

ESR study of paramagnetic centers in irradiated $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ and $\text{Ba}(\text{ClO}_3)_2 \cdot \text{D}_2\text{O}$ single crystals

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ESR study of γ -irradiated $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ revealed three main centers which are identified as O_3^- , ClO_2 , and $(\text{ClO}_2\text{-H}_2\text{O})$ radicals, trapped at two distinct sites. The parameters of the spin Hamiltonian have been determined from single crystal and powdered samples. The principal values for O_3^- and ClO_2 centers agree with those reported in other systems. The chlorine center having "superhyperfine" interaction with the two protons of water of crystallization has been identified as a $(\text{ClO}_2\text{-H}_2\text{O})$ radical. The principal values of the g tensor are $g_{xx}=2.0023$, $g_{yy}=2.0065$, and $g_{zz}=2.0150$; those of the A tensor are $a_{xx}=102.11$, $a_{yy}=53.22$, and $a_{zz}=7.79$ G. The parameters of the hyperfine coupling of ^{35}Cl with the first proton are $a_{xx}=8.6$, $a_{yy}=5.0$, and $a_{zz}=5.0$ G, with $a_{\text{iso}}=6.2$ G, and those for the second proton are $a_{xx}=2.5$, $a_{yy}=1.2$, and $a_{zz}=1.2$ G. The $(\text{ClO}_2\text{-H}_2\text{O})$ center is found to be bleached at temperatures (above 120°C), where the crystal loses its water of hydration. On exposing the irradiated crystal to uv light, the two chlorine centers ClO_2 and $(\text{ClO}_2\text{-H}_2\text{O})$ are fully bleached, followed by an increase in the concentration of the O_3^- center.

INTRODUCTION

Electron spin resonance (ESR) studies of a number of paramagnetic oxides of chlorine, produced by the process of radiolysis of different chlorates¹⁻⁵ and perchlorates⁶⁻⁸ have been reported by earlier workers. Byberg *et al.*⁷ identified the ClO_2 radical in KClO_4 , and Eachus *et al.*⁹ studied a number of paramagnetic oxides of chlorine, which are usually the fragments of the anion. However, not much work has been reported on the nature of paramagnetic centers trapped in divalent chlorates.

In this paper, ESR studies on the nature of paramagnetic centers trapped in barium chlorate monohydrate $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ and $\text{Ba}(\text{ClO}_3)_2 \cdot \text{D}_2\text{O}$ obtained by uv, x, γ -irradiations are reported. Fayet *et al.*¹⁰ have earlier reported some results on these crystals, and the present results are compared with the earlier results.

I. EXPERIMENTAL

Single crystals of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ are grown from aqueous solution by slow evaporation at room temperature. Starting materials are analytically pure reagents and are further purified by recrystallization. The crystals usually form with (110) face and are elongated along the c axis. Deuterated single crystals are grown by first dehydrating the monohydrate sample and then making a solution with heavy water (isotopic purity 99.4%) supplied by BARC-Bombay. These crystals are grown in water free atmosphere.

Crystals are irradiated with x rays from a molybdenum target operated at 30 kV and 15 mA for periods ranging from a few minutes to a few hours. A ^{60}Co - γ source capable of giving an effective dose rate of 0.156 M rad/hr is used for irradiation. In both cases, a dark brown color is observed. A 100 W mercury discharge tube is used for bleaching experiments with Wurtz filter (3600 Å).

The ESR spectra are recorded on a Varian E-4, x-band spectrometer operating at 9.5 GHz at temperatures ranging from -180 to $+150^\circ\text{C}$. The g factors are calculated using DPPH ($g=2.0036$) as standard and are ac-

curate to ± 0.0005 . The results are analyzed by Schonland's¹¹ method.

A. Crystal structure of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$

The crystal belongs to a monoclinic system with space group $I2/C$ having the lattice parameters¹² $a=8.916 \pm 0.010$ Å, $b=7.832 \pm 0.008$ Å, $c=9.425 \pm 0.010$ Å, and $\beta=93^\circ 39' \pm 7'$ with four molecules per unit cell. The structure contains Ba-O polyhedra and ClO_3 pyramids. The water molecule is situated at a position of relatively simple crystalline symmetry. The orientations of the interproton vectors were determined by Spence,¹³ Silvini,¹⁴ and McGrath^{14,15} using proton magnetic resonance studies. The atomic positions in the unit cell of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ are shown in Fig. 1.

