

PLATINUM ISOTOPES AND THEIR NUCLEAR SPIN.

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PLATINUM is one of the few elements which has so far not yielded its isotopic constitution by the mass-spectrograph method. Generally the hyperfine structure data have been interpreted in the light of the isotopic constitution as revealed by the mass-spectrograph. The present knowledge in regard to the hyperfine structure of spectral lines, especially with reference to isotopic effect, is often adequate for the determination of the isotopic constitution and nuclear spin. A study of the hyperfine structure of the arc lines of platinum was therefore undertaken.

Experimental.

The hollow cathode employed in this investigation is a double-walled copper cylinder (Fig. 1) hard-soldered at both ends with the inside hollow

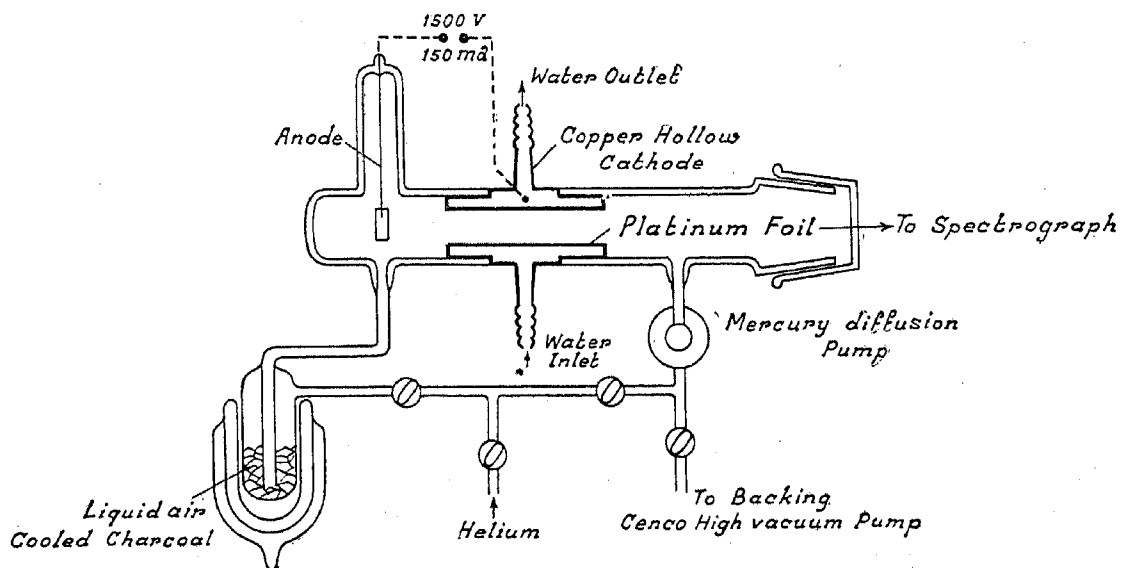


FIG. 1.

about 1 cm. in diameter and 6 cms. in length. Inlet and outlet tubes are provided so as to maintain a continuous flow of water in the space between the two cylinders during excitation. On to the shoulders cut in the outer copper cylinder are fitted pyrex glass tubings with a quartz window on one side and a ring anode on the other. The metal glass joint is rendered air-tight by Apiezon sealing wax and due to the continuous flow of water in the hollow cathode the joint continues to be air-tight under all conditions of discharge. The apparatus is set up *in situ* with a cylinder of platinum foil fitting tightly in the hollow cathode. The apparatus is next exhausted with a mercury diffusion pump backed by a Cenco Hyvac pump. The backing pump is then cut off and the activated charcoal is cooled by liquid air contained in a triple wall Dewar cylinder. Helium is now let in slowly, further purification being effected by its passage through the liquid air cooled charcoal. When the required pressure of helium (about 1 or 2 mms. of mercury) is reached the supply is cut off. Requisite amount of helium is thus allowed to circulate continuously through the hollow cathode by the operation of the diffusion pump. The repeated passage of helium through the liquid air cooled charcoal maintains its purity. A direct current dynamo of 1 kilowatt capacity is employed to send a discharge through the hollow cathode. For the excitation of the platinum lines a discharge current of 150 mA at 1500 v. is found satisfactory. At this stage the hollow cathode glow is intense and is accompanied with little or no positive glow. The discharge conditions can be maintained steady for hours together by replenishing the liquid air from time to time.

