

Physics. — *On the absorption spectra of the azobenzol crystal.* By J. W. OBREIMOW and W. J. DE HAAS. (Communication Phys. Lab. Leiden, N^o. 204c.)

(Communicated at the meeting of November 30, 1929).

Introduction. In two preceding papers ¹⁾ has been shown, that the change of colour of crystals at low temperatures is a general phenomenon for all crystalline bodies and that at low temperatures the absorption spectra of all crystals probably must be line spectra. The wide absorption band of most of the well-known crystals must split up into fine lines like the bands of the rare earths (J. BECQUEREL) or the wide bands of benzol (KÖNIGSBERGER and PRINGSHEIM). The change of colour of the crystals has been attributed to the contraction of the absorption bands.

We remarked that at the temperature of 20° K. the spectrum of the azobenzol is very regular. For want of a suited spectrograph however we could make no accurate measurements.

§ 1. Now Prof. D. S. ROSCHDESTWENSKY in Leningrad has lent us a very good grating (plane grating 8 cm. long, 14000 lines per inch, focal distance of the object-glass ca. 165 cm.). With this spectral apparatus we could obtain spectrograms suited for measurements.

The azobenzol crystallizes from an alcoholic solution in monocline plates ($a : b : c = 2, 11 : 1 : 1, 33$; $\angle (a, c) = 114^\circ.26'$). The plane of the plates is c (001). The plane of the optical axis is perpendicular to the plane of symmetry (010). At room temperature in transmitted light the azobenzol-plates are distinctly dichromatic. They have brick colour when the light vector is parallel with the b -axis and lemon colour when the light vector is perpendicular to the b -axis ²⁾).

At 20° K and lower temperatures azobenzol shows a beautiful line spectrum, when the light vector is parallel with the b -axis (red spectrum). We made spectral photographs in the first order of the grating at the temperatures 14° K (liquid hydrogen at 6 cm. pressure) and at 4.22° K. (liquid helium at atmospheric pressure). In the following tables the blackest absorption lines have been given :

¹⁾ J. W. OBREIMOW and W. J. DE HAAS, Proc. Roy. Soc., Amsterdam, **31**, 353, 1929.

J. W. OBREIMOW, Journ. d. Russ. Phys. Ges., 1927.

²⁾ The crystallographic data have been taken from P. GROTH, Chemische Krystallographie

TABLE I.
Azobenzol in liquid helium (4.22°). Red spectrum.

Indication of the line	$\lambda_{air}^1)$	$\nu_{vac} = 1/\lambda_{vac}$	a, b	$\nu_a - \nu_b$	ν_{calc}	$\nu_{calc} - \nu_{vac}$
0	5499.62	18178.03			18178.0	0.0
0'	5440.66	18375.03	0' - 0 =	197.00	18377.3	2.0
0 ₁ '	5427.13	18420.84	0 ₁ ' - 0' =	45.81		
0 ₂ '	5409.66	18480.33	0 ₂ ' - 0' =	105.30		
0''	5382.69	18572.92	0'' - 0' =	197.89	18576.6	3.7
0 ₁ ''	5369.29	18619.39	0 ₁ '' - 0'' =	46.47		
0 ₂ ''	5352.49	18677.64	0 ₂ '' - 0'' =	105.72		
0 ₃ ''	5339.15	18724.37	0 ₃ '' - 0'' =	153.45		
0 ₄ ''	5331.08	18752.72	0 ₄ '' - 0'' =	179.80		
1	5309.13	18830.25	1 - 0 =	652.22	18830.2	0.1
0 ₂ '''	5295.59	18878.40	0 ₂ ''' - 0 ₂ '' =	200.76		
0 ₃ '''	5283.15	18922.85	0 ₃ ''' - 0 ₃ '' =	198.48		
0 ₄ '''	5275.45	18950.47	0 ₄ ''' - 0 ₄ '' =	197.75		
1'	5253.54	19029.50	1' - 1 =	199.25	19029.5	0.0
1 ₁ '	5241.01	19074.99	1 ₁ ' - 1' =	45.44		
1 ₂ '	5225.49	19131.65	1 ₂ ' - 1' =	102.15		
1''	5199.50	19227.28	1'' - 1' =	197.78	19228.8	+ 1.5
1 ₁ ''	5187.38	19272.20	1 ₁ '' - 1'' =	44.92		
1 ₂ ''	5171.05	19333.06	1 ₂ '' - 1'' =	104.78		
1 ₃ ''	5159.48	19376.41	1 ₃ '' - 1'' =	149.13		
1 ₄ ''	5152.63	19402.18	1 ₄ '' - 1'' =	174.90		

In the tables I and II *all* measured lines have been given. Of the 42 measured lines only *two* do not fit into a series schema. This does not mean however, that their right values do not fit into our schema. The signs of interrogation and the remarks in Table II were added during the measurements viz. before the calculations.

