

NOTAS DE FÍSICA

VOLUME XVI

Nº 13

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IN A KCl LATTICE

by

R. P. A. Muniz, H. V. Vugman and J. Danon

CENTRO BRASILEIRO DE PESQUISAS FÍSICAS

Av. Wenceslau Braz, 71 - Botafogo - ZC-82

RIO DE JANEIRO, BRAZIL

1970

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R. P. A. Muniz, N. V. Vugman, J. Danon
Centro Brasileiro de Pesquisas Físicas
Rio de Janeiro, Brasil

(Received October 12, 1970)

ABSTRACT

Electron irradiation of the diamagnetic $Rh(CN)_6^{3-}$ ion in a KCl host lattice produces three paramagnetic species. EPR studies reveals that one of the species can be assigned as $Rh(CN)_4Cl_2^{4-}$, of D_{4h} symmetry, $4d^7$ low spin configuration, arising from the trapping of an electron in a d_z^2 orbital followed by the substitution of two axial cyanides by chloride ions. The experimental data have been interpreted in terms of a spin Hamiltonian yielding the principal values of the g and hyperfine tensors as $g_{||} = 1.995$, $g_{\perp} = 2.297$, $A_{||}^{Rh} = -40.8 \times 10^{-4} \text{ cm}^{-1}$, $A_{\perp}^{Rh} = -36.9 \times 10^{-4} \text{ cm}^{-1}$, $A_{||}^{Cl} = +27.8 \times 10^{-4} \text{ cm}^{-1}$, $A_{\perp}^{Cl} = +12.4 \times 10^{-4} \text{ cm}^{-1}$. Theoretical estimates of g values confirms this assignment. A semi-empirical estimate of the unpaired electron density on the metal and ligands is presented.

* * *

The first EPR work on a coordination compound of Rh(II) reports an investigation of the complex $(Bu_4N)RhS_4C_4(CN)_4$ in which the rhodium ion has a $4d^7$ low spin configuration and is coordinated to four sulfur atoms.¹ Maki et al² studied the same complex diluted in the isomorphous single crystals of

* Submitted by N. V. Vugman to the Universidade Federal do Rio de Janeiro as partial fulfillment of the requirements for the Master's degree.

$(\text{Bu}_4\text{N})\text{NiS}_4\text{C}_4(\text{CN})_4$. Townsend³ investigated Rh(II) in a single crystal of zinc tungstate obtaining for the first time detailed information on the hyperfine interaction with the rhodium nucleus. Dessy et al.^{4,5} studied the complexes $(\pi\text{-C}_5\text{H}_5)\text{Rh}(\pi\text{-C}_2\text{H}_4)_2$ and $(\pi\text{-C}_5\text{H}_5)\text{RhS}_2\text{C}_4\text{F}_6$ obtained by electrolytic oxidation but measured only the average g value of the first compound. Keller and Waver⁶ investigated $(\pi\text{-C}_5\text{H}_5)_2\text{Rh}$ without resolving the hyperfine structure of the spectrum.

References 1 and 2 study refer to a planar complex and Townsend's work treats the Rh(II) in a crystal field of almost octahedral symmetry.

Danon et al.^{7,8} succeeded in producing paramagnetic species of d^7 configuration irradiating with electrons diamagnetic d^6 low spin complexes. Following this line we have irradiated $\text{K}_3\text{Rh}(\text{CN})_6$, an octahedral complex of Rh(III), with a ground state configuration (t_{2g}^6), expecting that under favourable conditions, reduction effects be produced by electron trapping as reported in references 7 and 8.

Given the difficulties of obtaining single crystals, preliminary experiments were performed by irradiating polycrystalline samples. The results, however, were not very informative since many species were produced and the spectra obtained difficult to assign.

Other work^{9,10,11} suggested the possibility of diluting the Rh(III) complex in KCl whose cubic lattice has the appropriate symmetry and spacing to accommodate the $\text{Rh}(\text{CN})_6^{3-}$ ion. The KCl was chosen after a few trials with other alkali halides which did not give good results, probably due to the size of the unit cell, which is too small. In the KCl it enters substitutionally, replacing a KCl_6^{5-} group. Two positive ion vacancies must be formed in order

to keep neutrality.

Very conveniently the V_{K^-} -centers which are formed when alkali halides are irradiated disappear at room temperature.

EXPERIMENTAL

The potassium chloride crystals were obtained by slow crystallization of a saturated aqueous solution to which $K_3Rh(CN)_6$ was added in molar proportions of .1, .2, .4, .5, 1 and 2 percent. They were about 2 mm edge and the best ones were chosen by visual inspection.

Irradiation was performed both at room temperature and at 77°K. The samples irradiated at 77°K were brought to room temperature after irradiation in order to anneal away the undesired signals from V_K centers. All samples were irradiated for 20 seconds with 2 MeV electrons at a current of 5 microamperes.

The crystals irradiated at liquid nitrogen temperature and brought to ambient temperature became colorless. The ones irradiated at room temperature acquired a light pink color.