The hollow cathode glow is concentrated on a Hilger Lummer Gehrcke plate of quartz (3.45 mms. thick and 20 cms. long) by means of a quartz lens carrying a double image prism. One of the images is cut out and the light of the other, with its electric vector parallel to the plate, passes through. The pattern is focussed by a quartz achromatic lens on to the slit of a Hilger E 1 spectrograph with a quartz train. The hyperfine structure patterns of the platinum lines are photographed on hypersensitive panchromatic plates.

Results.

Ten arc lines of platinum are examined for hyperfine structure, two of which however do not exhibit their complete structure for want of sufficient exposure. Below is given a table containing the wavelengths of the lines, their classification and their hyperfine structure components. The intensities of the components inserted in brackets against each component are eye-estimates and are therefore subject to further confirmation by microphotometric study.

Wavelength in A.U.	Classification ¹	Structure in cm. ⁻¹	Remarks
3408·13	a ³ F ₄ -z ⁵ D ₄ ⁰	+0·161 (5), 0·000 (18) -0·086 (7), -0·176 (1) -0·314 (4)	Fig. 2 (Pl. XLVIII)
3042·63	a ³ F ₄ -z ⁵ G ₅ ⁰	+0·162 (5), 0·000 (18) -0·087 (7), -0·174 (1) -0·314 (4)	
2719·02	a ³ F ₄ -z ³ F ₄ ⁰	0·000 (18), 0·154 (12?)	Exposure insufficient.
2705·88	a ³ F ₄ -8 ₃ ⁰	0·000 (18), -0·145 (12?)	Exposure insufficient.
2650·84	a ³ F ₄ -z ⁵ F ₅ ⁰	+0·171 (5), 0·000 (18) -0·120 (7), -0·296 (4)	Pattern faint and measurements approximate
2997·97	a ³ D ₂ -z ³ F ₃ ⁰	+0·240 (5), 0·000 (25) -0·304 (4)	
2733·96	a ³ D ₂ -6 ₂ ⁰	+0·172 (5), 0·000 (25) -0·227 (4)	
2702·38	a ³ D ₂ -8 ₃ ⁰	0·201 (5), 0·000 (25) -0·262 (4)	
2929·79	a ³ D ₃ -z ³ F ₃ ⁰	+0·160 (4), 0·000 (25) -0·141 (5)	
2659·44	a ³ D ₃ -z ³ F ₄ ⁰	+0·248 (4), 0·000 (25) -0·187 (5)	

The two lines 3408·13 and 3042·63, besides having a common lower level in $5d^8 6s^2$ a ³F₄, are identical in structure; this leads to the conclusion that in either case the spin splitting of the upper levels is negligibly small. An examination of their structure leads to the indubitable conclusion that the three central components 0·000 (18), -0·086 (7) and -0·176 (1) have to be respectively ascribed to the even isotopes 196, 194 and 192, all of which have zero nuclear spin. The remaining two components 0·161 (5) and

¹ A. C. Haussmann, *Astrophys. Jour.*, 1927, 66, pp. 333-346; J. J. Livingood, *Phys. Rev.*, 1929, 34, pp. 185-198.

-0.314 (4) belong to the odd isotope 195; the relative intensity of the components as well as their number fixes the nuclear spin moment of Pt 195 as $\frac{1}{2} \frac{h}{2\pi}$. The centre of gravity of these components falls at -0.050 cm.^{-1} between the components ascribed to the isotopes 196 and 194; this fact makes the interpretation of the extreme satellites as being due to Pt 195 a certainty. The centre of gravity, as in the case of other elements like mercury, lies nearer to the lighter isotope 194 (Pl. XLVIII). The level a^3F_4 , arising as it does from an electronic configuration of the type $d^8 s^2$, is expected to show even isotope shift as in other spectra. The deeper levels $a^3D_{3,2}$ show no measurable isotopic displacement. The hyperfine levels of a^3F_4 are inverted. The spin separations and the interval factors for the multiplet levels here examined are given in Fig. 3, where it is seen that the hyperfine levels are