All measured lines have been plotted from fig. 1 in wave-number scale.

The spectrum looks as follows; it consists of several series of aequidistant lines:

0; 0'; 0''; 1; 1'; 1''; 1'''; 2; 2'; 2''; 2'''; 3; 3''.

¹⁾ Last figure not certain.

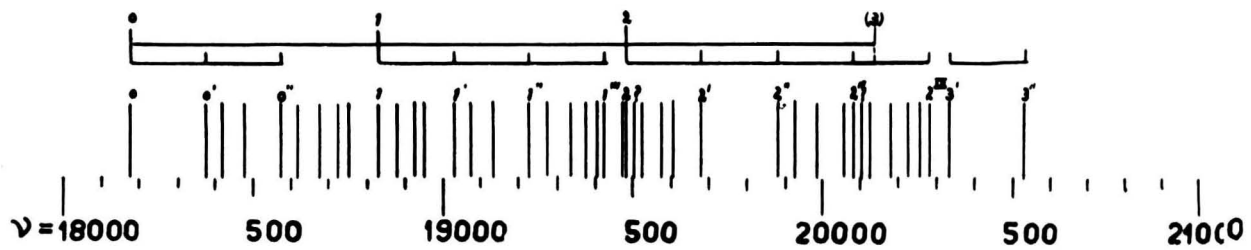


Fig. 1.

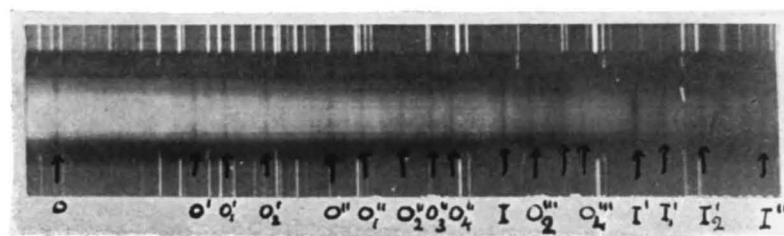


Fig. 3.