The spectra were obtained with a Varian 4500 X band spectrometer all at liquid nitrogen temperature. Q-Band measurements were performed to obtain angular variation and to check on the coherence of the species assignment.

For examination in the spectrometer the crystals were mounted on a cold-finger cryostat for EPR in such a way that they could be rotated around one of the principal axes. When any of the other two axes of the crystal is parallel to the applied magnetic field one obtains, in one scanning, both the parallel and the perpendicular features of the spectrum. This gives an immediate check on the axial symmetry of the species under study.

The spectra observed reveal, in the irradiated sample, the presence of three paramagnetic species (fig. 1) which we label A, B and C. All three have axial symmetry. Species A, which is the main object of this paper, exhibits a well resolved spectrum. The other two spectra are under study.

Species A only forms when the crystal is irradiated at room temperature. Samples irradiated at 77°K show the signal corresponding to this species in such a low intensity that it is hardly measurable. Annealing for about two hours at 200°C of the samples irradiated at liquid nitrogen strongly enhances the signal.

The intensity of the species A spectrum is notably influenced by concentration of $\text{Rh}(\text{CN})_6^{3-}$ present in the doped sample. For low concentrations (up to about .3%) the intensity of the signal increases linearly with concentration. As the amount of added $\text{Rh}(\text{CN})_6^{3-}$ increases this intensity passes by a maximum and then decreases in an exponential fashion.

Angular variation studies show that species A has axial symmetry (Figs. 2, 3). Both g values and hyperfine splittings can be fitted to the familiar $\cos^2\theta$ law for these parameters, and have the same principal axes, oriented along the crystalline axes.

The spectrum of species A is shown in figs. 4 and 5 in which one can see respectively the parallel and perpendicular features. It will be noticed the strong similarity of the parallel spectrum of species A with the spectrum of V_k -centers as presented in Kanzig's work¹². This similarity suggests that, as in V_k -centers, there is interaction with two equivalent chlorines. Species A, however, has a) different symmetry axes, b) different g values and c) is stable at room temperature.

By assigning species A as $\text{Rh}(\text{CN})_4\text{Cl}_2^{4-}$, with the two Cl^- in the axial positions, the semi empirical reconstitution of the spectra reproduced in figs. 4 and 5 was made in terms of a spin hamiltonian of the following form:

$$\mathcal{H} = \beta_e H \cdot g \cdot S + \sum_{i=1}^2 S \cdot A_{\text{Cl}_i} \cdot I_{\text{Cl}_i} + S \cdot A_{\text{Rh}} \cdot I_{\text{Rh}}$$

which splits into three partial hamiltonians corresponding to the three possible pairs of chlorine isotopes $\text{Cl}_{35} - \text{Cl}_{35}$, $\text{Cl}_{35} - \text{Cl}_{37}$ and $\text{Cl}_{37} - \text{Cl}_{37}$ one has to consider to account for the whole spectrum. The parameters obtained for species A, together with the g values for species B and C are shown in table I.

The natural abundances of these isotopes are taken respectively as 75% and 25%. As one can see in the figures it is possible to account for all the lines observed.

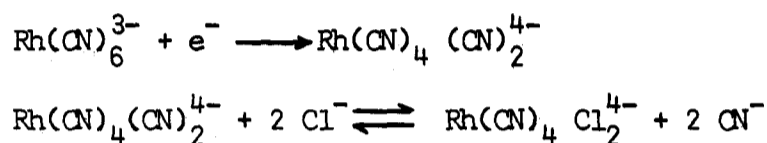
The same line of reasoning leads to the reconstruction of the perpendicular feature in good agreement with the observed spectrum.

DISCUSSION

The hyperfine splittings observed in both the parallel and perpendicular features of species A, the observed axial symmetry, and the g values measured strongly suggests that species A, as mentioned earlier in this work, is $\text{Rh}(\text{CN})_4\text{Cl}_2^{4-}$. Earlier work by Danon et al. ^{7, 8} on irradiated d^6 low spin transition metal complexes has shown that the axial cyanides are the ones usually affected by the electron trapping in a d_{z^2} orbital. This is to be expected since this is an antibonding orbital normally empty in these complexes.

The trapping of the electron increases the energy of the system loosening, therefore, the bond of the axial cyanides. In our case the equatorial cyanides remain in their positions and the axial cyanides have their binding energies reduced to a point that thermal agitation is enough to exchange them for chlorines. This interpretation is supported by the fact that samples irradiated at liquid nitrogen temperature form very little of species A whereas those irradiated at room temperature show very strong signals due to species A. The fact that samples irradiated at 77°K and annealed at 200°C will show the spectrum of species A gives further support to this interpretation.

These results suggest the following reaction scheme:



The first reaction corresponds to the trapping of the electron in the anti-bonding orbital ¹³. The second reaction is influenced by concentration and only proceeds above certain temperature as the annealing experiments show. The increase in concentration of $\text{Rh}(\text{CN})_6^{3-}$ shifts the equilibrium towards the left. This explains qualitatively the decrease of intensity of the signal due to species A at higher concentration of this ion in the sample.

