

Magnetic Hyperfine Structure Due to Rotation in $^1\Sigma$ Molecules*

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INTRODUCTION

THE ground state of an overwhelming majority of gaseous molecules is the $^1\Sigma$ electronic state, that is, a state in which the total electronic orbital and spin angular momenta are both separately zero. The net lack of angular momentum is caused by a pairing of electrons from the different atoms of the molecule in such a manner as to cancel the individual electronic angular momenta which are not in general zero. There exists a small number of molecules containing an odd number of electrons making total cancellation not possible, and a smaller number of molecules containing an even number of electrons in which cancellation does not occur. These kinds of molecules are discussed elsewhere, and will not be treated here.

In a $^1\Sigma$ molecule the magnetic dipole-dipole interactions between any nuclear magnetic moment and the electronic spins of the molecule will sum to zero. The internuclear magnetic dipole interaction will be small, usually less than a kilocycle,¹ and in most instances too small for experimental detection. This type of nuclear spin-spin interaction is in any case fairly straightforward and will not be considered here. If the total orbital angular momentum of the $^1\Sigma$ molecule were rigorously zero, the magnetic field arising from electronic angular momentum would also be expected to be zero, and no interaction of the nuclear magnetic moments with this field could be observed.

Actually, however, the electronic orbital angular momentum is zero only for the nonrotating molecule and departs slightly but significantly from zero for a rotating molecule. The associated magnetic field interacts with each nuclear magnetic moment to produce an energy which for certain common cases has the form $c_i(\mathbf{I}_i \cdot \mathbf{J})$, where \mathbf{I}_i is the spin of the i th nucleus, \mathbf{J} is the angular momentum of molecular rotation, and c_i the magnetic coupling constant. This energy is of the order of a few kilocycles for most molecules, but may be over one hundred kilocycles for certain very light molecules. Such an interaction in $^1\Sigma$ molecules was first observed by Rabi *et al.*² while investigating the hydrogen mole-

cule using a molecular beam technique. A similar technique was later extended to the alkali halides, detecting an $\mathbf{I} \cdot \mathbf{J}$ interaction in many instances.³ The first measurement of such a magnetic interaction by microwave absorption was made by Gilbert, Roberts, and Griswold⁴ in ClF. Recently the spectra of a number of molecules have been sufficiently accurately measured by improved microwave techniques to reveal this magnetic interaction. The molecules so investigated have been DI, NH₃, OCS, OCSe, HCN, ClCN, CH₃Cl, SiH₃Cl, and GeH₃Cl.⁵ The purpose of this paper is to assemble the results already published, present those not previously published, and to give an integrated discussion of the available data.

THEORY

The theory of magnetic interactions in $^1\Sigma$ molecules has been treated in considerable detail for the case of the diatomic molecule, stimulated by the very accurate experimental data obtained by molecular beams methods, particularly by Ramsey⁶ on hydrogen. Henderson⁷ and Gunther-Mohr *et al.*⁸ have discussed a more general case in reference to the ammonia molecule, as have Townes and Schawlow⁹ in a general discussion of second-order interactions in gaseous molecules. Since the data to be interpreted in this paper embrace a variety of molecular types, it seems profitable to present here a unified and general description of the relevant quantities.

If one assumes in the conventional manner that the nuclei of a molecule form a rigid frame, and separates out the coordinates of translational motion, one can write the Hamiltonian, exclusive of internal interactions other than monopole Coulombic attraction as

$$H = \frac{1}{2} \sum_g \frac{N_g^2}{A_g} + \frac{1}{2m} \sum_g \sum_i (P_g)_i^2 + V(x, y, z), \quad (1)$$

where N_g is the instantaneous angular momentum of

³ The references of Tables II and III and reference (d) of Table IV give the instances in which an $\mathbf{I} \cdot \mathbf{J}$ energy was detected by molecular beam techniques.

⁴ Gilbert, Roberts, and Griswold, *Phys. Rev.* **76**, 1723 (1949).

⁵ References on these molecules are given in Tables IV, V, and VI.

⁶ N. F. Ramsey, *Phys. Rev.* **90**, 232 (1953); *Phys. Rev.* **87**, 1075 (1952); *Phys. Rev.* **85**, 60 (1952); *Phys. Rev.* **78**, 699 (1950).

⁷ R. S. Henderson, *Phys. Rev.* **74**, 104 (1948); erratum *Phys. Rev.* **74**, 626 (1948).

⁸ Gunther-Mohr, White, Schawlow, Good, and Coles, *Phys. Rev.* **94**, 1184 (1954); Gunther-Mohr, Townes, and Van Vleck, *Phys. Rev.* **94**, 1191 (1954).

⁹ C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy of Gases* (McGraw-Hill Book Company, Inc., New York, 1955).

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¹ Energy values, $h\nu$, where h is Planck's Constant and ν is the frequency in cycles per sec, are abbreviated in this article by giving only the number of cycles per sec.

² Kellogg, Rabi, Ramsey, and Zacharias, *Phys. Rev.* **56**, 728 (1939); Kellogg, Ramsey, Rabi, and Zacharias, *Phys. Rev.* **57**, 677 (1939).

the nuclear frame referred to the principal axes of inertia $g=a, b, c$ fixed in the molecule; A_g is a principal moment of inertia of the nuclear frame; $(P_g)_j$ is the instantaneous linear momentum of the j th electron referred to the principal axis of inertia g ; m is the electronic mass, and V is the potential function for electronic motion and involves only the relative coordinates of the particle.

