carbon bond is in agreement with the observation that the Si–C distances in all the methylsilanes are significantly less than that expected from the addition of covalent radii.[29]

It should also be mentioned that the heat of formation of the silyl radical, taken with the heat of formation of disilane,[5] leads to a bond dissociation energy $D(H_3Si–SiH_3)$ = 82 kcal. mole^{-1}. This result is much higher than the recent E(Si–Si) = 46.4 kcal. mole^{-1} [5,30] and the earlier estimates[26] of D from the activation energy for the pyrolysis of disilane. However, it is in better accord with the observation[31] that silicon–silicon bonds are in some cases more stable thermally than the corresponding carbon–carbon bond.[32] The large difference between E and D implies a large energy difference between the free silyl radical and the silyl group in its bonding state.

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[29] See F. G. A. Stone, "Hydrogen Compounds of the Group IV Elements," Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962.

[30] This becomes 49 kcal. mole^{-1} using the values given in footnote 27.

[31] A. G. MacDiarmid in "Advances in Inorganic Chemistry and Radiochemistry," Vol. III, eds., H. J. Emeleus and A. G. Sharpe, Academic Press, Inc., New York, N. Y., 1961, p. 207.

[32] NOTE ADDED IN PROOF.—We have recently measured $A_p(SiH_3^+)$ from disilane which leads to a value of 81.3 kcal. mole^{-1} for $D(H_3Si–SiH_3)$. See W. C. Steele and F. G. A. Stone, *J. Am. Chem. Soc.*, **84**, 3599 (1962). This result is in excellent agreement with that predicted from the results presented here.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y.]

A Raman Study of Gallium Bromide Solutions[1]

BY JAMES NIXON[2] AND ROBERT A. PLANE

RECEIVED JUNE 4, 1962

Raman spectral intensity measurements were made for gallium bromide solutions which contained various ratios of these two ions. The only spectrum evident was that of the tetrahedral $GaBr_4^-$ ion. The frequencies, depolarization ratios and intensities, relative to ν_1 of this species, were found to be: ν_1, 210 cm.$^{-1}$, $\rho = 0.10$, (1); ν_2, 71 cm.$^{-1}$, $\rho = 0.76$, 0.55; ν_3, 280 cm.$^{-1}$, $\rho = 0.83$, 0.22; ν_4, 102 cm.$^{-1}$, $\rho = 0.84$, 0.74. From Raman intensities, the concentration of $GaBr_4^-$ in a variety of solutions at temperatures up to 95° was found and used to evaluate the thermodynamic parameters for its formation in solution. The enthalpy and entropy values were found to be independent of temperature but varied somewhat with solution composition. At an ionic strength of 10 M, the enthalpy of formation was found to be +9.5 kcal./mole and the entropy 12.5 cal./mole-degree. Because of partial cancellation of the ionic strength changes of entropy and enthalpy, the association equilibrium quotient was reasonably constant. At 25° the average value for the log of the association quotient was determined to be −4.3. Finally, the entropy of hydration of $GaBr_4^-$ was evaluated as −63 cal./mole-degree.

A recent study involving $ZnBr_2$ and $CdBr_2$ solutions showed that Raman spectroscopy can be applied to study quantitatively complex ion equilibria in aqueous solution.[3] In that study it was concluded that Raman spectra can show the extent to which complex ion formation occurs in a stepwise manner. Thus, for the Zn^{++}–Br^- system it was found that in addition to $ZnBr_4^=$, two complexes containing less Br were present in measurable concentrations. For the Cd^{++}–Br^- system, relative to $CdBr_4^=$, lower species were of much less importance than for the Zn case. The present study was undertaken partly to determine the extent of lower species for a similar system of different charge type, Ga^{+3}–Br^-. In addition, the study was extended to higher temperatures in order to determine enthalpy and entropy changes accompanying complex ion formation. It should be noted that Raman measurements require relatively concentrated solutions so that the results cannot be extrapolated to infinite dilution. Thus the enthalpy and entropy values obtained apply to these solutions and necessarily include enthalpy and entropies of dilution. Change of temperature is relatively easily accomplished experimentally for Raman studies. The interpretation of such measurements is made simple through use of an internal standard which compensates for the small changes in refractive index of solutions and changes in their density with temperature. Furthermore, the temperature dependence of the inherent Raman intensity is known.[4]

Woodward and Nord obtained the Raman spectrum of 1.5 M gallium solution prepared by dissolution of the metal in 10.5 M HBr.[5] The four-line spectrum obtained was that of a tetrahedral $GaBr_4^-$ species. The study was not designed to investigate either the quantitative aspects of the equilibrium nor the possible existence of lower species. These questions have not previously been investigated for gallium bromide; although for gallium chloride there is both Raman[6] and anion exchange[7] evidence that only $GaCl_4^-$ forms in solution.