The data on species A, which we have assigned as $\text{Rh}(\text{CN})_4\text{Cl}_2^{4-}$ are consistent with the idea that we have a $4d^7$, low spin, complex with a D_{4h} symmetry.

Indeed, the crystal field treatment of the problem, assuming the unpaired electron to be in a d_{z^2} orbital, i.e., a ground state configuration $e^4 b_2^2 a_1$, including in the hamiltonian the spin orbit interaction and L.I interaction, ¹⁴ leads to the following formulas for the spin hamiltonian parameters:

$$g_{\parallel} = 2$$

$$g_{\perp} = 2 + 6y$$

$$A_{\parallel}^{\text{Rh}} = P(g_{\parallel} - K + \frac{4}{7} - \frac{6}{7}y)$$

$$A_{\perp}^{\text{Rh}} = P(g_{\perp} - K + \frac{2}{7} + \frac{3}{7}y)$$

where

$$y = \frac{\xi_{4d}}{\Delta} \langle 4, P = 2g_{\parallel}^{\text{Rh}} \beta_N \beta_N \langle r^{-3} \rangle, \rangle$$

$g_{\parallel} = g_{\parallel} - 2$, $g_{\perp} = g_{\perp} - 2$, K is a measure of the Fermi contact interaction, and Δ is the energy difference between the 2A_1 ground configuration and the first excited 2E configuration.

TABLE

Species	A	B	C
Symmetry	axial	axial	axial
g-Values	$g_{\parallel} = 1.995$	$g_{\parallel} = 1.997$	$g_{\parallel} = 1.990$
	$g_{\perp} = 2.297$	$g_{\perp} = 2.128$	$g_{\perp} = 2.160$
A^{Rh}	$A_{\parallel} = -40.8 \times 10^{-4} \text{ cm}^{-1}$... (a)
	$A_{\perp} = -36.9 \times 10^{-4} \text{ cm}^{-1}$		
A^{Cl}	$A_{\parallel} = +27.8 \times 10^{-4} \text{ cm}^{-1}$		
	$A_{\perp} = +12.4 \times 10^{-4} \text{ cm}^{-1}$		
Stability	Stable at room temp. Well resolved parallel multiplet consisting of two V_K -Center-like spectra offset by the Rh splitting. The perpendicular feature consists of ten main lines with the same characteristics.	Stable at room temp.	Stable at room temp.
Assignment	$[\text{Rh}^{\text{II}}(\text{CN})_4\text{Cl}_2]^{4-}$		
Conditions under which is formed	Irradiation at rm. temp. of KCl single crystals doped with low concentrations of $\text{Rh}(\text{CN})_6^{3-}$. Crystals irradiated at 77°K or with high doping show this spectrum when annealed for a few hours at 200°C.	These form when the crystal is irradiated either at room temperature or at 77°K, and with any concentration of $\text{Rh}(\text{CN})_6^{3-}$.	

Note: The signs of the hyperfine couplings are discussed in the text.

G. Rossman¹⁵, in preliminary optical measurements of the irradiated sample observed a peak at 505 nm ($19,800 \text{ cm}^{-1}$) which can be assigned to the ${}^2E \rightarrow {}^2A_1$ transition. This will give a $g_{\perp} = 2.37$, in reasonable agreement with the experimental data, which supports our unpaired electron orbital assignment.

Measured values of the hyperfine coupling constants bring no information about their signs. These can be inferred for the rhodium from the study of the formula of P obtained from eqs. 2 and 3, which can be solved simultaneously for P and K and from the value of $\langle r^{-3} \rangle$ obtained from the expression (5). Since $g_N^{\text{Rh}} < 0$, according to (5) P must be negative. The value of $\langle r^{-3} \rangle$ for the complex species must be smaller than the theoretical free Rh(II) ion value, 6.80 a.u.^{17} . The only combination of signs that will satisfy these conditions is both A_{\parallel} and A_{\perp} negative.

Taking $A_{\parallel}^{\text{Rh}} = -40.8 \times 10^{-4} \text{ cm}^{-1}$ and $A_{\perp} = -36.9 \times 10^{-4} \text{ cm}^{-1}$, $y = 0.061$ and the experimental g values one obtains $\langle r^{-3} \rangle = 1.49 \text{ a.u.}$, which is consistent with the delocalization of the electron to the ligands, as indicated by the chlorine hyperfine splittings observed.