The total angular momentum, \mathbf{J} , of the molecule exclusive of spin angular momenta is composed of two components, one nuclear and one electronic in origin. Thus,

$$\mathbf{J} = \mathbf{N} + \mathbf{L}, \quad (2)$$

where

$$\mathbf{L} = \sum_j \mathbf{r}_j \times \mathbf{P}_j. \quad (3)$$

Here \mathbf{r}_j is the radius vector from the center of gravity of the molecule to the j th electron. Inserting (2) into (1), one obtains

$$\begin{aligned} H = & \frac{1}{2} \sum_g \frac{J_g^2}{A_g} - \sum_g \frac{J_g L_g}{A_g} + \frac{1}{2} \sum_g \frac{L_g^2}{A_g} \\ & + \frac{1}{2m} \sum_g \sum_j (P_g)_j^2 + V(xyz). \end{aligned} \quad (4)$$

If the rotating molecule were in a true ${}^1\Sigma$ state, L_g would be zero to all orders of approximation. However, measurements on molecular magnetic moments, dielectric susceptibilities, and in the present case internal magnetic interactions all indicate that L_g , though small, is definitely nonzero. One is led to assume that the pure ${}^1\Sigma$ state exists only for the nonrotating molecule, and that for the rotating molecule, the term

$$- \sum_g \frac{J_g L_g}{A_g} \quad (5)$$

acts as a perturbation which causes excited electronic states of nonzero L_g to exist. Since $L_g \ll J_g$, one subdivides the Hamiltonian into an unperturbed Hamiltonian H^0 and two perturbations H^1 and H^2 of descending order of magnitude. Thus,

$$\begin{aligned} H = & \left\{ \frac{1}{2} \sum_g \frac{J_g^2}{A_g} - \frac{1}{2m} \sum_g \sum_j (P_g)_j^2 + V(xyz) \right\} \\ & + \left\{ - \sum_g \frac{J_g L_g}{A_g} \right\} + \left\{ \frac{1}{2} \sum_g \frac{L_g^2}{A_g} \right\}. \end{aligned} \quad (6)$$

Denoting the electronic state of the rotating molecule by a subscript, one has to a first approximation

$$\Psi_0^1 = \Psi_0^0 + \sum_n \sum_{g'} \frac{J_g'(h|L_{g'}|0)}{A_{g'}(E_n - E_0)} \Psi_n^0. \quad (7)$$

where the summation in n is over the excited molecular

electronic states. Using this wave function one obtains

$$\begin{aligned} (0|L_g|0)^1 &= (0|L_g|0)^0 \\ &+ \sum_n \sum_{g'} \frac{(0|L_g|n)(n|L_{g'}|0) + (0|L_{g'}|n)(n|L_g|0)}{E_n - E_0} \\ &\quad \times \frac{J_{g'}}{A_{g'}} + \text{higher-order terms} \end{aligned} \quad (8)$$

with

$$(0|L_g|0)^0 = 0. \quad (9)$$

Consider now the energy of interaction of the magnetic moment of the i th nucleus with the surrounding magnetic field. The magnetic moment of the nucleus is given by

$$\mathbf{u}_i = g_I \mu_{0N} \mathbf{I}_i, \quad (10)$$

where g_I is the gyromagnetic ratio of the nucleus under consideration, μ_{0N} is the nuclear magneton, and \mathbf{I}_i the spin angular momentum. The field at the i th nucleus is

$$\mathbf{H} = - \sum_{j \neq i} \frac{q_j (\mathbf{v}_j \times \mathbf{r}_{ij})}{c r_{ij}^3}, \quad (11)$$

where q_j is the algebraic charge on the j th particle of the molecule, \mathbf{v}_j , its velocity, and \mathbf{r}_{ij} , the radius vector from the i th nucleus to this particle. For purposes of analysis we will divide the summation over j into two sections: the sum over other nuclei, producing H_n ; and the sum over all electrons, producing H_e .

The energy of interaction with \mathbf{H} will be

$$\begin{aligned} W_N = - \mathbf{u} \cdot \mathbf{H} &= \mu_{0N} g_I \sum_i \sum_g \sum_{g'} \sum_{g''} \frac{q_j}{c r_{ij}^3} \\ &\times \left[\frac{(r_{ij})_{g'} (r_{ij})_{g''} J_{g'} J_{g''}}{A_{g'}} - \frac{r_{ij}^2}{A_g} \right] I_g J_g. \end{aligned} \quad (12)$$

The expression for W_N is obtained by expanding the vector product $(\mathbf{v}_j \times \mathbf{r}_{ij})$ after expressing \mathbf{v}_j in terms of the molecular angular momenta and moments of inertia. For the general case this does not reduce. For a nucleus on the symmetry axis, z , of a symmetric top molecule the expression simplifies to

$$\begin{aligned} W_N = \mu_{0N} g_I \sum_i \frac{q_j}{c r_{ij}^3} &\left\{ \frac{(r_{ij})_z^2 - r_{ij}^2}{A_x} \right. \\ &+ \left. \left[\frac{(r_{ij})_z^2 - r_{ij}^2}{A_z} - \frac{(r_{ij})_x^2 - r_{ij}^2}{A_x} \right] \frac{K^2}{J(J+1)} \right\} \mathbf{I} \cdot \mathbf{J}. \end{aligned} \quad (13)$$

For a linear molecule

$$W_N = - \mu_{0N} g_I \sum_i \frac{q_j}{c r_{ij} A_x} \mathbf{I} \cdot \mathbf{J}. \quad (14)$$

In this expression \mathbf{J} has been used in cases where \mathbf{N} is the quantity required. Since N_g differs from J_g by

TABLE I. Hydrogen.