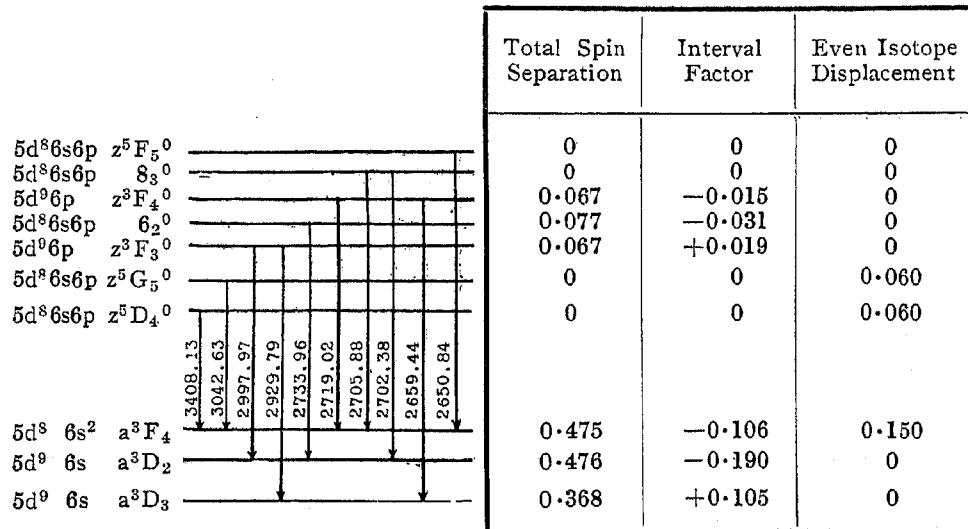


FIG. 3. Arc Lines of Platinum Analysed.

inverted in some cases and erect in others. The scheme suggested is the result of an adjustment to cover the observational data recorded in this paper. Fig. 4

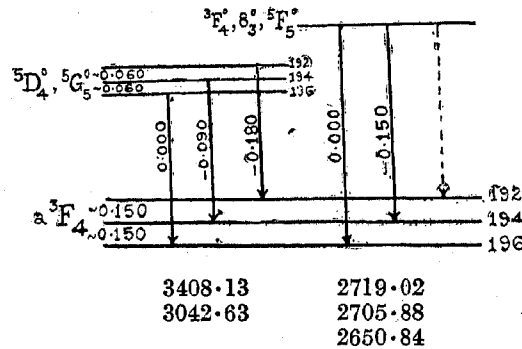


FIG. 4. Even Isotope Displacement.

gives the observed even isotope displacements in lines arising from transitions

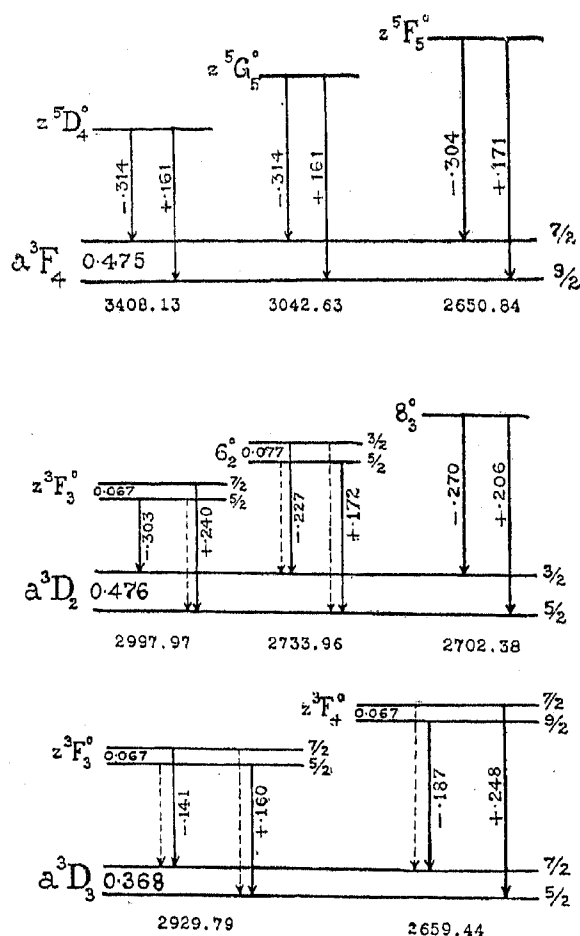


FIG. 5. Hyperfine Structure of Pt, I lines arising from a nuclear spin of $\frac{1}{2} \frac{h}{2\pi}$ in the Odd Isotope 195 of Platinum.

to the level a^3F_4 . Fig. 5 accounts for the remaining components as arising from $f-f$ transitions in the isotope 195. All transitions that are too faint to be observed are shown by broken lines. The observed structure, when compared with Figs. 4 and 5, shows complete agreement with theoretical expectations. Any complication arising out of self-reversal is entirely ruled out, because the lines arising from transitions to the ground term a^3D_3 , such as 2929.79, show sharp main lines without any doubling due to self-reversal. The observed isotope shift in 3408.13 is not due to any such cause as the two bright central components are of unequal intensity; besides this line is poorly absorbed as compared with any other line here examined.² The observed intensity of absorption is in the ratio of 4 : 30 for 3408.13 and 2929.79 in under-water spark discharge.