In order to attribute signs for the chlorine hyperfine coupling constants we start from the formula.

$$A_{\text{aniso}} = (A_{\parallel} - A_{\perp})/3 = 2/5 P$$

derived under the assumption a) that the wave function of the unpaired electron on the chlorines is of character p, b) that the orbital angular momentum is totally quenched and c) that the chlorine hyperfine interaction is due exclusively to dipolar interaction¹⁶. P is defined as in (5). Choosing $A_{\text{Cl}}^{\text{Cl}} = + 27.8 \times 10^{-4} \text{ cm}^{-1}$ and $A_{\perp} = + 12.4 \times 10^{-4} \text{ cm}^{-1}$ one obtains a positive P (positive g_N), a value of $\langle r^{-3} \rangle = 0,74 \text{ a.u.}$ (which is less than the theoretical value 6,71 a.u. for the free Cl¹⁷) and a small isotropic contents in the hyperfine coupling.

From a molecular orbital standpoint one consider the wave function of the unpaired electron as a linear combination of metal and ligand functions of the form

$$\psi = N \phi_M^d + \sum_L \alpha_L \phi_L^p$$

where the sum extends over all ligands and s densities are considered small and neglected. $|N|^2$ and $|\alpha_L|^2$ will be a measure of the spin density respectively on the metal d orbital and in the ligands p orbitals.

Calculating $\langle r^{-3} \rangle$ with this wave function we will have:

$$\langle r^{-3} \rangle = \langle \psi | r^{-3} | \psi \rangle = |N|^2 \langle \phi_M^d | r^{-3} | \phi_M^d \rangle + \text{terms}$$

involving integrals of the type $\langle \phi_M^d | r^{-3} | \phi_L^p \rangle$ and $\langle \phi_L^p | r^{-3} | \phi_L^p \rangle$, which can be considered small.

The $|N|^2$ value is, in this approximation:

$$|N|^2 = \frac{\langle r^{-3} \rangle}{\langle \phi_M^d | r^{-3} | \phi_M^d \rangle}$$

The denominator is the theoretical value calculated by Hartree Fock method reported by Freeman and Watson¹⁷ as 6.80 for Rh(II). Admitting that the numerator corresponds to the semi-empirical value obtained from experimental values of the hyperfine constants and crystal field theory (1,49 a.u. for Rh(II) in $\text{Rh}^{\text{II}}(\text{CN})_4\text{Cl}_2^{4-}$), we can write

$$|N|^2 = \frac{\langle r^{-3} \rangle_{\text{exp}}}{\langle r^{-3} \rangle_{\text{theor}}}$$

This gives $|N|^2 = 0,22$ as the spin density on the d orbital.

One could obtain similar expression for the $|\alpha_L|^2$ putting the origin of the coordinate system on the ligand L. Then, for the chlorine p orbital, $|\alpha_L^{\text{Cl}}|^2 = 0,11$.

The s density on the chlorine can be estimated by the ratio of the isotropic part of the hyperfine splitting to the theoretical value¹⁶ neglecting polarization of internal shells. This places $|\alpha_s|^2$ in the vicinity of 1%.

Remains to be estimated the real s density on the metal. In order to do that one has to separate the effects of polarization on the ns^2 inner shells. It can be shown that

$$A_{\text{iso}}^{\text{pol}} (\text{cm}^{-1}) = 2/3 (g_e \beta_e g_N \beta_N) (2S\chi)/hca_0^3$$

where χ is the core polarization hyperfine field per unit spin²⁰ and a_0 the Bohr radius. χ can be obtained from ref. 18 and is approximately constant for the 4d elements. Assuming that the value of χ for Pd^{3+} (-8.62 a.u.) is the same as that for Rh^{2+} , which has the same configuration, one finds $A_{\text{iso}}^{\text{pol}} (\text{Rh}^{2+}) = 32,1 \times 10^{-4} \text{ cm}^{-1}$ and, by difference:

$$A_{\text{exp}}^{5s} = - 70.3 \times 10^{-4} \text{ cm}^{-1} .$$

The total 5s density calculated theoretically¹⁹ for Rh^{1+} is $- 790 \times 10^{-4} \text{ cm}^{-1}$. A candid estimate of the total 5s density for Rh^{2+} can be made if one observes that the ratio of the calculated real s isotropic interaction for V^{1-}

and V° , Cr^{1-} and Cr° , Mn^{1-} and Mn° 19 is of the order of 2.5. This will place $A_{5s}^{Rh^{2+}} = -2000 \times 10^{-4} \text{ cm}^{-1}$, leading to a 5s spin density on the Rh in our complex of 3.5%.

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ACKNOWLEDGEMENTS

This work was supported by the National Research Council of Brazil. We thank Dr. J. B. Raynor for enlightening discussions.

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CAPTIONS TO THE FIGURES

1. Spectrum of single crystals of KCl doped with 1% M $K_3 Rh(CN)_6$, irradiated at ambient temperature. To the left the perpendicular feature of species A. The two peaks at the center are the perpendicular feature of species C and B. The parallel features are superimposed on the extreme right. Spectrum taken with the magnetic field parallel to one of the crystalline main axes.
2. g-values angular variation of species A, obtained by rotation of the crystal around one of the main axes. 0° and 90° correspond to the other two axes.
3. Angular variation of the hyperfine splitting due to interaction with Rh and Cl nuclei.
4. Perpendicular feature of the spectrum of species A. a) Reconstitution made assuming interaction with Rh and Cl. b) Recorded spectrum at $77^\circ K$.
5. Parallel feature of species A. a) Reconstitution assuming interaction with Rh and Cl. b) Recorded spectrum at $77^\circ K$.