Mole- cule	Refer- ence	Nu- cleus	C_i (Kc)	C_i (bare nuclei) (Kc)	C_i (elec- trons) (Kc)	$\frac{c_i(\text{electronic})\hbar^2}{8\mu_0 N \mu_0 B g_I}$ $\left(= \frac{1}{r^3} \sum_n \frac{ (0 L_\theta n) ^2}{E_N - E_0} \right)$ gm cm ⁻¹	g^J (mol)	g^J (nuclear frame)	g^J (electrons)	$\frac{g^J(e)\hbar^2}{4-B}$ m
										$\left(= \sum_n \frac{ (0 L_\theta n) ^2}{E_N - E_0} \right)$ gm cm ²
H ₂	a	H	-113.904 ±0.030	-203	89.1	2.65×10 ⁻²⁰	+0.8787 ±0.0070	+1.0000	-0.1213	1.54×10 ⁻⁴⁵
HD	b	H	-87.00 ±0.85	-152	65.0	2.60×10 ⁻²⁰	+0.6601 ±0.0050	+0.8333	-0.1732	1.52×10 ⁻⁴⁵
		D	-12.6 ±0.3	-23.3	10.7	2.77×10 ⁻²⁰				
D ₂	a	D	-8.445 ±0.056	-15.58	7.13	2.77×10 ⁻²⁰	+0.4406 ±0.0030	+0.5000	-0.0594	1.52×10 ⁻⁴⁵

^a Harrick, Barnes, Bray, and Ramsey, Phys. Rev. **90**, 260 (1953).

^b Kellogg, Ramsey, Rabi, and Zacharias, Phys. Rev. **57**, 677 (1939).

^c Referred to center of charge of molecule (see text).

only a few parts in a thousand for $^1\Sigma$ molecules, the error introduced into the energy calculation by substitution will usually be too small to be detected experimentally. On the other hand, though the electrons contribute but little to the total mechanical angular momentum, the electronic gyromagnetic ratio is nearly two thousand times greater than that of nucleons, so the electronic participation in magnetic interactions associated with angular momentum is at least the same order as that of the nuclear frame.

The energy of interaction of the nucleus with H_e is

$$\begin{aligned}
 W_e &= -\mathbf{u} \cdot \mathbf{H}_e = -\frac{e}{c} \mu_0 N g_I \mathbf{I}_i \cdot \sum_j \frac{\mathbf{v}_j \times \mathbf{r}_{ij}}{r_{ij}^3} \\
 &= -\frac{e}{mc} \mu_0 N g_I \mathbf{I}_i \cdot \sum_j \frac{\mathbf{P}_j \times \mathbf{r}_{ij}}{r_{ij}^3} \\
 &= 2\mu_0 B \mu_0 N g_I \mathbf{I}_i \cdot \sum_j \frac{\mathbf{r}_{ij} \times \mathbf{P}_j}{r_{ij}^3},
 \end{aligned} \quad (15)$$

where $\mu_0 B$ is the Bohr magneton. To reduce this expression to a more useful and tractable form we must call in some detail upon knowledge of molecular structure. It is convenient to divide the electrons into two classes: (1) Tightly bound electrons in closed shells which may be assigned to a specific nucleus and (2) valence electrons which are not in closed shells and which may be associated with more than one nucleus. Closed-shell electrons belonging to nucleus i will cancel one another out in the summation over j since their total spatial distribution is spherically symmetric about the nucleus. Closed-shell electrons on another nucleus can possess no angular momentum about that nucleus and will have angular momentum relative to nucleus i due only to the motion of their center of mass. In the rotating molecule these shells may be likened to the chairs on a ferris wheel, preserving their orientation while the frame rotates. Since the effective Z for closed inner shells is relatively high, such electron shells may to a

first approximation be considered to have shrunk down onto their respective nuclei, decreasing the effective nuclear charge.¹⁰ Their effect may be handled formally by omitting them from the summation in j of Eq. (15) but reducing the nuclear charge q_j , in expressions (11) through (14) to an effective charge q_j' equal to the nuclear charge minus the number of inner shell electrons. We are left then with only the valence electrons to consider.