Experimental

Measurements were made with a Cary model 81 Raman spectrophotometer using the same techniques described previously.[3] In some experiments, a Kodak 2-A Wratten gelatin filter was used to improve the background by removal of the 4047Å. line of the mercury arc which may excite fluorescences in trace impurities. In every case, the ν_1 line of ClO_4^- in the solution measured served as internal standard. All intensities were corrected for the temperature change of inherent intensity through multiplication by the factor $[1 - \exp(-h\nu/kT)]$.

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[1] This work was supported by the United States Air Force through the Air Force Office of Scientific Research and Development Command, under Contract No. AF 49(638)-279. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] Based on work performed for partial fulfillment of requirements for the degree of Doctor of Philosophy.

[3] W. Yellin and R. A. Plane, *J. Am. Chem. Soc.*, **83**, 2448 (1961).

[4] G. W. Chantry, *J. Chem. Phys.*, **32**, 222 (1960).

[5] L. A. Woodward and A. A. Nord, *J. Chem. Soc.*, 2655 (1955).

[6] T. F. Young, L. F. Maranville and H. M. Smith, "The Structure of Electrolytic Solutions," Edited by W. J. Hamer, John Wiley and Sons Inc., New York, N. Y., 1959, pp. 60, 61.

[7] K. A. Kraus and F. Nelson, *ibid.*, pp. 349–351.

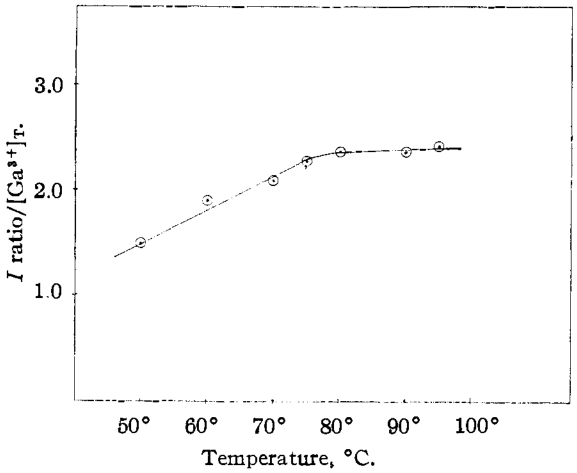

Fig. 1.—Approach to limiting molar intensity as temperature is raised for solution with 0.456 M total gallium and 7.19 M total bromide.

$GaBr_3$ was prepared by a method similar to one used for making $AlBr_3$.[8] Bromine was added dropwise to 99.9% Ga metal, which had been cleaned with CCl_4. About two-thirds the stoichiometric amount of Br_2 was added. Then, the mixture was refluxed in a nitrogen atmosphere until it became colorless. Finally, the $GaBr_3$ was distilled and collected under nitrogen. $Ga(ClO_4)_3 \cdot 6H_2O$ was prepared by dissolution with heating of the cleaned metal in perchloric acid; it was crystallized, filtered and dried under vacuum at 128°.[9] The other reagents, LiBr, NaBr, $HClO_4$, were AR grade, used without further purification.

Gallium analyses were performed by precipitation and the weighing of gallium 8-hydroxyquinolate.[10,11] Perchlorate analyses were performed by precipitation at 90° from a solution *ca.* 0.01 M in perchlorate and 1.3 M in NaCl by dropwise addition of a 50% excess of tetraphenylarsonium chloride. After standing some 3 hours the precipitate was filtered off on sintered glass, washed with small quantities of ice-water, dried 2 hours at 110° and weighed as anhydrous $(C_6H_5)_4AsClO_4$.

Results

For all solutions studied, only four Raman lines associated with gallium and bromide were observed. The frequencies of these lines, 71, 102, 210 and 280 cm.$^{-1}$, show them to be the same lines previously assigned by Woodward and Nord[5] to the tetrahedral species $GaBr_4^-$. The depolarization ratio, ρ, of each of these lines and its intensity relative to ν_1 are given in Table I.