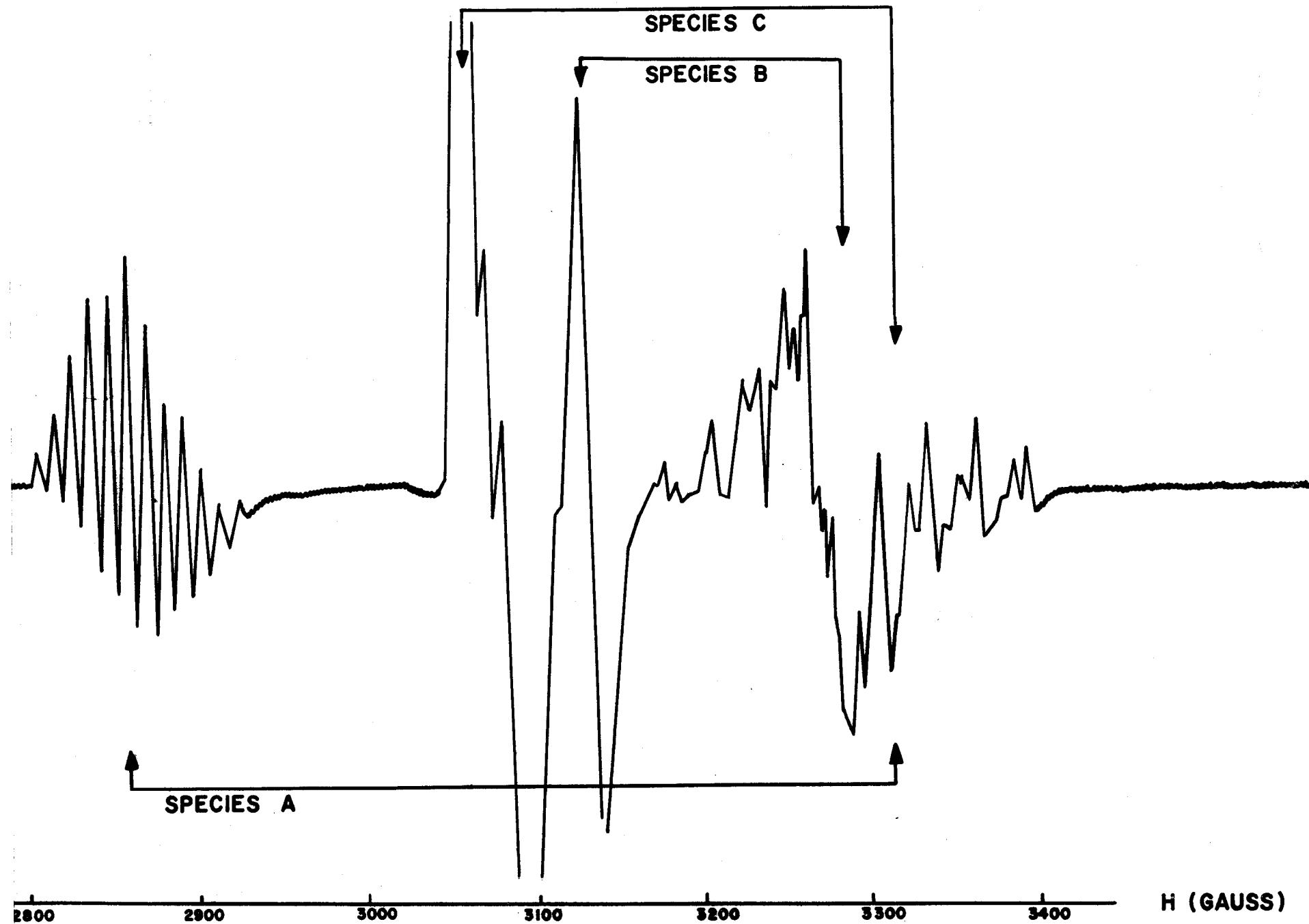


FIG. 1