We know that for a true $^1\Sigma$ molecule $\sum_j \mathbf{r}_{0j} \times \mathbf{P}_j = \mathbf{L} = 0$, referred to the molecular center of mass. Though $\sum_j (\mathbf{r}_{0j} \times \mathbf{P}_j / r_{0j}^3)$ is not readily calculable, it might be expected that the cancellation characteristic of the numerator would prevail, and the sum be small for a $^1\Sigma$ molecule. Further, just as a small amplitude of excited electronic states of nonzero \mathbf{L} provide the only nonzero contribution to $\sum_j \mathbf{r}_{0j} \times \mathbf{P}_j$, so also would these same excited states dominate $\sum_j (\mathbf{r}_{0j} \times \mathbf{P}_j / r_{0j}^3)$. We have shown earlier that the molecular rotation serves to introduce excited electronic states, so making the additional assumption that only one electron at a time will enter an excited state, and that this electron will be a valence electron, we approximate the contribution of the valence electrons to (15) by

$$2\mu_0 B \mu_0 N g_I \mathbf{I}_i \cdot \sum_j' \frac{\mathbf{r}_{ij} \times \mathbf{P}_j}{r_{ij}^3} = 2\mu_0 B \mu_0 N g_I \langle 1/r^3 \rangle_{Av} \mathbf{I}_i \cdot \mathbf{L}. \quad (16)$$

Where \sum_j' is restricted to the valence electrons, $\langle 1/r^3 \rangle_{Av}$ is averaged over the excited electronic wave function, and \mathbf{L} is given by expression (8). Thus we have

$$\begin{aligned}
 W_e &= 2\mu_0 B \mu_0 N g_I \langle 1/r^3 \rangle_{Av} \sum_n \sum_g \sum_{g'} \\
 &\quad \times \frac{(0|L_\theta|n)(n|L_{g'}|0) + (0|L_{g'}|n)(n|L_\theta|0)}{E_n - E_0} \\
 &\quad \times \frac{J_{g'} \cdot I_g}{A_{g'}}. \quad (17)
 \end{aligned}$$

¹⁰ A more formal derivation of this result, starting with the equivalent of Eq. (15), is given in Chap. 8, of reference 9.

TABLE II. Alkali halides. Data from electron resonance molecular beams.

Molecule	Reference	Nucleus	C_i (Kc)	C_i (rigid frame) (Kc)	C_i (valence electrons) (Kc)	$\frac{c_i(\text{electronic})\hbar^2}{8\mu_0 N \mu_0 B g_I}$	$\frac{ (0 L_y n) ^2}{\sum_n \frac{ (0 L_y n) ^2}{E_n - E_0}}$
						$\left(\left\langle \frac{1}{r^3} \right\rangle_{Av} \sum_n \frac{ (0 L_y n) ^2}{E_n - E_0} \right)$ (gm cm ⁻¹)	(gm cm ²)
Li ⁶ F ¹⁹	a	F ¹⁹	37.3±0.3	-2.3	39.6	0.422×10 ⁻¹⁸	1.88×10 ⁻⁴⁴
		Li ⁶	0±0.5				
Li ⁷ F ¹⁹	b	F ¹⁹	32.9±0.1	-2.1	35.0	0.420×10 ⁻¹⁸	1.87×10 ⁻⁴⁴
		Li ⁷	+2.2±0.6	+0.9	+1.3	0.039×10 ⁻¹⁸	
KF	c	F ¹⁹	0±10		0±10	0±0.65×10 ⁻¹⁸	0±2.63×10 ⁻⁴⁴
Rb ⁸⁵ F ¹⁹	d	F ¹⁹	11±3	-0.24	11.2	0.95×10 ⁻¹⁸	3.85×10 ⁻⁴⁴
Rb ⁸⁷ F ¹⁹	d	F ¹⁹	14±4	-0.23	14.2	1.20×10 ⁻¹⁸	4.90×10 ⁻⁴⁴
CsF ¹⁹	e	F ¹⁹	16±2	-0.2	16.2	1.64×10 ⁻¹⁸	6.65×10 ⁻⁴⁴

^a J. C. Schwartz and J. W. Trischka, Phys. Rev. **88**, 1085 (1952).

^b R. Braunstein and J. W. Trischka, Phys. Rev. **90**, 348 (1953).

^c L. Grabner and V. Hughes, Phys. Rev. **79**, 819 (1950).

^d V. Hughes and L. Grabner, Phys. Rev. **79**, 314 (1950).

^e J. W. Trischka, Phys. Rev. **74**, 718 (1948).

For a nucleus on the axis of a symmetric top, expression (17) reduces to

$$W_e = 4\mu_0 B \mu_0 N g_I \langle 1/r^3 \rangle_{Av} \sum_n \left[\frac{|(0|L_x|n)|^2}{A_x} \times \left(\frac{|(0|L_x|n)|^2}{A_z} - \frac{|(0|L_x|n)|^2}{A_x} \right) \frac{K^2}{J(J+1)} \right] \times \frac{\mathbf{I} \cdot \mathbf{J}}{E_n - E_0}. \quad (18)$$

For a linear molecule (17) becomes

$$W_e = 4\mu_0 B \mu_0 N g_I \langle 1/r^3 \rangle_{Av} \sum_n \frac{|(0|L_x|n)|^2}{E_n - E_0} \mathbf{I} \cdot \mathbf{J}. \quad (19)$$

The total energy of magnetic interaction will be given by the sum of expressions (12) and (17) with the q_j of (12) replaced by q_j' , as previously noted. Attention is called to the fact that for a nucleus on the axis of a symmetric top the magnetic interaction has the form $c\mathbf{I} \cdot \mathbf{J}$, where c is the sum of two terms of opposite sign, e.g., for the linear molecule

$$W = \frac{\mu_0 N g_I}{A_x} \left[4\mu_0 B \langle 1/r^3 \rangle_{Av} \sum_n \frac{|(0|L_x|n)|^2}{E_n - E_0} - \sum_i \frac{g_j'}{c r_{ij}} \right] \mathbf{I} \cdot \mathbf{J}. \quad (20)$$