II. RESULTS

A. Description and interpretation of the spectra

ESR spectra are recorded by varying the orientation of the crystal with the magnetic field in intervals of every 5° in each of the three orthogonal planes—(001*), (010), and (100). The spectra with the magnetic field along the [100] direction is shown in Fig. 2 for γ -irradiated $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ crystal. It consists of three types of paramagnetic centers; a single lined spectrum marked as (A) with no hyperfine splitting, and two others marked as (B) and (C) with hyperfine splitting (characteristic of a nuclear spin $I=\frac{3}{2}$). The most probable nucleus with $I=\frac{3}{2}$ in this crystal being chlorine, the centers B and C are attributed to two chlorine species. The lines due to ^{35}Cl and ^{37}Cl isotopes are seen with the expected intensity ratio 3:1 and magnetic moment ratio 1:0.83. Furthermore, the chlorine center C, with the largest hyperfine separation, reveals superhyperfine interaction with the two protons of the water of crystallization. This fact was confirmed on deuteration, for which the observed splitting is very small and is governed by the expected proton-deuteron magnetic moment ratio of 3.32:1. It is further observed that the center C is relatively more intense in γ -irradiated crystal than in x-irradiated crystal.

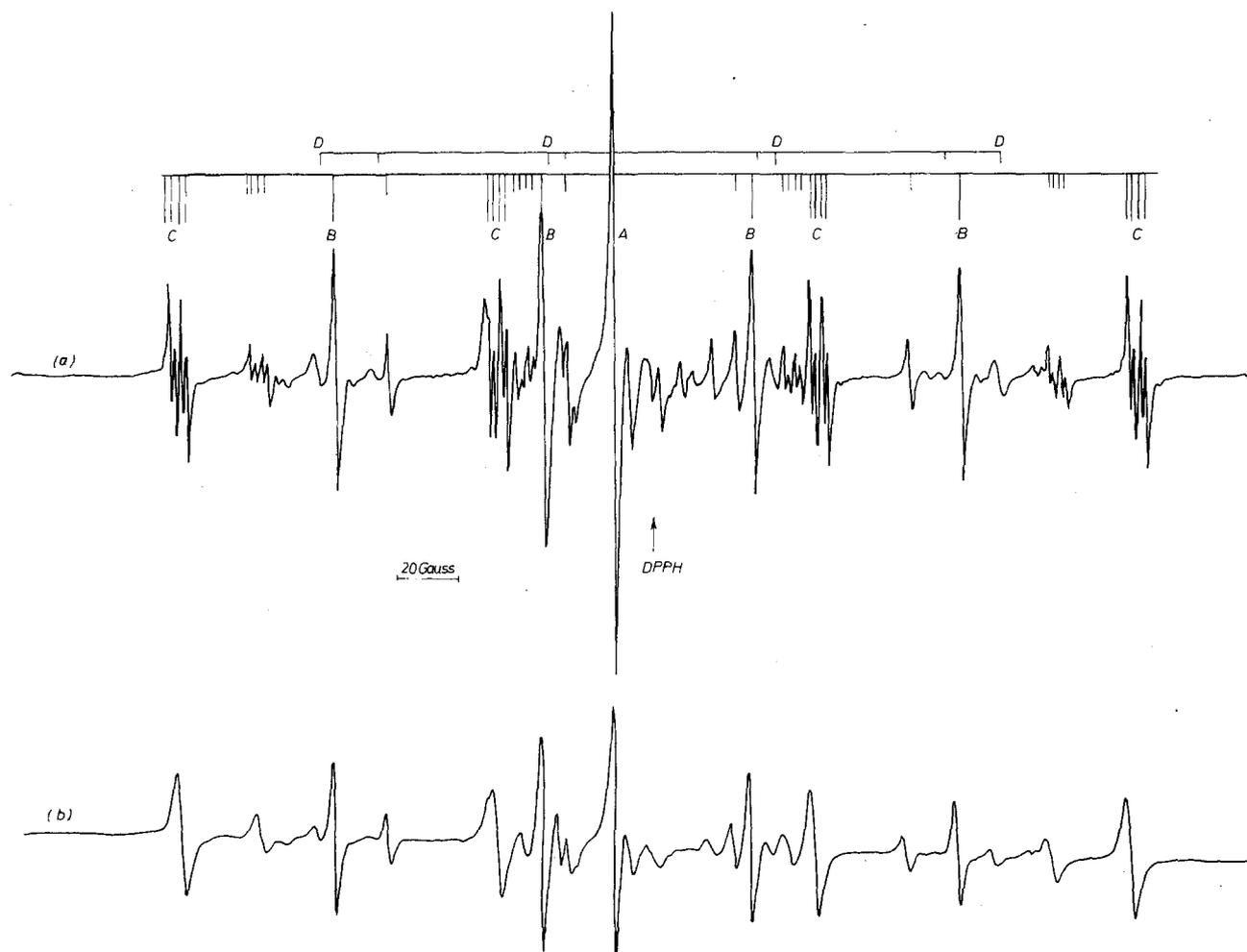


FIG. 2. ESR spectra of γ -irradiated (a) $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ and (b) $\text{Be}(\text{ClO}_3)_2 \cdot \text{D}_2\text{O}$. The positions of the lines of A, B, and C centers are indicated at the top of the figure. D is an unidentified chlorine center.