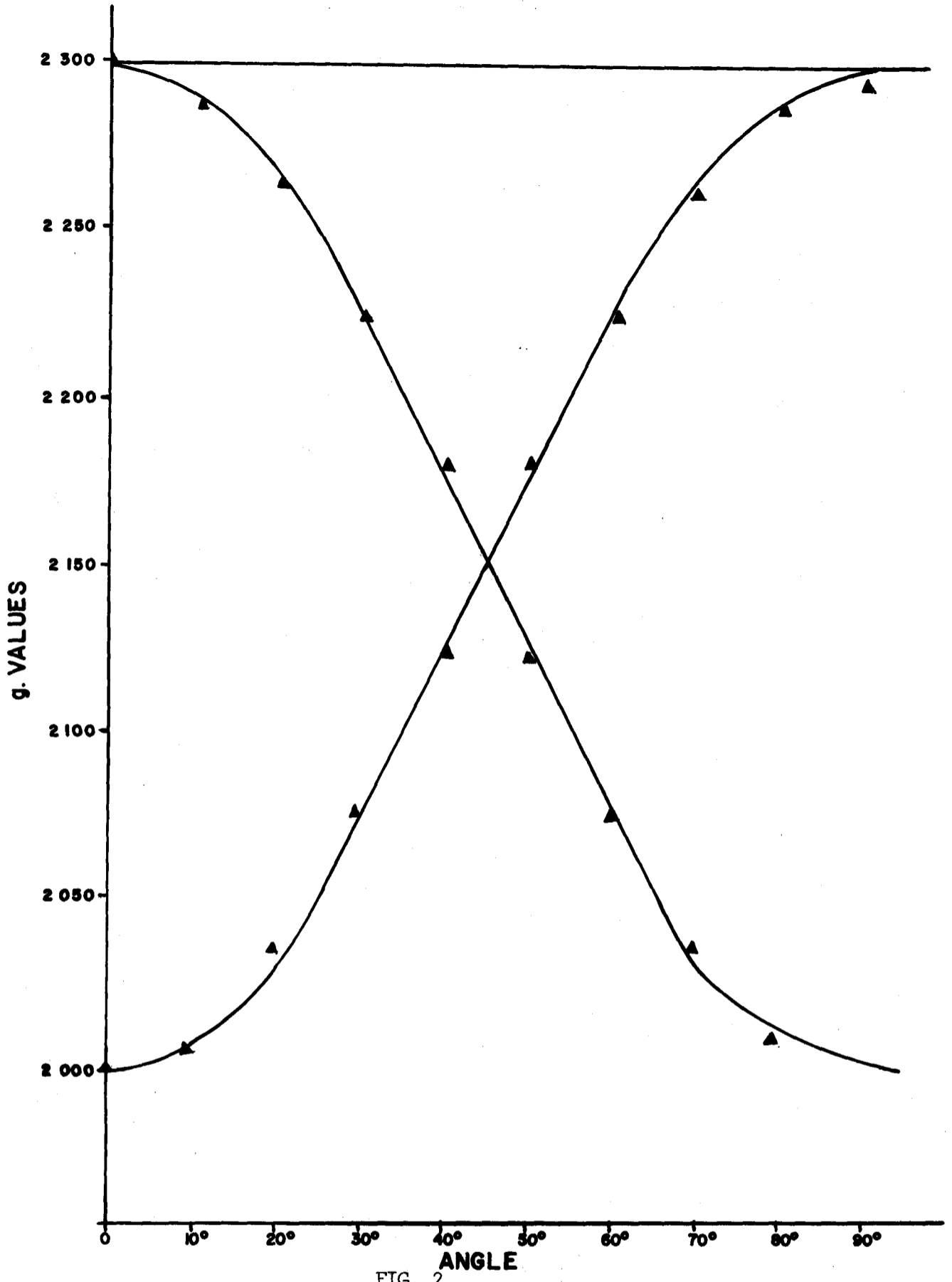


FIG. 2

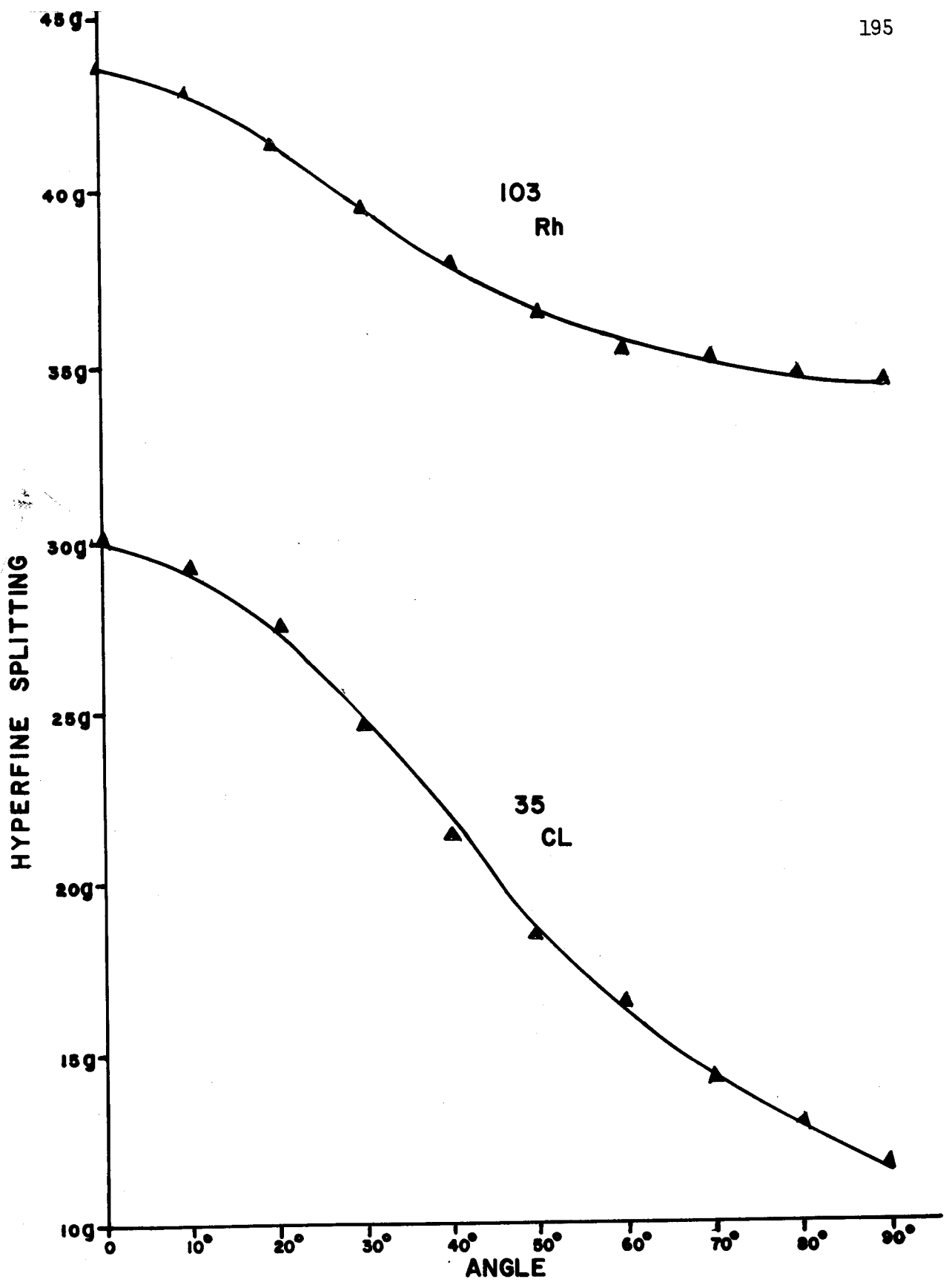
