LINEWIDTH OF E.P.R. OF LIQUID SOLUTIONS OF THE ETHYLENE-GLYCOL COMPLEX FOR EVEN AND ODD CHROMIUM ISOTOPES

PHYSICS

1968

SovietRxiv

Abstract

Full Text

UDC 538.113

PHYSICS

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LINEWIDTH OF E.P.R. OF LIQUID SOLUTIONS OF THE ETHYLENE-GLYCOL COMPLEX FOR EVEN AND ODD CHROMIUM ISOTOPES

(Presented by Academician E. K. Zavoisky, March 22, 1967)

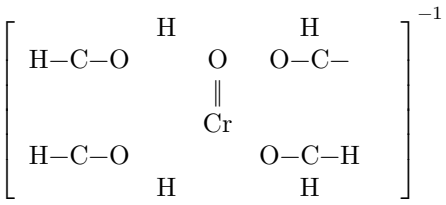
Earlier [1] an e.p.r. spectrum was discovered in an aqueous solution of the complex ion Cr(V), obtained by reduction of K_2CrO_4 or $K_2Cr_2O_7$ with glycerol. An intense line from the even isotopes of Cr(V) with $g = 1.975$ and $\delta H \simeq 2$ Oe, and a 4-component hyperfine structure from the magnetic isotope Cr^{53}, were observed. In a frozen aqueous-glycerol solution of the same ion at 77° K, a practically isotropic broad line from the even chromium isotopes with $g = 1.978$ and two components of a partially resolved anisotropic hyperfine structure with $A_{\parallel} = 37$ Oe were observed. Assuming identical signs, the constant $A_{\perp} \simeq 12$ Oe was also calculated [2].

In the present work we report the results of an e.p.r. investigation of Cr(V) complexes obtained by reduction, upon heating, of ethylene-glycol solutions of compounds of hexavalent chromium (CrO_3; $K_2Cr_2O_7$; $(NH_4)_2CrO_4$; K_2CrO_4). The same complex can be obtained by dissolving pentavalent chromium (K_3CrO_8) in glycol at room temperature. The e.p.r. measurements were carried out at a frequency of 9320 MHz at temperatures from 320 to 77° K.

In liquid solution the spectrum consists of a line from the even isotopes and a 4-component hyperfine structure from the isotope Cr^{53} (Fig. 1a). At room temperature, in highly dilute solutions, the line from the even isotopes is split into 9 very narrow components of an additional hyperfine structure (d.h.f.s.) with a binomial distribution of intensities close to 1 : 8 : 28 : 56 : 70 : 56 : 28 : 8 : 1 (Fig. 1b). The width of the narrowest central component proved to be 0.32 Oe. When the temperature is raised or lowered from 290° K, the width of the hyperfine components increases somewhat. The distance between the maxima of the d.h.f.s. is 0.64 ± 0.01 Oe. As for the 4 hyperfine components observed from the isotope Cr^{53}, they do not give additional splitting because of the considerably greater width of each d.h.f.s. component. For the hyperfine components with $I_z = \pm 3/2$, the width is $\delta H = 3$ Oe, and for the components

with $I_z = \pm 1/2$, $\delta H = 2.3$ Oe.

The additional h.f.s. on the line from the even chromium isotopes is evidently caused by 8 equivalent protons. It may therefore be assumed that the structure of our complex has the form



Thus, owing to the exceptional narrowness of the lines, in the present example it was possible to observe an additional hyperfine structure from protons bound to chromium through oxygen and carbon atoms.

It should be noted that narrow lines from liquid solutions of paramagnetic ions can be observed only for electron spin $S = 1/2$, which in the case under consideration is possible only for pentavalent chromium, since the formation of a low-spin complex with monovalent chromium in the nearest environment of oxygen atoms is excluded.

The spectrum of a liquid solution can be described by the spin Hamiltonian

$$\mathcal{H} = g\beta HS + A_1 I_1 S +$$

$$+ A_2 I_2 S,$$

where $S = 1/2$; $g = 1.981 \pm 0.001$; A_1 is the h.f.s. constant from Cr^{53} with $I_1 = 3/2$, equal to 17.6 oersted; A_2 is the constant of the additional h.f.s. from 8 protons with $I_2 = 4$, equal to 0.64 oersted. Upon cooling to 218°K, a single broad, practically isotropic line from the even chromium isotopes with $g = 1.981$ is observed, with $\delta H = 7.8$ oersted (see Fig. 1b). With such a width the h.f.s. from protons is, naturally, not resolved.