TABLE I

RAMAN LINES OF $GaBr_4^-$

	Frequency, cm.$^{-1}$	ρ	Rel. I.
ν_1	210	0.10	(1)
ν_2	71	.76	0.55
ν_3	280	.83	.22
ν_4	102	.84	.74

The values are also consistent with the previous photographic determinations and the assignments.[5]

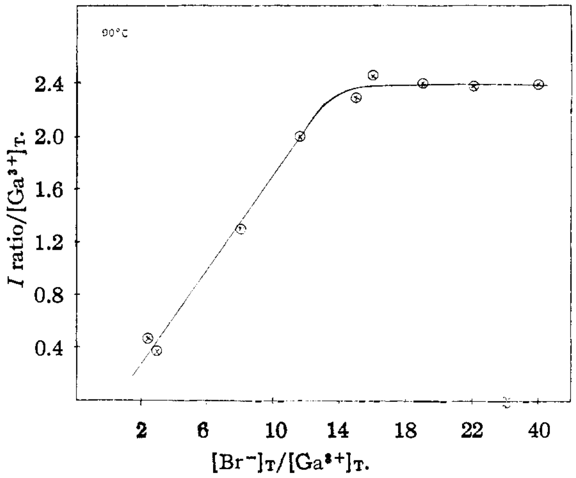

Fig. 2.—Approach to limiting molar intensity as Br^-/Ga^{+3} ratio is increased at 90°.

Spectra were taken of solutions prepared with ratios of bromide to gallium of one, two and three. In none of these were any new Raman lines observed.

For the determination of $GaBr_4^-$ concentration, the ν_1 line was used and its intensity was in every case compared with the molar intensity of the ν_1 line of ClO_4^- dissolved in the same solution. Both lines were corrected for temperature dependence of inherent intensity.[4] This corrected relative intensity, here abbreviated I_{cor} is listed (per molar total gallium) for various solutions at various temperatures in Table II. The table contains most of the data obtained; however, a few points taken at other intermediate and lower (*cf.* Fig. 3) temperatures have been omitted for brevity. It will be noted that as the temperature was raised, the molar intensity increased, and as the ratio Br/Ga was raised (downward in table), it also increased. A limiting value at high temperature and high bromide, of 2.40 was reached which was unchanged by addition of more bromide and thus was taken as the molar intensity of the species $GaBr_4^-$. Figure 1 shows the approach to this limiting molar intensity as the temperature is increased for a solution containing stoichiometric concentrations of Ga = 0.456 M and of Br = 7.19 M. Figure 2 shows the approach at 90° as the ratio Br/Ga is increased.

Using the molar intensity determined for $GaBr_4^-$, its concentration in all solutions at all temperatures was determined. This value was then used to determine values of the equilibrium quotient for the association reaction

$$K = [GaBr_4^-]/[Ga^{+3}][Br^-]^4$$

The logarithms of the quotients for each solution at various temperatures were found to give straight line plots when plotted *versus* the reciprocal of the absolute temperature. Typical plots are shown as Fig. 3. Apparently the enthalpy for the association is a constant over the temperature range studied. From the straight line plots, the best value of log K at 80° was found. This value, along with the enthalpy and entropy of association, also at 80°, is listed in Table III. The solutions

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[8] D. G. Nicholson, P. Winter, and H. Fineberg, "Inorganic Syntheses," Vol. III, Ed. by L. F. Audrieth, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 33.

[9] L. S. Foster, Inorganic Syntheses, Vol. II, Ed. by W. C. Fernelius, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 29.

[10] W. Geilman and W. Wrigge, *Z. anorg. Chem.*, **209**, 129 (1932).

[11] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, "Applied Inorganic Analysis," 2nd. Ed., John Wiley and Sons, Inc., New York, N. Y., 1953.