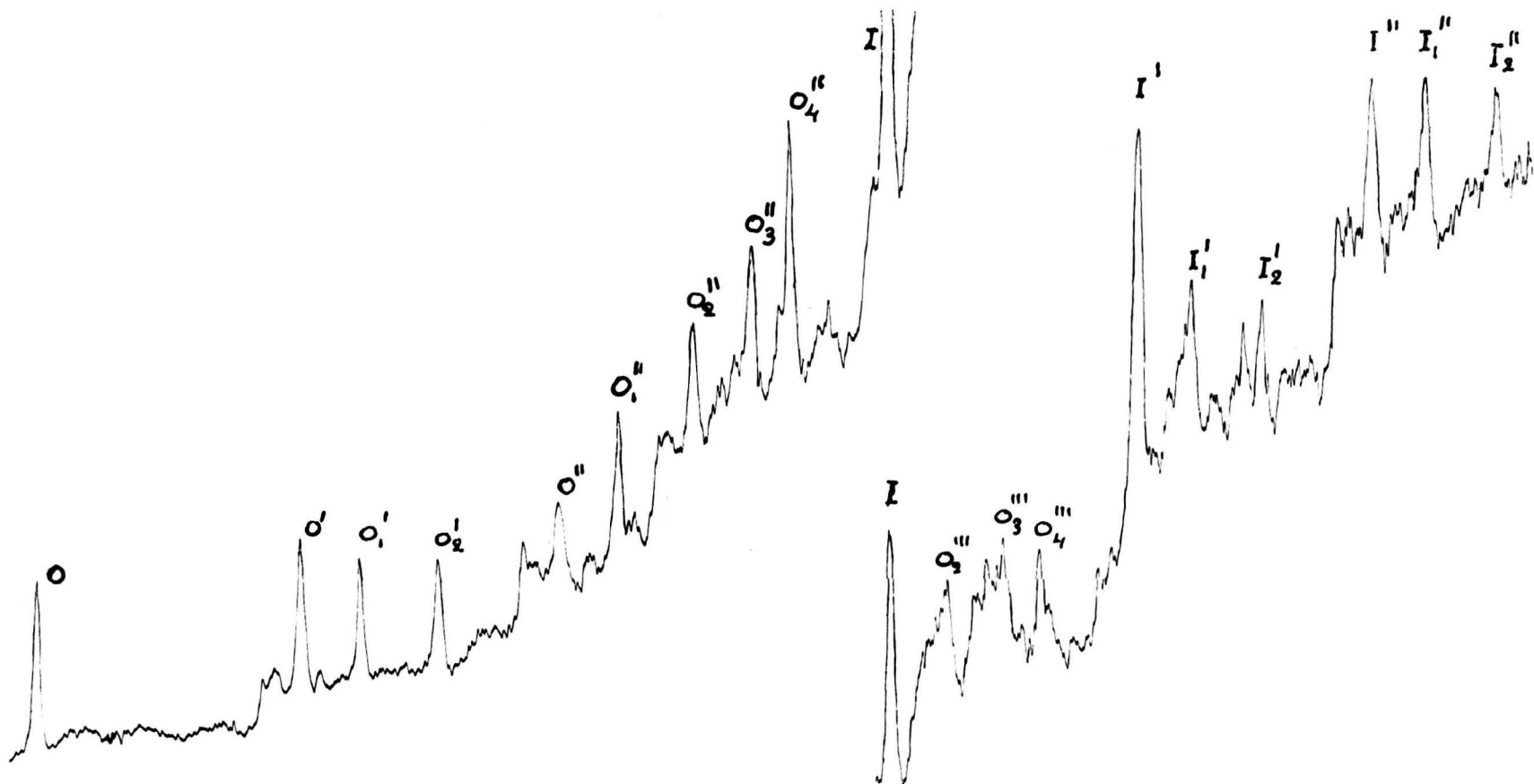


Fig. 2.

where m and n are whole numbers 0, 1, 2, 3, and ν_0 , a , b constants :

$$\left. \begin{aligned} \nu_0 &= 18178.0^3 \\ a &= 199.3 \\ b &= 652.2 \end{aligned} \right\} \dots \dots \dots (2)$$

In column 5 of tables I and II we have given the wavenumbers calculated with formula (1) and the constants (2).

But the whole spectrum measured is more complicated. All lines without index, but often also those with the index ' are single, e.g. the lines: 0, 1, 2, 2', 3'.

The next lines (0' ; 1' ; 2'' and as can be seen but not measured 3'') are accompanied by two lines: 0' by the companion lines 0'_1, and 0'_2. 1' by the companion lines 1'_1 and 1'_2. One of the companion lines has a mean distance of 45.0, the other one of 104.0 from the principal line.

The next principal lines are accompanied not only by these two companion lines but by several other companion lines. Among these the satellites 0_3'' ; 1_3'' ; 2_3''' have a mean distance of 147.2 and 0_4'' ; 1_4'' ; 2_4''' of 176.13 from the principal line.

A peculiar aspect of the spectrum is due to the distribution of the intensity in several lines. Let us e.g. consider the group 0.

The line 0 is single or we can say, that the intensity of the lines 0_1, 0_2 is practically zero.

In the reiteration 0' the lines 0' ; 0_1' ; 0_2' ; have nearly equal intensities. The lines 0_3' ; 0_4' however are lacking.

These two last lines only occur in the next reiteration 0'' ; here however the intensity of the line 0'' is smaller than the intensity of the line 0_1'' and the line 0_1'' is weaker than 0_2''. In the fourth reiteration however the lines 0''' and 0_1'''' are failing ; but the lines 0_2''' ; 0_3''' ; 0_4''' are still present. The same holds for the other groups.

From the microphotogram (fig. 2) of the spectrum of the azobenzol (fig. 3) at 4.22° K. it is evident, that in fact the spectrum is still more complicated. There exist more lines than we have measured. Beside the rather sharp lines we can also see diffuse bands. All these lines and bands constitute a continuous background. This background is weak in the neighbourhood of the line 0 and becomes stronger towards the violet of the spectrum till it is so dark, that no black lines can be discerned against it. That is why in the measurements with the comparator only the lines 0 ; 0' ; 0_1' ; 0_2' are discernable. Further towards the violet the lines become less and less distinct. For this reason we could not measure a line beyond 3''. Even in helium we could only extend the measurements till 1_4'', the "helium" crystal being thicker than the "hydrogen" crystal.

Unfortunately we therefore cannot compare the observations in helium and in hydrogen. At 4.22° K. the absorption lines are considerably sharper than at 14° K. It is however remarkable that both at 4.22° K. and at 14° K. the same lines occur with nearly the same distribution of the intensity.

This shows, that our series scheme is also the energy scheme viz. that our fundamental level is also the zero energy level.

From the tables I and II it is evident that at 4.22° K. the position of the lines is shifted with respect to that at 14° K. over 0.2 \AA towards the short wavelengths. The amount at this shifting is uncertain and falls beyond the accuracy of our measurements. The constant a too increases with ν , but our measurements were not accurate enough to give the term with ν^2 .

We also investigated the absorption spectrum of the azobenzol for the component of the light perpendicular to the b -axis, but we could find no structure in this spectrum, not even at 4.22° K. We observed a continuous absorption in the violet without discrete bands.

Azobenzol vaporizes without decomposition. At 70° C. already the azobenzol vapour seems to have a greenish yellow colour. But in the absorption spectrum of the vapour (saturated vapour at 70° C. ; 200° C. and 300° C. in vacuum ; thickness of the layer 10 cm.) we could find no lines or bands. The absorption increased regularly from the red towards the violet.