Attention is also called to the similarity in form of the electronic contribution to the magnetic energy and the electronic contribution to the molecular g -factor. The latter may be written¹¹

$$[g_J(\text{electronic})]_g = \frac{\mu_0 B}{\mu_0 N} L_g, \quad (21)$$

and L_g can then be obtained from (8), and one has,

¹¹ J. R. Eshbach and M. W. P. Strandberg, Phys. Rev. **85**, 24 (1952).

e.g. for the linear molecule,

$$g_J(\text{electronic}) = \frac{2\mu_0 B}{\mu_0 N A_x} \sum_n \frac{|(0|L_x|n)|^2}{E_n - E_0}. \quad (22)$$

Since c_i and g_j are known, one therefore can calculate $\langle 1/r^3 \rangle_{Av}$, a fact which will be used in later sections of this paper as a check on the assumptions to be made concerning $\langle 1/r^3 \rangle_{Av}$.

EXPERIMENTAL EVIDENCE

As was indicated in the introduction, the experimental evidence on magnetic interaction in $^1\Sigma$ molecules comes from two sources; molecular beam experiments and measurement of microwave absorption spectra. The data vary widely in quality, uncertainty in the constant in hydrogen being only about 0.03% as compared to 50% for some of the heavier molecules. All experimental information currently available is presented in Tables I through VI.

The tables contain a number of quantities in addition to the interaction constants themselves, and are not entirely self-explanatory. Results are presented in the order of ascending complexity of the molecule involved, starting with hydrogen and proceeding through the other diatomic molecules to linear polyatomic and finally symmetric top molecules. In each case the interaction constant or constants are presented and the derived quantity

$$\frac{c_i(\text{electronic})\hbar^2}{8\mu_0 N \mu_0 B g_I} = \langle 1/r^3 \rangle_{Av} \sum_n \frac{|(0|L_y|n)|^2}{E_n - E_0} \quad (23)$$

listed, where c_i is the interaction constant in cycles per second and B , the rotational constant, is equal to $h(8\pi^2 A)$. The equality sign holds only if certain approximations given in the theory section and discussed further in the interpretation section below, are valid.

TABLE III. Alkali halides. Data from magnetic resonance molecular beams.

Molecule	Nucleus	Transition used and reference	C_i (measured) (Kc)	C_i (rigid frame) (Kc)	Comments
NaF	Na	$(J\pm 3/2) \leftrightarrow (J\pm 1/2)$ (reference a)	$ \sim 1 $		
NaCl	Na	$(J\pm 3/2) \leftrightarrow (J\pm 1/2)$ (reference a)	$ \sim 1 $ $ 0.37 $	+0.045	
		Data of reference a Interpreted in reference b $(J\pm 1/2) \leftrightarrow (J\mp 1/2)$	-0.16		See text for comments on reference b
NaBr	Na	$(J\pm 3/2) \leftrightarrow (J\pm 1/2)$ (reference b)	$ 0.67 $	+0.030	
		$(J\pm 1/2) \leftrightarrow (J\mp 1/2)$ (reference b)			Fit of existing theory to observed line not possible.
NaI	Na	$(J\pm 1/2) \leftrightarrow (J\mp 1/2)$ (reference b)	-0.23	+0.022	
		$(J\pm 3/2) \leftrightarrow (J\pm 1/2)$ (reference c)	$ 0.69 $		
KBr	Br ⁷⁹ Br ⁸¹	$(J\pm 1/2) \leftrightarrow (J\mp 1/2)$ (reference b)	+1.21 +1.30	-0.010	The eqQ reported in this reference is considerably different from that of Fabricand, Carlson, and Lee. ^d Latter detect considerable change in eqQ with v .
RbF	Rb ⁸⁷	$(J\pm 3/2) \leftrightarrow (J\pm 1/2)$ (reference e)	$ 1.1 \pm 0.1$		
RbCl	Rb ⁸⁷	$(J\pm 3/2) \leftrightarrow (J\pm 1/2)$ (reference e)	$ 1.0 \pm 0.1$		
LiF	F ¹⁹	Data of reference c Interpreted in reference f	$ 20 $	-2.3	$C_i = 32.9$ Kc from electric resonance molecular beams. ^g
CsF	F ¹⁹	Data of reference c Interpreted in reference h	$ 7.2 $	-0.2	$C_i = 16$ Kc from electric resonance molecular beams. ^h

^a H. J. Zeiger and D. I. Bolef, Phys. Rev. **85**, 788 (1952).

^b R. E. Cote and P. Kusch, Phys. Rev. **90**, 103 (1953).

^c W. A. Nierenberg and N. F. Ramsey, Phys. Rev. **72**, 1075 (1947).

^d Fabricand, Carlson, Lee and Ravi, Phys. Rev. **91**, 1403 (1953).

^e D. I. Bolef and H. J. Zeiger, Phys. Rev. **85**, 799 (1952).

^f R. Braunstein—private communication.