TABLE II

RELATIVE INTENSITY OF ν_1 FOR $GaBr_4^-$

Stoichiometric concn.				$I_{cor}/[Ga_T]$					
Ga^{+3}	Br^-	ClO_4^-	H^+	50°	60°	70°	80°	90°	95°
2.21	5.93	1.11	0.40	0.16			0.37	0.41	
2.23	6.70	0.27	.27	.29	0.37	0.41	.49	.56	0.57
3.35	10.05	.27	.27	.70	.74	.86	.79	.98	0.86
3.55	10.64	.51	.51	.85	.76	.79	.78	.97	1.01
1.01	3.12	3.30	.29				.13	.35	
1.05	5.16	3.39	.23	0.25	0.35	0.43	.50		
1.05	6.01	1.62	.57	0.41	.49	.57	.67		
0.89	7.04	0.22	.22		.75	.95	1.07	1.28	1.34
.50	5.83[a]	1.75	.24		1.46	1.62	1.86	2.01	2.30
.49	7.18	2.13	.25			1.91	2.33	2.30	2.30
.46	7.19	1.66	.29	1.51	1.89	2.10	2.35	2.45	2.52
.41	7.88	1.38	.28	1.85	2.18	2.18	2.30	2.40	2.47
.25	5.62[a]	0.97	.25		1.14	2.14	2.42	2.34	2.45
.18	7.39[a]	0.76	.23				2.31	2.37	

[a] Most of Br^- added as LiBr; in all other cases, NaB only added.

TABLE III

THERMODYNAMIC DATA

Stoichiometric concn.					Ionic	80°		
Ga^{+3}	Br^-	ClO_4^-	H^+	Na^+	strength	$-\log K$	ΔH	ΔS
0.50	5.83	1.75	0.24	5.83[a]	6.0	2.01	13.1	27.7
0.89	7.04	0.22	.22	4.36	7.5	3.00	11.4	18.4
1.01	3.12	3.30	.29	3.13	9.0	3.08	10.4	15.3
1.05	6.00	1.62	.57	3.91	9.9	3.11	9.6	12.6
1.05	5.16	3.39	.23	5.16	10.4	3.10	9.3	12.2
2.23	6.70	0.27	.27	0	11.0	3.36	8.8	9.7
2.21	5.93	1.11	.40	0	11.5	3.40	9.2	10.5
3.35	10.05	0.27	.27	0	13.6	3.30	7.9	7.1
3.55	10.64	0.51	.51	0	14.9	3.51	8.4	7.7

[a] $Na^+ = 1.56\ M$, $Li^+ = 4.27\ M$.

are listed in order of increasing ionic strength which was calculated after correcting for the association reaction.

Discussion

A major difference between gallium bromide solutions and the zinc and cadmium bromide solutions is the lack of species having less than four Br per Ga. The explanation for this preference of the fully coördinated species does not lie simply in the inherent stability of the complex formed. Thus Cd has the greatest affinity for 4 bromides, Zn is intermediate and Ga shows the smallest affinity.[3] Yet, Zn shows the greatest tendency to form lower species relative to its tendency to form the tetrabromide, Cd is intermediate, and Ga shows the least tendency. *A priori* it would seem that for the metal of lowest bromide affinity (relative to its affinity for H_2O), the lower complexes should be of greater importance relative to the fully coördinated species. Not only should the successive addition of each ligand become more difficult, but the statistical entropy favoring the lower species should be relatively more important compared to the weaker bond energies.

It appears that the major difference between Ga^{+3} and Zn^{++} and Cd^{++}, which might account for the Ga^{+3} not forming lower bromide complexes, is the difference of positive charge. Certainly, for all three metals the affinities for successive addition of Br^- do not fall off as fast as might be expected from an electrostatic model. However, there must be contributions to over-all stability from electrostatic repulsions. These repulsions will be a maximum for addition of a negative ligand to an already negative complex. This, however, cannot occur for a +3 ion such as Ga^{+3} which forms at maximum $GaBr_4^-$. In general, one might expect that lower complexes should be of greater importance for metals of lower charge.

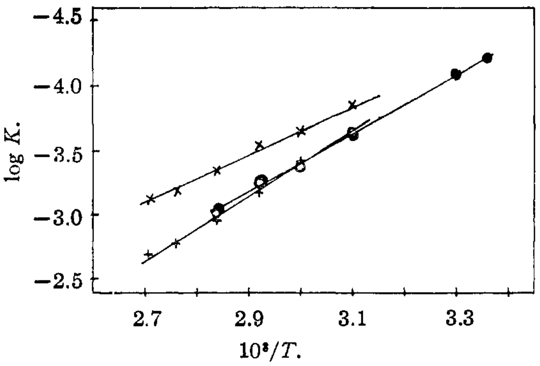

Fig. 3.—Temperature dependence of equilibrium quotients for various solutions.