similar to those reported by Fayet *et al.*¹⁰ and those found in other chlorates and perchlorates by earlier investigators.^{7,9} The optical absorption studies by the authors¹⁷ have revealed a strong band, at 350 μ , characteristic of ClO_2 . The paramagnetic center C has not been fully analyzed earlier, and its g and A tensor results show that it is probably the radical complex ($\text{ClO}_2\text{-H}_2\text{O}$). Since the results on radical A have been reported earlier, details regarding the two centers B and C are discussed further.

The ClO_2 center has C_{2v} symmetry and is isoelectronic with O_3^- . The axes system is chosen such that the two-

fold axis corresponds to the principal Z axis. The Y axis is parallel to the O-O direction, and the X axis is perpendicular to the molecular plane. The maximum principal value of the g tensor (g_{yy}) lies along the O-O direction, and the minimum value (g_{xx}) lies perpendicular to the ClO_2 plane. The experimental direction cosines of $g_{yy}(\text{ClO}_2 \text{ site I})$ given in Table I (80° , 68° , 24°) are in good agreement with the calculated direction cosines of $\text{O}'_1\text{-O}'_1$ vector (Fig. 1), forming angles (84° , 67° , 23°) with the crystal axes. The g_{xx} and g_{zz} directions agree in a similar manner. Similarly, the g_{yy} direction for the second site of ClO_2 (not presented in Ta-

TABLE II. Possible forms of the hyperfine tensor for ($\text{ClO}_2\text{-H}_2\text{O}$), together with the breakdown into isotropic and anisotropic contributions.

	Trial I	Trial II	Trial III	Trial IV	Trial V	Trial VI	Trial VII	Trial VIII
a_{11}	+102.11	-102.11	-102.11	+102.11	-102.11	+102.11	+102.11	-102.11
a_{22}	+53.22	-53.22	+53.22	-53.22	-53.22	-53.22	-53.22	+53.22
a_{33}	+7.79	-7.79	+7.79	-7.79	+7.79	+7.79	-7.79	-7.79
a_{1so}	+54.37	-54.37	-13.7	+49.18	-49.18	+18.89	+13.7	-18.89
b_{11}	+47.74	-47.74	-88.41	+52.93	-52.93	+83.22	+88.41	-83.22
b_{22}	-1.15	+1.15	+66.92	+4.04	-4.04	-72.11	-66.92	+72.11
b_{33}	-46.58	+46.58	+21.49	-56.97	+56.97	-11.10	-21.49	+11.10

