated that I considered the extrapolation of LANGLEY's dispersion curve as quite uncertain, and that in the tables the direct data of observation (angles of minimum deviation) were given, because I did not like to have my results inseparably connected with a possible incorrectness of the dispersion curve. The passage in question seems not to have been noticed by W. W. COBLENTZ, for in his excellent work „Investigations of Infra-red Spectra”, published by the Carnegie Inst. of Washington, 1905, he says on p. 135, after alluding to LANGLEY's extrapolation of the dispersion curve in a straight line: „JULIUS, with apparently less hesitation, has applied this extrapolation to his work”.

²⁾ WINKELMANN, *Handbuch der Physik*; KAYSER, *Handbuch der Spectroscopie*; CHWOLSON, *Lehrbuch der Physik*.

³⁾ *Recherches bolométriques dans le spectre infra-rouge*. *Arch. néerl.* 22, p. 310—388 (1888).

Die Licht- und Wärmestrahlung verbrannter Gase, Berlin, Simion. 1890.

Bolometrisch onderzoek van absorptiespectra, l. c.

the investigation, described on p. 69 of "Die Licht und Wärmestrahlung verbrannter Gase" that many pains were taken to reduce this source of error. There the CO_2 -maximum of the BUNSEN flame was found at minimum deviation $38^\circ 54' 20''$, the refracting angle of the prism being $59^\circ 53' 20''$ and the temperature 10° . From this follows $n = 1.52103$. Had the temperature been 20° , then the deviation would have been found smaller by $1' 50''$, giving for the index of refraction: $n = 1.52069$.

If we suppose this value to be exact, then the angles of minimum deviation given in my first paper in Arch. néerl. 22, and on pages 47—68 of "Die Licht- und Wärmestrahlung" are too small by nearly $3'$, owing to an instrumental error. In "Bolometrisch onderzoek van absorptiespectra" the deviation of the CO_2 -maximum has been found $38^\circ 52' 40''$ instead of $38^\circ 54' 20''$; $1'$ of this difference results from the fact that the refracting angle of the prism, then in use, was smaller than that of the other one by $1'$; only the remaining $40''$ were owing to an instrumental error.

I have now applied the corrections resulting from this re-examination, and calculated the indices of refraction for 20° , the temperature to which the dispersion curves as compared by Mr. MOLL also refer. In finding the wave-lengths corresponding to the indices, advantage has been taken of elaborate tables, prepared by Dr. MOLL for a research of his own, and which he was kind enough to put at my disposal.

Emission-spectrum of:	Indices of refraction for the maxima (Temp. 20)	Wave-lengths according to the dispersion curve		Intensity ¹⁾
		of RUBENS	of LANGLEY	
BUNSEN-flame	1.5268	1 905	1.953	0.5
	1.5247 H ₂ O	2 760	2.831	3—5
	1.52069 CO ₂	4.410	4.462	10
Flame of carbon monoxide or of cyanogen	1.52445 CO ₂	2 883	2 947	1
	1.52069 CO ₂	4.410	4.462	10
Hydrogen flame	1.5247 H ₂ O	2.77	2.83	10
	1.5176	5.41	5.46	2
Luminous gasflame. . .	1.5270 C	1.84	1.89	²⁾
	1.5247 H ₂ O	2 77	2 83	²⁾
	1.5207 CO ₂	4.41	4.46	²⁾
Hydrog. burning in chlor.	1.5226 HCl	3.68	3.74	
Flame of sulfur	1.5093 SO ₂	7.49	7 52	
Flame of carb. disulphide	1.5247	2.77	2 83	1
	1.5207 CO ₂	4.41	4 46	10
	1.5125 COS(?)	6 76	6.80	3—0 ²⁾
	1.5093 SO ₂	7.49	7.52	2—3 ²⁾
Absorption-spectrum of:				
C (diamond)	1.5238	3.18	3.24	
	{ 1.5202	4.58	4.63	10
	{ 1.5183	5.20	5.25	
	1.5088 etc. ³⁾	7.59	7.62	10
H ₂ O	1.5287	1.41	1.43	1
	1.5265	2 01	2.06	1
	1.5236	3 25	3 31	9 s
	1.5194	4.85	4 90	
	1.5146	6.24	6.28	

¹⁾ In each spectrum the intensity of the highest maximum is indicated by 10. The letter s following an intensity figure means, that the band is rather sharp.

²⁾ The relative intensity of these bands varies much with the place in the flame.

³⁾ The addition "etc." behind an index of refraction indicates, that the band marks the beginning of an extensive region of strong absorption.