In both the present study and that concerning zinc bromide, a notable feature is the relative constancy of the various equilibrium quotients with changing solution composition. Part of the explanation for this result can be deduced from the values in Table III. Thus, it is seen that with increasing ionic strength, both the enthalpy and entropy of association decrease. Were it not for this compensation of changes in both activity coefficients and their temperature derivatives, the equilibrium quotient would vary considerably.

From the data of Table III, equilibrium constants can be calculated for 25°. In making the calculation it is assumed that the constancy of ΔH and ΔS extends downward in temperature to 25°. This was tested directly for the fourth experiment in the table and the results, plotted in Fig. 3, show that the assumption is justified. The values of the association quotient found for 25° are more constant than those at 80°. Except for the first experiment of Table III ($\log K(25°) = -3.54$) all the other values of log K at 25° lie between −4.12 and −4.56. Incidentally, the first experiment differs significantly from the others in that it contains a high concentration of lithium ion.

The only factor favoring the formation of $GaBr_4^-$ in solution is the entropy change. Since the association of the bare ions must result in a loss of entropy, the entropy gain must come as a result of differences of hydration. In order to assess these changes, the following calculation was made. The entropy change for the gas phase association was determined to be −123 cal. deg.$^{-1}$ mole^{-1}. This value results from a loss of translational entropy of 151 cal. deg.$^{-1}$ mole^{-1} and a gain of rotational entropy of 28 cal. deg.$^{-1}$ mole^{-1}. If the entropy change for the reaction in solution is taken from the values of Table III to be 15 cal. deg.$^{-1}$ mole^{-1}, and the entropy of hydration of Ga^{+3} and Br^- taken to be −122 and −19.8, respectively, as given by Powell and Latimer,[12] the entropy of hydration of $GaBr_4^-$ is found to be

(12) R. E. Powell and W. M. Latimer, *J. Chem. Phys.*, **19**, 1139 (1951).

-63 cal. deg.$^{-1}$ mole^{-1}. This entropy loss is considerably in excess of the value for a simple -1 ion, such as Br^- for example, and seems large even if all the rotational entropy (28 cal. deg.$^{-1}$ mole^{-1}) were lost. Thus, it seems probable that the $GaBr_4^-$ ion has an abnormally large ordering effect on the solvent due either to its large size or to a retention of a certain amount of ionic charge by the component atoms. In the latter case, the ion should not be considered simply as a large -1 ion, but as one having over short distances, a greater effective charge.

[CONTRIBUTION FROM THE SCIENTIFIC LABORATORY, FORD MOTOR COMPANY, DEARBORN, MICHIGAN]

Electron Magnetic Resonance of X-Irradiated Potassium Hydrogen Maleate

BY H. C. HELLER AND T. COLE

RECEIVED JUNE 22, 1962

X-Irradiation of a single crystal of potassium hydrogen maleate HOOCCH=CHCOOK has been found to produce a free radical in which the unpaired electron interacts with only two protons. The electron magnetic resonance of this radical, shown to be ·OOCCH=CHCOO$^-$, indicates that it is oriented in the host crystal in the same way as the parent hydrogen maleate ion. The principal values of the proton hyperfine tensors of the radical are: -19.0, -28.4, and -6.0 Mc. These rather small principal values and their directions indicate that the unpaired electron in the radical is in a $p\pi$ orbital delocalized over the whole radical, including the carboxyl groups. The directions of the principal values are in agreement with the *cis*-structure of the parent molecule. The utilization of e.m.r. spectra in differentiating between *cis*- and *trans*-structures of radicals is briefly discussed.

Introduction

Several free radicals produced by high-energy radiation in dicarboxylic acids have been studied by means of electron magnetic resonance (e.m.r.).[1-6] The unpaired electron in these radicals was shown to be in a $p\pi$-orbital localized on one of the carbon atoms[7] forming the backbone of the radical. Recently, an allyl-type radical, *i.e.*, HOOC—CH=CH—·CH—COOH was found[8] to be formed in X-irradiated glutaconic acid. The odd electron in this radical was found to be in a delocalized $p\pi$-orbital, the delocalization extending only over the radical's three central carbons. We here report the e.m.r. study of a radical produced in X-irradiated potassium hydrogen maleate KOOCCH=CHCOOH, in which there is considerable unpaired spin delocalization onto the π-orbitals of the carboxyl groups.