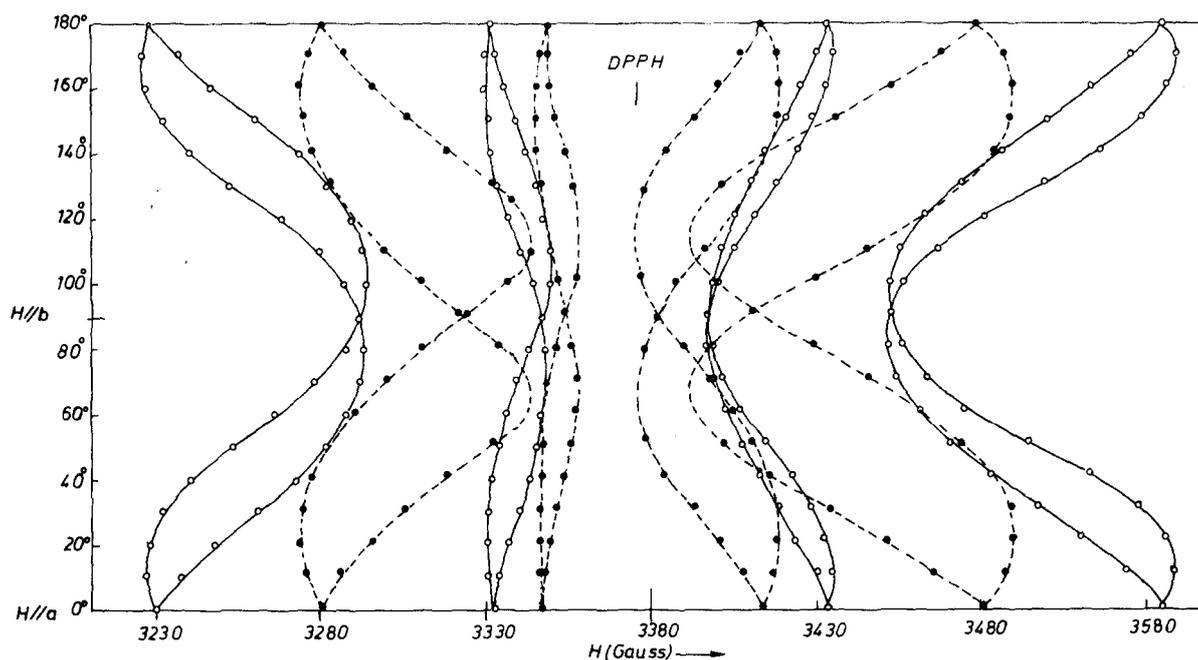


FIG. 3. Positions of experimental ESR lines for ^{35}Cl components of the B and C center of deuterated crystal in (001^*) plane. Angular dependence of the lines is shown taking DPPH line as center. The lines with open circles correspond to center C. The dashed lines with dark circles correspond to center B.

ble I) is coinciding with the direction of $\text{O}_I''-\text{O}_{II}''$ vector (Fig. 1). It is interesting that the symmetry of the experimental results show that ClO_3^- always lose a particular oxygen to give rise to the two inequivalent sites. It should be mentioned that the ClO_3^- group in barium chlorate is not completely symmetric, having the O-O distances 2.385, 2.384, and 2.363 Å.¹² In KClO_3 , similar

conclusions were drawn.^{9,18} The crystal structure (Fig. 1) suggests eight such possible ClO_2 sites obtainable from the eight chlorate groups of the unit cell. However, four pairs can be made by suitable glide operation and they can be further reduced to two by pairwise inversion. The two possible ClO_2 sites are inclined 90° with respect to each other.