² W. F. Meggers & O. Laporte, *Phys. Rev.*, 1926, 28, pp. 642-664.

Neglecting isotopes of small abundance, whose presence cannot be discovered by hyperfine structure study, the isotopes of platinum, in decreasing order of their relative abundance, are 196 (18), 195 (9), 194 (7) and 192 (1). The relative isotopic abundance here given is from eye-estimates of the intensities of the components. It is needless to attempt any calculation of atomic weight, until their relative abundance is definitely fixed by microphotometric measurement. As platinum is at present devoid of any mass-spectrum data,³ this derivation of its isotopic constitution purely from hyperfine structure study is of interest.

Platinum exhibits a positive isotope shift consistent with our previous generalisation that even atomic number "elements whose nuclei contain an odd number of α -particles exhibit positive isotope shift and those with even number a negative displacement".⁴

Abstract.

An examination of the hyperfine structure of some ten lines in the arc spectrum of platinum has led to the determination of the isotopic constitution and the nuclear spin of this element. The isotopes are 196 (18), 195 (9), 194 (7) and 192 (1). The relative abundance of the isotopes will be checked by microphotometric study. The nuclear spin of the odd isotope 195 is $\frac{1}{2} \frac{h}{2\pi}$. The isotopic displacement is observed to be positive.

³ F. W. Aston, *Proc. Roy. Soc.*, 1935, 149, p. 404.

⁴ B. Venkatesachar & L. Sibaiya, *Proc. Ind. Acad. Sci.*, 1934, 1, pp. 8-13.

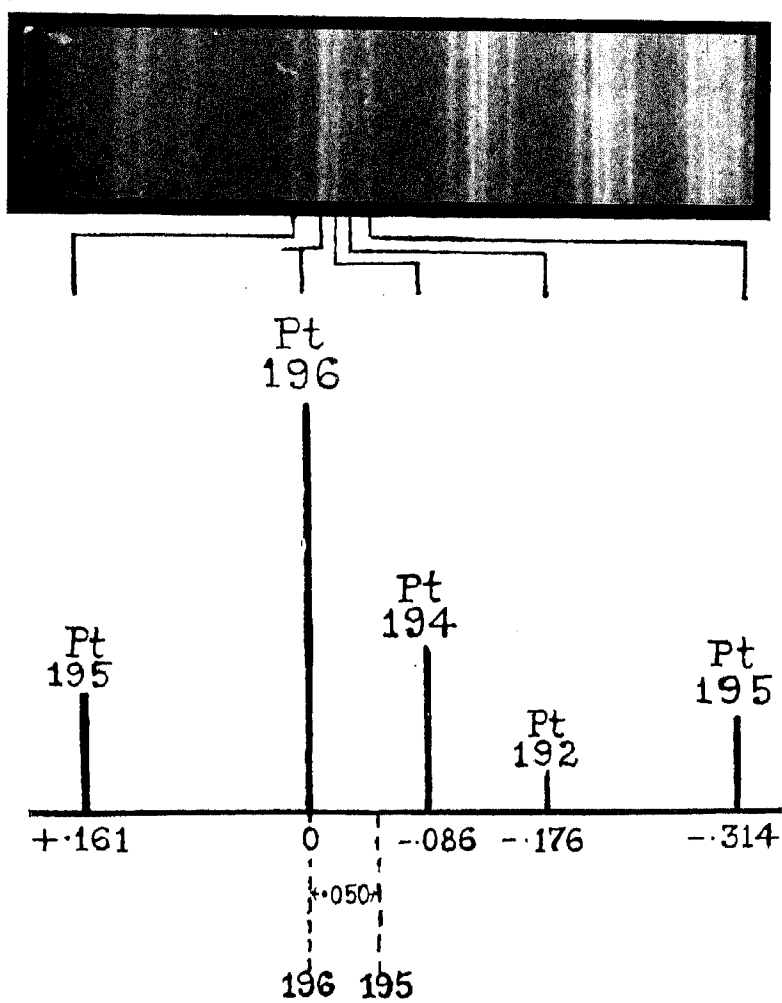


FIG. 2. Structure Pattern of 3408.13 Å.