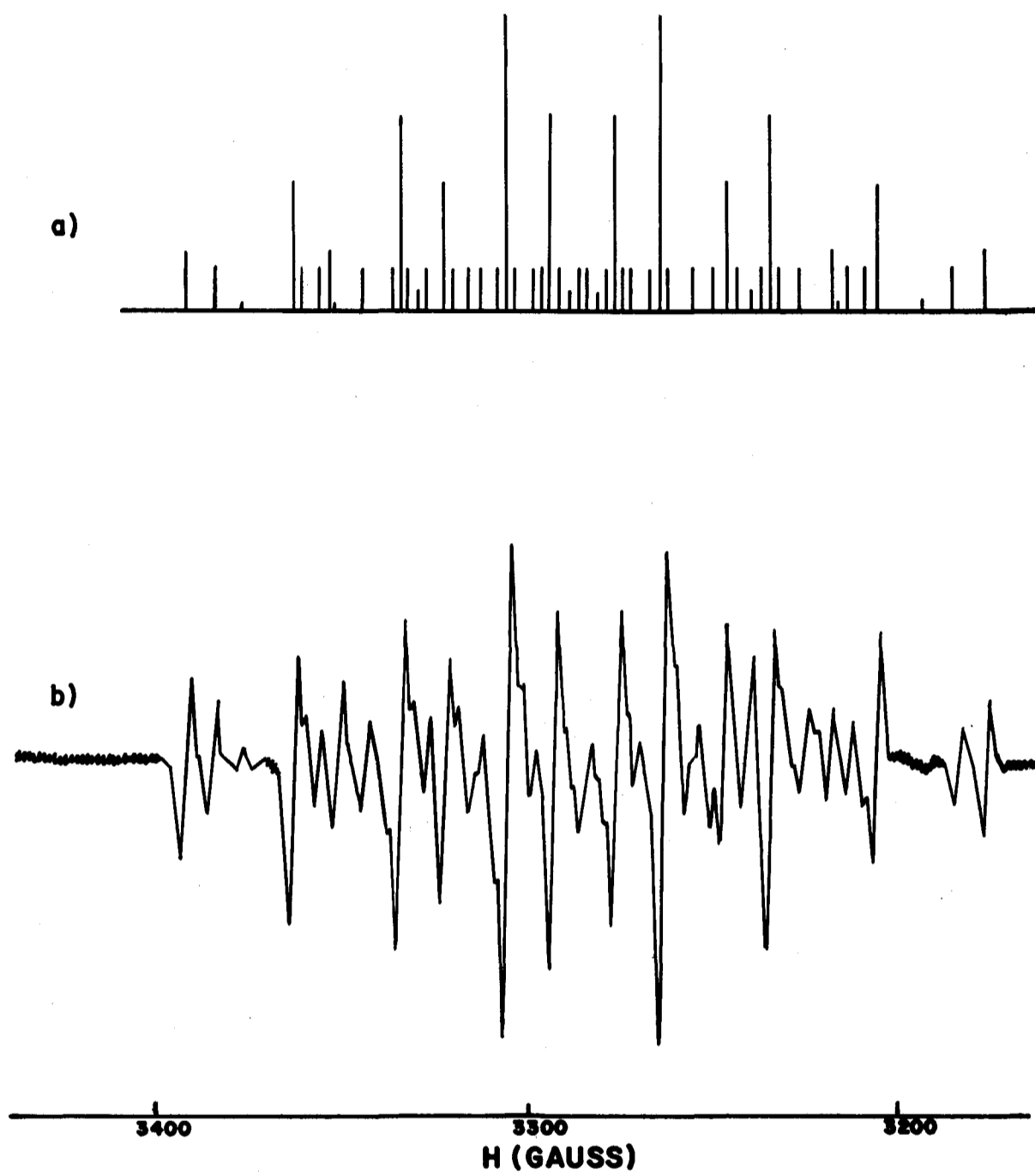