The hyperfine structure from the odd isotope Cr^{53} proved to be anisotropic and only partially resolved. From analysis of the spectrum it was possible to determine $A_\parallel = 35$ oersted. As for $A_\perp$, if the relation $A_{av} = (A_\parallel + 2A_\perp)/3$ is assumed valid and if the signs of $A_\parallel$ and $A_\perp$ are the same, the latter quantity should be equal to 8.9 oersted.

Fig. 1. EPR spectra in ethylene-glycol complexes of Cr(V) and Mo(V) at $\nu = 9320$ MHz. Isotropic spectra in liquid solutions, $T = 290$°K: *a*–from even and odd Cr isotopes; *b*–from even Cr isotopes; *d*–spectrum of the ethylene-glycol complex of Mo. Anisotropic spectra at $T = 218$°K: *v*–from even isotopes;

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Let us turn to discussion of the results. First of all, a very unexpected fact attracts attention: the practical isotropy of the g-factor in the frozen solution (within the line width of ~ 8 oersted) despite the considerable anisotropy of the hyperfine interactions (Fig. 1g). The only attempt to explain such isotropy of the g-factor, first put forward in Ref. ([3]) in connection with a discussion of EPR spectra in $K_3Mo(CN)_8$, consists in the assumption of an "accidental" equality between $g_\parallel$ and $g_\perp$, where, without taking covalency of the bond into account, $g_\parallel = 2 - 8\lambda/\Delta$ and $g_\perp = 2 - 2\lambda/\delta$, i.e., the condition $4\delta \approx \Delta$ must be satisfied. Of course, this

This explanation is quite strained, especially if one takes into account the undoubted covalency of the bonds in our complex. In this case $g_\parallel = 2 - 8\alpha^2\gamma^2\lambda/\Delta$ and $g_\perp = 2 - 2\alpha^2\beta^2\lambda/\delta$, and, in order to preserve the condition $g_\parallel \approx g_\perp$, it is additionally required that $\beta^2 \approx \gamma^2$. Another explanation of the "isotropy" of the g-factor, possible at first glance and consisting in the assumption of a very high symmetry of the complex for $S = 1/2$, is contradicted both by the narrowness of the observed EPR lines and by the very long spin-lattice relaxation times. The anisotropy of the hyperfine structure also argues against a high symmetry of the complex.

Let us turn to the question of the nature of the relaxation times in liquid solutions of our complex. It seems that such narrow lines have been observed by us for the first time; this made it possible to detect the dependence of the width of the individual components on the magnetic moment of the chromium isotope. Indeed, according to McConnell [4],

$$\Delta\nu \simeq \frac{1}{T_1} + \frac{1}{T_2},$$

where

$$\frac{1}{T_1} = \frac{8\pi^2}{15} \frac{(\Delta g \beta H_0 + BI_z)^2 h^{-1} \tau_c}{1 + 4\pi^2 \nu_0^2 \tau_c^2},$$

$$\frac{1}{T_2^2} = \frac{32\pi}{45} (\Delta g \beta H_0 + bI_z)^2 h^{-2} \arctan \frac{2\tau_c}{T_2},$$

with $\Delta g = g_\parallel - g_\perp$ and $b = A_\parallel - A_\perp$.

It follows from this that for the even chromium isotopes ($I = 0$), with a very small Δg, one should expect very long relaxation times and, consequently, very narrow EPR lines. For the odd isotope Cr^{53}, the presence of a nonzero term bI_z must broaden the components of the hyperfine-structure lines, with the lines for components with $I_z = \pm 3/2$ being broader than for components with $I_z = \pm 1/2$. This broadening makes a noticeable contribution even to the total width of the hfs lines of Cr^{53}, which consist of unresolved hyperfine structure due to protons.

In the Cr(V) compounds studied by us so far, the value of Δg was apparently so large that the contribution of the term bI_z to the line width was practically not manifested.

In conclusion, we note that the analogous ethylene-glycol complex of Mo(V), obtained by us by heating a solution of ammonium molybdate in ethylene glycol, proved to be much less stable; however, we succeeded in obtaining its EPR spectrum in liquid solution (Fig. 1d), with the parameters: $g = 1.959 \pm 0.001$, $\delta H = 5$ Oe, $A = 72.6$ Oe. Because the line width from the even isotopes for this complex was considerably greater than the magnitude of the additional splittings from protons, only a single line is observed. Calculations of the spin densities in the complex studied will be reported separately.

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Received
20 February 1967

References

1. N. S. Garifyanov, N. F. Usacheva, *DAN*, **145**, 565 (1962).
2. N. S. Garifyanov, *FTT*, **4**, 2450 (1962).
3. R. M. Golding, A. Carrington, *Molecular Phys.*, **5**, 378 (1962).
4. H. M. McConnell, *J. Chem. Phys.*, **25**, 709 (1956).

Note: Figure translations are in progress. See original paper for figures.