^g R. Braunstein and J. W. Trischka, Phys. Rev. **90**, 348 (1953).

^h J. W. Trischka, Phys. Rev. **74**, 718 (1948).

For most of the molecules an approximation to $\langle 1/r^3 \rangle_{Av}$ is also made, and the further approximate quantity $\sum_n (|0|L_g|n\rangle|^2/E_n - E_0)$ listed. The quantity c_i (electronic) is obtained from c_i (total) by subtracting out c_i (rigid frame) calculated for the nuclear frame plus closed-shell electrons. In illustration of the rigid-frame calculation, a net charge of $+e$ would be considered to reside at the Li nucleus and a net charge of $-e$ to reside at the F -nucleus. For some molecules the

molecular g -factors are available. When this is the case the g -factor is given as well as the derived quantity

$$\frac{g_J(\text{electronic})\hbar^2}{\frac{M}{4-B}m} = \sum_n \frac{|0|L_g|n\rangle|^2}{E_n - E_0}, \quad (24)$$

where m and M are the electron and proton masses,

TABLE IV. Diatomic molecules: DI, ClF, CS, TICl.

Molecule	Reference	Nucleus	C_i (Kc)	C_i (rigid frame) (Kc)	C_i (valence electron) (Kc)	$\frac{c_i(\text{electronic})\hbar^2}{8\mu_0 N \mu_0 B B g I}$ ($= \langle \frac{1}{r^3} \rangle_{Av} \sum_n \frac{ 0 L_g n\rangle ^2}{E_n - E_0}$) (gm cm ⁻¹)	$\sum_n \frac{ 0 L_g n\rangle ^2}{E_n - E_0}$ (gm cm ²)
DI	a	I ¹²⁷	+140	-1.03	141	3.88×10^{-18}	0.67×10^{-43}
ClF	b	Cl ³⁵	+22±3	-0.8	22.8	8.00×10^{-18}	3.27×10^{-43}
		Cl ³⁷	+18±3	-0.8	18.8	8.15×10^{-18}	3.33×10^{-43}
CS	c	S ³³	+19±15	-0.6	19.6	6.95×10^{-18}	4.06×10^{-43}
TICl	d	Tl ²⁰⁷	73±2	+0.6	72.4	25.7×10^{-18}	6.35×10^{-43}
		Cl ³⁵	1.4±0.1	-0.10	1.5	2.65×10^{-18}	1.08×10^{-43}

^a C. A. Burrus and W. Gordy, Phys. Rev. **92**, 1437 (1953).

^b Table VII.

^c R. C. Mockler and G. Bird, Phys. Rev. (to be published).

^d Carlson, Lee, and Fabricand, Phys. Rev. **85**, 784 (1952).

TABLE V. Linear molecules.

Mole- cule	Nu- cleus	Refer- ence	C_i (Kc)	$\frac{c_i \hbar^2}{B\mu_0 B\mu_0 N B g_I}$		g_i	Refer- ence	g_i (rigid frame)	$ g_i $ (elect)	$\frac{g_J(e)\hbar^2}{4\frac{M}{m}}$
				$\left(\frac{1}{r^3}\right) \sum_n \frac{ (0 L_x n) ^2}{E_n - E_0}$ gm cm ⁻¹	$\sum_n \frac{ (0 L_x n) ^2}{E_n - E_0}$ gm cm ²					$\left(\sum_n \frac{ (0 L_x n) ^2}{E_n - E_0}\right)$ gm cm ²
O ¹⁷ C ¹² S ³²	O ¹⁷	a	-4.0 ± 1.5	2.70 × 10 ⁻¹⁸	2.75 × 10 ⁻⁴³	-0.025	b	+0.025	0.050	1.90 × 10 ⁻⁴³
O ¹⁶ C ¹² S ³³	S ³³	c	+2 ± 1	2.03 × 10 ⁻¹⁸	1.78 × 10 ⁻⁴³	±0.002				
O ¹⁶ C ¹² Se ⁷⁹	Se ⁷⁹	d	-3.2 ± 1.0	8.25 × 10 ⁻¹⁸	3.75 × 10 ⁻⁴³	-0.019 ±0.002	e	+0.021	0.040	2.27 × 10 ⁻⁴³
HCN ¹⁴	N ¹⁴	f	+10 ± 4	1.67 × 10 ⁻¹⁸	2.98 × 10 ⁻⁴³					
DCN ¹⁴	N ¹⁴	f	+8 ± 3	1.64 × 10 ⁻¹⁸	2.92 × 10 ⁻⁴³					
Cl ³⁵ CN ¹⁴	N ¹⁴	g	+2.5 ± 0.8	3.12 × 10 ⁻¹⁸	5.55 × 10 ⁻⁴³	No informa-				
Cl ³⁵ CN ¹⁴	Cl ³⁵	h	+3.0 ± 1.0	2.78 × 10 ⁻¹⁸	1.70 × 10 ⁻⁴³					
Cl ³⁵ CN ¹⁵	Cl ³⁵	i	+3.5 ± 0.6	3.34 × 10 ⁻¹⁸	2.04 × 10 ⁻⁴³	tion available				

^a Table XIII.

^b J. R. Eshbach and M. W. P. Strandberg, Phys. Rev. **85**, 24 (1952).

^c Table VIII.

^d Table IX.