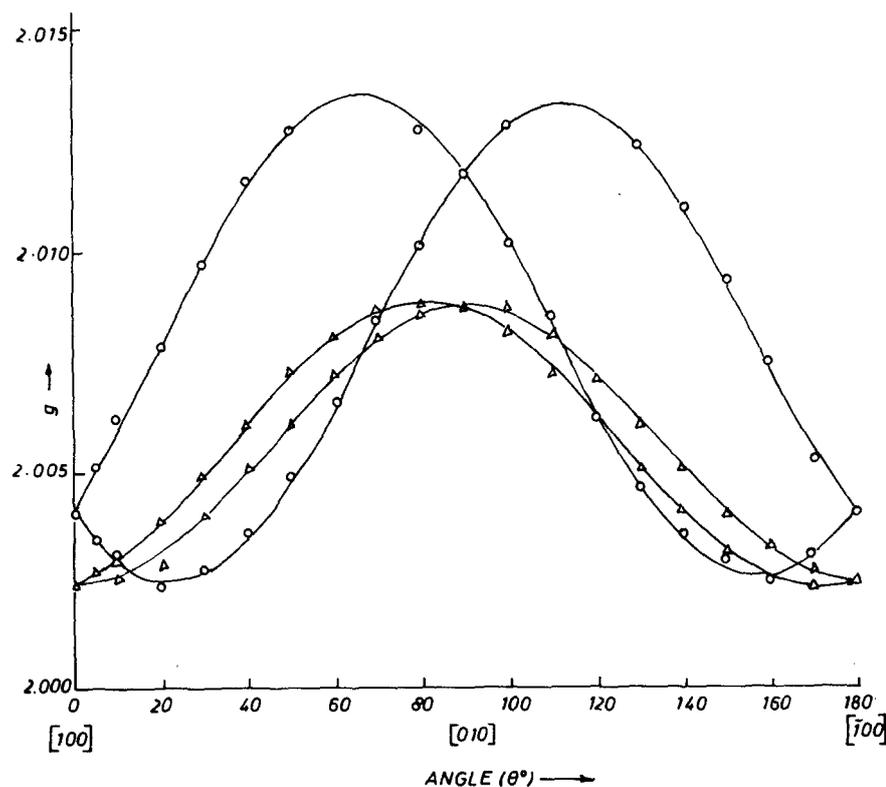


FIG. 4. The variation of g with angle θ for the mean position of the lines of groups B and C in (001^*) plane, fitted with least squares. The open circles are for center B and the triangles are for center C. The solid line represents theoretical lines.

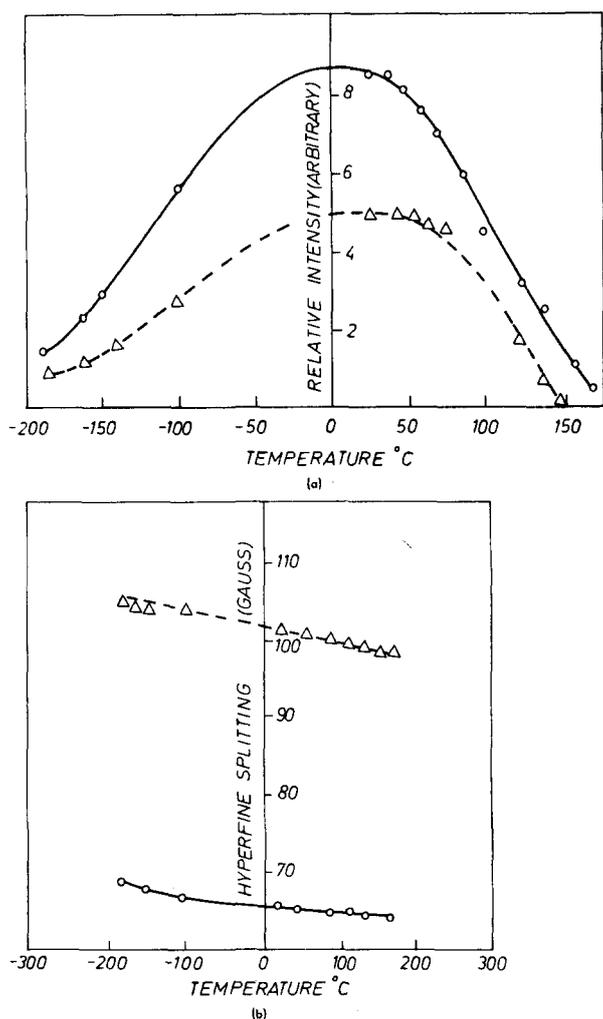


FIG. 5. (a) Plot of the relative intensity of Centers B and C with respect to their intensity at room temperature for various temperatures. Circles for center B and triangles for center C. (b) The temperature dependence of hyperfine splitting of centers B and C.