Experimental

Potassium hydrogen maleate (KHM) was prepared by neutralizing maleic acid with an appropriate amount of potassium carbonate. Single crystals were grown by the slow evaporation of saturated aqueous solutions. KOOC-CH=CHCOOD was obtained by exchange of KHM with D_2O, and several crystals of the deuterated acid salt were grown from D_2O solutions.

The KHM crystal is reported to be orthorhombic[9,10] and contains four molecules per unit cell. The HM^- ion in the crystal is planar,[9,10] with carboxyl proton H_1 forming an intramolecular hydrogen bond between the carboxyl groups (Fig. 1 upper). There is a plane of symmetry perpendicular to the ion and passing through H_1 and the midpoint of the double bond.

KHM crystals were X-irradiated at room temperature with a tungsten target tube operating at 50 kv. and 50 ma. Irradiation time was one hour.

E.m.r. spectra were observed at room temperature with a spectrometer of conventional design employing 100 kc. field modulation and operating at X-band frequency (~9750 Mc.). Spectra were taken every 10° during rotation of the magnetic field about the *a*, *b*, and *c* axes. Initial orientations of the crystals were made by means of an optical goniometer. An n.m.r. servo system was used to continuously monitor and control the magnetic field. A K-band spectrometer (~24,000 Mc.) was used to observe spectra for certain orientations of the crystal (see Results and Analysis section). The spectroscopic splitting factor **G** was obtained in a manner described previously.[6]

Results and Analysis

Simple e.m.r. spectra are obtained with the external magnetic field along the *a*, *b*, and *c*-axes, and also for rotations about the *a* and *b*-axes. The molecules in the unit cell are magnetically equivalent for these directions. These simple spectra consist of either four main lines with an integrated intensity ratio of approximately 1:1:1:1 (Fig. 2C) or three lines with a ratio of 1:2:1 (Figs. 2A, 2B, and 2D). "Forbidden" transitions[1] are also evident, especially with the field along the *c*-axis (Fig. 2B). Calculations (details of which are given elsewhere[1]) show that the probability of these transitions should be almost zero for spectra obtained at higher fields. The simple spectrum at Fig. 2D, obtained at K-band frequencies (~24,000 Mc.), is in agreement with these calculations (compare Fig. 2B and 2D). E.m.r. spectra for rotations about other axes, *e.g.*, the *c*-axis, are more complex. A crystal in which the carboxyl proton was replaced by a deuteron via exchange with D_2O gave similar spectra, but with narrower and sharper lines. The main spectra, therefore, do not arise from hyperfine (h.f.) coupling to the carboxyl proton.

All the e.m.r. spectra show that the unpaired electron in the free radical, formed by the X-irradiation, is coupled to two protons. The total magnetic interaction may be described by the spin Hamiltonian, where β_n and β are the nuclear and electronic Bohr magnetons, respectively, $\mathbf{g}$ is the electronic spectroscopic splitting tensor, g_n is the nuclear spectroscopic splitting factor, $\mathbf{B}_0$ is the

$$\mathcal{H} = -\beta \mathbf{S}\cdot\mathbf{g}\cdot\mathbf{B}_0 + \Sigma_i g_n \beta_n \mathbf{I}_i\cdot\mathbf{B}_0 + \mathbf{S}\cdot\Sigma_i \mathbf{A}_i\cdot\mathbf{I}_i \qquad (1)$$

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(1) H. M. McConnell, C. Heller, T. Cole and R. W. Fessenden, *J. Am. Chem. Soc.*, **82**, 766 (1960).

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(3) D. Pooley and D. H. Whiffen, *Mol. Phys.*, **4**, 81 (1961).

(4) A. Horsfield, J. R. Morton and D. H. Whiffen, *ibid.*, **4**, 169 (1961).

(5) J. R. Morton and A. Horsfield, *ibid.*, **4**, 219 (1961).

(6) C. Heller, *J. Chem. Phys.*, **36**, 175 (1962).

(7) H. M. McConnell and R. W. Fessenden, *ibid.*, **31**, 1688 (1959); T. Cole and C. Heller, *ibid.*, **34**, 1085 (1961).

(8) C. Heller and T. Cole, *ibid.*, **37**, 243 (1962).

(9) S. F. Darlow and W. Cochran, *Acta Cryst.*, **14**, 1250 (1961).

(10) S. F. Darlow, *ibid.*, **14**, 1257 (1961).