^e Hardy, Silvey, Townes, Burke, Strandberg, Parker, and Cohen, Phys. Rev. **92**, 1532 (1953).

^f J. A. Klein and A. H. Nethercot, Quarterly Report, CU Radiation Lab., October 30, 1953.

^g Table X.

^h Table XI.

ⁱ Table XII.

respectively. The expression is exact, but approximations are usually necessary in obtaining g_J (electronic), the electronic contribution to the molecular g -factor, from the total molecular g -factor g_J . Only the total g -factor, g_J is experimentally observed.

Table I presents excellent experimental data on hydrogen in its various isotopic forms. Tables II and III give the results on the alkali halides. The results of electric resonance molecular beam experiments and magnetic resonance molecular beams experiments are given separately since there is strong evidence, discussed later, that values of c_i so far obtained by the latter technique are not reliable in many instances. The magnetic interaction data on diatomic molecules other than hydrogen and the alkali halides are tabulated in Table IV. Since the microwave spectrum of ClF was originally measured some years ago it was deemed desirable to remeasure this spectrum using the more refined techniques now available. This was done and the remeasured spectrum from which the magnetic constant of Table IV was calculated is given in Table VII. No g_J values are available for any of the diatomic molecules other than hydrogen.

Table V represents the magnetic constants, all calculated from microwave absorption spectra, and the molecular g -factors when available for linear polyatomic molecules. The spectra of O¹⁷CS, HCN, and DCN have previously been published.^{12,13} The spectra of the remaining molecules were measured for the purposes of this paper on a high-resolution bridge-type spectrometer, and the resulting determinations are given in

Tables VIII through XII. Details of the spectrometer^{8,14} and the techniques of measurement using it have been published elsewhere.^{8,15} The interpretation of the O¹⁷CS spectrum as originally published did not include consideration of the magnetic interaction. The improvement in fit of the theoretical spectrum to the experimental spectrum upon inclusion of the magnetic interaction is detailed in Table XIII.

A similar situation concerning sources of information prevails for the symmetric top molecules tabulated in Table VI. All the magnetic interaction constants are derived from microwave spectra measured on the aforementioned spectrometer. The results on NH₃ have been previously published⁸ as part of an extensive treatment of the energy levels of that molecule. The microwave data from which the magnetic constants of the other molecules were obtained are given in Tables XIV through XVIII of the appendix.

INTERPRETATION OF RESULTS

For the linear molecule, of which the diatomic molecule is a special case, Eq. (20) of the theory section applies and we have subject to the approximation made in derivation:

$$c_i = \frac{\mu_0 N g_J}{A_x} \left[4\mu_0 B \langle 1/r^3 \rangle_{av} \sum_n \frac{|(0|L_x|n)|^2}{E_n - E_0} - \sum_i \frac{q_i'}{c r_{ij}} \right]. \quad (25)$$

For purposes of interpretation it is desirable to obtain $\sum_n (|(0|L_x|n)|^2/E_n - E_0)$ explicitly to compare with the same quantity calculated from the molecular

¹² Geschwind, Gunther-Mohr, and Silvey, Phys. Rev. **85**, 474 (1952).

¹³ J. A. Klein and A. H. Nethercot, Columbia University Radiation Laboratory Progress Report, October 30, 1953.

¹⁴ S. Geschwind, thesis, Columbia University, 1951 (unpublished); see also S. Geschwind, Ann. N. Y. Acad. Sci. **55**, 751 (1952).

¹⁵ R. L. White, J. Chem. Phys. **23**, 249 (1955).

TABLE VI. Symmetric top molecules.

Molecule	Nucleus	Refer- ence	$C_{zz} (=C_{zz})$ (Kc)	C_{zz} (Kc)	C rigid frame (Kc)	C valence electron (Kc)	$\left(\left\langle \frac{1}{r^3} \right\rangle \sum_n \frac{ (0 L_x n) ^2}{E_n - E_0} \right)$ gm cm ⁻¹	$\frac{c(v.e.)^2}{8\mu_0 N \mu_0 B g I}$	$\left(\left\langle \frac{1}{r^3} \right\rangle \sum_n \frac{ (0 L_x n) ^2}{E_n - E_0} \right)$ gm cm ²	g_{zz} (= g_{zz})	Refer- ence	g rigid frame	g valence electron	$\frac{g(v.e.)^2}{4 \frac{M}{m} B}$ (= $\sum_n \frac{ (0 L_x n) ^2}{E_n - E_0}$) gm cm ²
CH ₃ C ¹³	C ¹³	a	+1.2±1.0	—	<0.1	+1.2	0.70×10 ⁻¹⁸		1.24×10 ⁻⁴⁸		b			
SF ₆ C ¹⁹	C ¹⁹	c	+1.8±1.0	—	<0.1	1.8	1.18×10 ⁻¹⁸		2.08×10 ⁻⁴⁸					
GeH ₃ C ¹³	C ¹³	d	0.5±0.7	—	<0.05	0.5	0.66×10 ⁻¹⁸		1.16×10 ⁻⁴⁸					
C ¹³ CN ¹⁵	C ¹³	f	—	+8±5	<0.1	8	0.48×10 ⁻²⁰		2.60×10 ⁻⁴⁶					
NH ₃	N ¹⁴	g	+6.5±0.2	6.1±0.2	-3.6	10.1	2.50×10 ⁻¹⁹		0.58×10 ⁻⁴⁸	0.560	h	0.886	0.326	0.25×10 ⁻⁴⁸
					-3.0	9.1	3.56×10 ⁻¹⁹		0.85×10 ⁻⁴⁸	—		1.000	0.516	0.63×10 ⁻⁴⁸

^a Table VII, Appendix.