D. Characteristic features of center C

The nature of the ESR spectrum of this center suggests that it must be a chlorine center. Optical absorption studies have revealed that the primary product of radiolysis, viz., ClO_3 , is present in the crystal as diamagnetic dimer¹⁷ Cl_2O_6 with an absorption band at 515 $\text{m}\mu$. Further ClO_3 has C_{3v} symmetry and is expected to have very little anisotropy. In the present case, center C has a large anisotropy with the $g_{av} = 2.008$ close to that of ClO_2 . Furthermore, the temperature variation of the relative intensity of centers B and C suggest that they may be of the same origin. When center C disappears after dehydration (at 120 °C), only centers A and B remain. Hence, it is suggested that this center is the paramagnetic complex ($\text{ClO}_2\text{-H}_2\text{O}$) formed such that the unpaired electron on the chlorine is having superhyperfine interaction with two protons of the water of crystallization. However, it is interesting that only some of the ClO_2 interacts with H_2O although each ClO_2 has a similarly located water molecule near it. The direction cosines of center C (Table I) suggest that considerable "rearrangement" of the atoms in this radical complex might have taken place, so that the molecular axes lie

parallel to the crystallographic a , b , and c axes. It can be suggested that the atoms can find different environments when displaced from their original positions owing to irradiation.

The assignment of proper sign to the components of the hyperfine tensor of center B (ClO_2) is done on the basis of earlier results.⁹ The signs of the components of the hyperfine tensor for center C are not known. Hence, the principal values of the hyperfine tensor are assigned with all possible sign combinations, and the corresponding isotropic and anisotropic parts are shown in Table II. The principal hyperfine coupling constant a_{xx} would be positive, as for ClO_2 , since the magnitude of g_{xx} suggests that the unpaired electron is largely confined to p_x orbital. This reduces it to four possible choices to be considered from Table II. It is assumed that the isotropic term will be positive and that the dipolar term will be approximately axial and of the form $(2B, -B, -B)$. Assuming all components to be positive, the principal values of the hyperfine tensor are 102.11, 53.22, and 7.79 G, with 54.37 G as the isotropic hyperfine interaction.

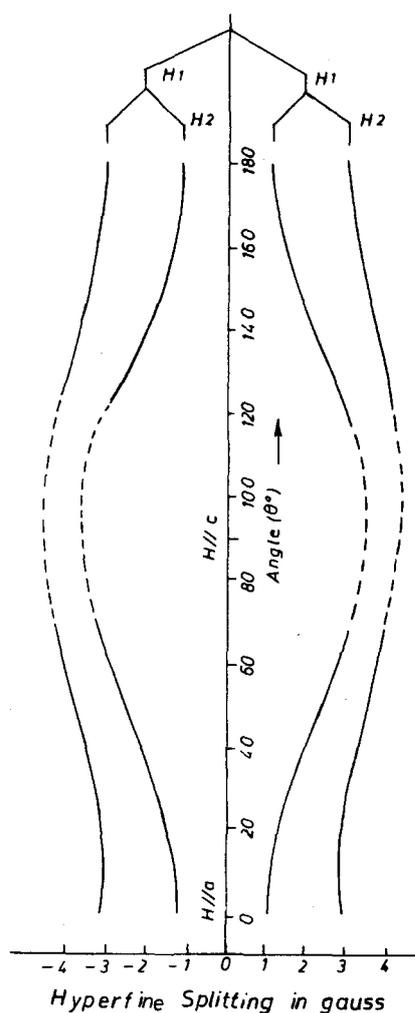


FIG. 6. The super hyperfine splitting of the ^{35}Cl lines of center C is expanded and the separation of the individual component of the four fingered pattern is measured with respect to their common center of gravity, and the angular dependence of this interaction is shown in (010) plane. The dashed line is extrapolated part.

E. Proton interaction

The observed spectrum of the chlorine center C can be explained by assuming superhyperfine interaction (SHF) with two nonequivalent protons. This (SHF) splitting also has considerable anisotropy, and the angular dependence of the proton splitting in the (010) plane is shown in Fig. 6. This is characterized by a major and a minor proton interaction, respectively. The major proton coupling in (010) plane has its maximum value (8 G) when the magnetic field is along the $[001^*]$ direction; minor proton coupling is maximum (2.5 G) along $[100]$ and minimum (1 G) along the $[001^*]$ direction. A similar study is made on the other two planes, and the principal values of the major proton coupling are obtained as (8.6, 5.0, and 5.0 G), with an isotropic part of 6.2 G and anisotropic part of (2.4, -1.2, and -1.2 G). The principal values of the minor proton coupling are (2.5, 1.2, and 1.2 G).