Absorption-spectrum of:	Indices of refraction for the maxima (Temp. 20°)	Wave-lengths according to the dispersion curve		Intensity
		of RUBENS	of LANGLEY	
CS ₂	1.5203	4.55	4.60	6 s
	1.5129	6.67	6.71	10
S ₂ Cl ₂	1.5219	3.96	4.02	1
	1.5163	5.78	5.82	1
	1.5090	7.55	7.58	7 s
	1.5049	8.36	8.39	1
	1.5020	8.90	8.93	1
	1.4992	9.41	9.44	8 s
	1.4942	10.28	10.31	10
PCl ₃	1.5221	3.88	3.94	0.5
	1.5082	7.72	7.75	10 s
	1.5030	8.73	8.76	0.5
	1.4944	10.25	10.28	10
Si Cl ₄	1.5172	5.53	5.57	6 s
	1.5154	6.03	6.07	1
	1.5058	8.19	8.22	10 s
	1.5014	9.02	9.05	10
	1.4974	9.73	9.76	10
Si HCl ₃	1.5234	3.34	3.40	0.5
	1.5173	5.50	5.54	1 s
	1.5058	8.19	8.22	2
	1.5014	9.02	9.05	10
	1.4974	9.73	9.76	3
C Cl ₄	1.5137	6.47	6.51	9 s
	1.5058	8.19	8.22	10 s
	1.4942	10.28	10.31	5 s
C H Cl ₃	1.5234	3.34	3.40	3
	1.5131	6.62	6.66	3 s
	1.5115	6.99	7.03	4
	1.5058	8.19	8.22	10
	1.4980	9.62	9.65	7

Absorption-spectrum of:	Indices of refraction for the maxima (Temp. 20°)	Wave-lengths according to the dispersion curve		Intensity
		of RUBENS	of LANGLEY	
CH Br ₃	1 5235	3 30	3.36	3 s
	1 5207	4.40	4.45	3 s
	1 5164	5.76	5.80	4 s
	1 5116	6 97	7 01	3
	1 5083	8.19	8.22	7 s
	1 5024	8 83	8 86	10
	1 4992	9 41	9.44	6
C ₆ H ₆	1 5259	2.25	2 31	1
	1.5236	3 25	3 31	4 s
	1 5211	4.26	4 31	1
	1 5173	5.50	5.54	6 s
	1 5128	6 69	6.73	10 s
	1.5107	7.18	7 21	3 s
	1 5088	7 59	7.62	1
	1 5060	8 15	8.18	2
	1.5039	8 56	8.59	7
(C ₃ H ₇) ₂	1 5259	2.25	2 31	2
	1.5230	3 51	3.57	7 s
	1 5154	6.03	6.07	1
	1.5118	6 93	6.96	10 s ¹⁾
	1 5097	7.40	7.43	6
	1 5068	7 99	8.02	4
	1 5032	8.69	8 72	6 s
	1.4980	9 63	9.66	5
	1.4942	10 28	10 31	5
CH ₃ OH	1.5259	2 25	2.31	1
	1.5229	3 56	3.62	10
	1 5194	4 85	4 90	2 s
	1.5145 etc.	6.27	6.31	10
C ₂ H ₅ OH.	1.5259	2 25	2 31	1
	1 5229	3 56	3.62	10
	1.5183	5 20	5.25	2 s
	1.5154	6 03	6.07	2
	1.5126 etc.	6.74	6.78	10

¹⁾ Sharply limited only toward the smaller wave-lengths.

Absorption-spectrum of:	Indices of refraction for the maxima (Temp. 20°)	Wave-lengths according to the dispersion curve		Intensity
		of RUBENS	of LANGLEY	
C ₃ H ₇ OH	1.5230	3.51	3.57	10
	1.5152	6.09	6.13	3
	1.5126 etc.	6.74	6.78	10
C ₄ H ₉ OH (normal). .	1.5230	3.51	3.57	10
	1.5162	5.81	5.85	3
	1.5126 etc.	6.74	6.78	10
C ₄ H ₉ OH (iso). . .	1.5230	3.51	3.57	10
	1.5192	4.92	4.97	1
	1.5154	6.03	6.07	2
	1.5126 etc.	6.74	6.78	10
C ₅ H ₁₁ OH	1.5230	3.51	3.57	10
	1.5192	4.92	4.97	1
	1.5154	6.03	6.07	3
	1.5126 etc.	6.74	6.78	10
(C ₂ H ₅) ₂ O	1.5327	0.95 _s	0.95 _s	1
	1.5293	1.30	1.32	1
	1.5259	2.25	2.31	2
	1.5230	3.51	3.57	8 s
	1.5183	5.20	5.25	3 s
	1.5164	5.76	5.80	1
	1.5116	6.97	7.01	10
	1.5099	7.35	7.39	4
	1.5078	7.80	7.83	4 s
	1.5045 etc.	8.44	8.47	10
C ₂ H ₅ SH	1.5256	2.38	2.44	1
	1.5230	3.51	3.57	5
	1.5221	3.88	3.94	3
	1.5183	5.20	5.25	1
	1.5162	5.81	5.85	1
	1.5115	6.99	7.03	10
	1.5074	7.88	7.91	10
	1.5001	9.25	9.28	8
	1.4936	10.39	10.42	9