FIG. 3



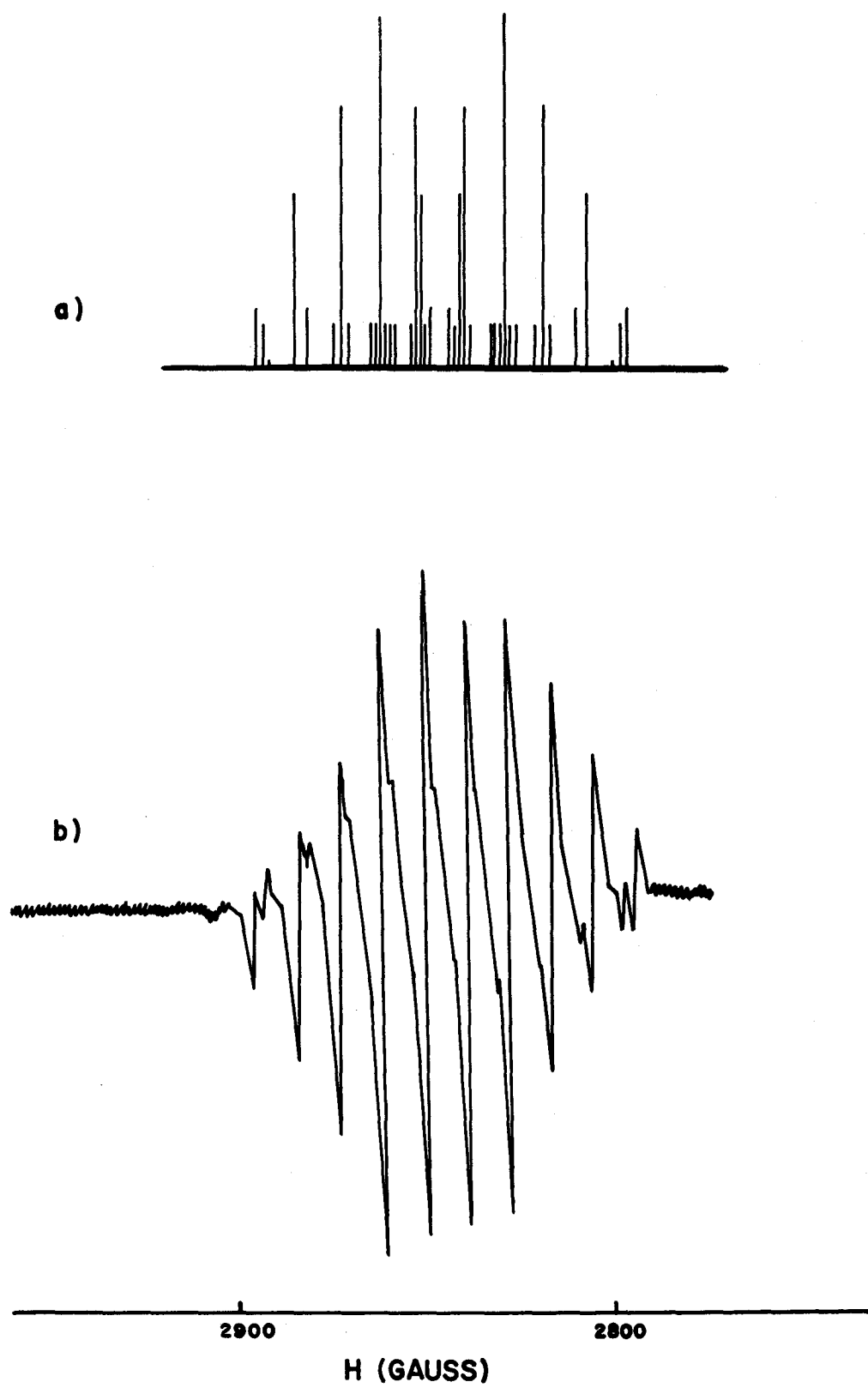


FIG. 5