The two protons, coupled to the unpaired spin of ClO_2 in the complex ($\text{ClO}_2\text{-H}_2\text{O}$), are at distances 2.98 Å and 4.23 Å from the chlorine atom, as calculated from the crystal structure data.¹² Since the proton coupling is mainly dipolar in nature, the maximum splitting (ΔH) is proportional to $\langle r^{-3} \rangle$, where r is the distance between the chlorine and the particular proton. The ratio of the maximum splitting due to the two protons must be in the ratio of $(r_1/r_2)^3 = (2.98/4.23)^3 = 0.35$, which agrees well with the experimental value of $\Delta H_2/\Delta H_1 = 0.30$. Furthermore, the calculated values of the magnitudes of the hyperfine interaction between the chlorine and the protons also agree with the experimental observation.

III. DISCUSSION

The spectra for center C in the absence of quadrupolar effects can be interpreted using the spin Hamiltonian

$$\begin{aligned} \mathcal{H} = & \beta(g_{xx}H_xS_x + g_{yy}H_yS_y + g_{zz}H_zS_z) + A_{xx}I_xS_x + A_{yy}I_yS_y \\ & + A_{zz}I_zS_z + A'I'_zS_z + B'(I'_xS_x + I'_yS_y) + A''I''_zS_z \\ & + B''(I''_xS_x + I''_yS_y) + g_N\beta_N I - g'_N\beta'_N I' - g''_N\beta''_N I'' \end{aligned}$$

where the nonprimed hyperfine and nuclear Zeeman components refer to the ^{35}Cl interaction, single primed ones to the major proton ($I' = \frac{1}{2}$), and doubly primed ones to the minor proton ($I'' = \frac{1}{2}$). The other parameters have their usual meaning. For ClO_2 , using Walsh's¹⁹ notation for a 19-electron molecule, the odd electron occupies a $2b_1$ molecular orbital which has the form

$$|2b_1\rangle = -C_1(3p_n^{C1}) + C_2(2p_n^{O1} + 2p_n^{O11})/\sqrt{2}$$

Using the value of the isotropic coupling of ^{35}Cl due to 3s-atomic orbital (1680 G),²⁰ the observed isotropic coupling of 16.21 G for center B (ClO_2) gives an s-character of about 1%. The anisotropic part of center B is (55.73, -31.49, and -24.25 G), which can be separated into an axially symmetric dipolar tensor (58.14, -29.07, and -29.07 G) due to chlorine 3P-orbital, the remaining part (-2.41, -2.41, and 4.82 G) denoting the deviation from axial symmetry. Using the anisotropic coupling

constant (i.e., $2B = 100 \text{ G}$)²¹ for ^{35}Cl , the unpaired spin density on the chlorine 3P-orbital is obtained as 58.1%. This leads to a spin density of about 18% on each oxygen atom by difference. These molecular parameters of $\text{ClO}_2(\text{B})$ are in good agreement with those reported for ClO_2 in other systems.⁹

For center C ($\text{ClO}_2\text{-H}_2\text{O}$), it is not appropriate to decompose the anisotropic part in the same manner as for ClO_2 , since the form of the tensor representing the deviation from axial symmetry is not uniquely known. From the projection diagram given in Fig. 1, it can be seen that there is hydrogen bonding¹² to one of the oxygens (216) of ClO_2 in the center ($\text{ClO}_2\text{-H}_2\text{O}$). This would also considerably modify the contribution from the oxygen 2p orbitals to the total unpaired spin density. Further, efforts are needed to give a quantitative analysis of the hyperfine tensor of the complex ($\text{ClO}_2\text{-H}_2\text{O}$).

IV. CONCLUSIONS

ESR studies of x and γ -irradiated $\text{Ba}(\text{ClO}_3)_2\text{H}_2\text{O}$ have revealed three main centers A, B, and C, which are trapped at two distinct sites:

(1) Center A is identified as O_3^- with $g_{av} = 2.0087$ giving an absorption band at 435 m μ .

(2) Center B is identified as ClO_2 , with the absorption maximum at 350 m μ . The g and A values agree well with those reported in other systems. The direction cosines are in good agreement with the crystal structure data.

(3) The unpaired electron of chlorine center C is interacting with the two protons that are at distances 2.98 Å and 4.23 Å, respectively. The large anisotropy of the g and A values, together with the similarity of its behavior with that of ClO_2 , suggest that this can be the ($\text{ClO}_2\text{-H}_2\text{O}$) center.

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