^b C. K. Jen, Phys. Rev. **81**, 197 (1951).

^c Tables VIII(a) and VIII(b), Appendix.

^d Table IX, Appendix.

^e Excited bending vibrational state

^f Table X, Appendix.

^g Gunther-Mohr, White, Schawlow, Good, and Coles, Phys. Rev. **94**, 1184 (1954).

^h J. R. Eshbach and M. W. P. Strandberg, Phys. Rev. **85**, 24 (1952).

g -factor. Therefore some approximation for $\langle 1/r^3 \rangle_{Av}$ for the excited electronic states is needed. If it is assumed that the dominant state in the sum over excited states is the π state, the lowest lying state of nonzero orbital angular momentum, one would expect the excited-state electron to behave essentially as a p -electron in the vicinity of a nucleus. We will therefore in many instances make the approximation

$$\left(\frac{1}{r^3} \right)_{Av} \left[\begin{array}{c} \text{for excited state} \\ \text{molecule} \end{array} \right] = \frac{1}{N} \left(\frac{1}{r^3} \right)_{Av} \left[\begin{array}{c} \text{for atomic} \\ p\text{-orbital} \end{array} \right], \quad (26)$$

where N is the number of atoms in the molecule. The factor $1/N$ must be included to express the fact that the molecular electron divides its time among several atoms. A convenient tabulation of $\langle 1/r^3 \rangle_{Av}$ for atomic p -orbitals has recently been prepared by Smith and Barnes.¹⁶ The validity of the $\langle 1/r^3 \rangle$ assumptions may be tested by comparing $\sum_n (|0|L_x|n)|^2/E_n - E_0$ calculated from one nucleus with that calculated from other nuclei in the same molecule, or with the identical quantity calculated from the molecular g -factor. Both methods will be used in subsequent parts of this section.

Only for hydrogen has a serious attempt been made to correlate the magnetic interaction with other molecular properties. The magnetic coupling constants and molecular g -factors of the various isotopic species of hydrogen have been measured with an accuracy orders of magnitude better than for any other molecule, and the theoretical treatment pushed to a corresponding degree of refinement. The effort here will not be toward further refinement of the interpretation. Since a comparative treatment of a number of molecules is one of the aims of this paper, hydrogen will suffer in that it will be given a rather coarse-grained interpretation commensurate with that possible for other molecules.

The most recent values of c_i and g_j for H₂, HD, and D₂ are presented in Table I. Note that the c_i are all negative,¹⁷ indicating that the magnetic field due to the rotating nuclei exceeds that of the electrons. This is true in only two instances of all those reported in this paper; for hydrogen and for the protons in ammonia. In both instances the nucleus involved is hydrogen, which because of its small Z is ineffective in producing a large $\langle 1/r^3 \rangle_{Av}$ for the valence electrons, and in both instances the molecule involved exhibits large electronic slippage. By this is meant that an appreciable fraction of the total molecular electronic wave function is spherically symmetric about the molecular center of mass, hence does not rotate with the molecular frame. That such slippage occurs in large measure for H₂ and NH₃ is evidenced by their large diamagnetic susceptibility.¹¹ When slippage occurs the electronic contribu-

¹⁶ R. G. Barnes and W. V. Smith, Phys. Rev. **93**, 95 (1954).

¹⁷ Ramsey gives c as positive, reflecting only the fact that he has taken the Hamiltonian term to be $-c(\mathbf{I} \cdot \mathbf{J})$ rather than $+c(\mathbf{I} \cdot \mathbf{J})$ as is done here.

tion to magnetic fields associated with the molecular rotation would of course be expected to be reduced. Moreover, since the field produced by nuclei is proportional to the reciprocal of the internuclear separation, the small internuclear distances in H_2 and NH_3 help enhance this field.

Confining the discussion specifically to hydrogen now one finds closely related to the aforementioned properties a concomitant small degree of excitation of electronic states of nonzero orbital angular momentum. The quantity $\sum_n (| \langle 0 | L_x | n \rangle |^2 / E_n - E_0)$ hereinafter abbreviated as $\sum_n (L_n)$ is taken to be a measure of this property. Since good values of the molecular g -factor are available, it is possible in the case of hydrogen to calculate $\sum_n (L_n)$ without any assumption about $\langle 1/r^3 \rangle_{Av}$. As will be seen in subsequent comparisons the $\sum_n (L_n)$ obtained here is exceptionally small. It should be remarked that in Table I, $\sum_n (L_n)$ for HD has been calculated relative to the center of charge, rather than about the center of mass, in order to render comparison with H_2 and D_2 immediate.

Knowing $\sum_n (L_n)$ from g_J , and $\langle 1/r^3 \rangle_{Av} \sum_n (L_n)$ from the electronic contribution to the magnetic interaction, one can calculate $\langle 1/r^3 \rangle_{Av}$ for the excited electronic states. The value is

$$\langle 1/r^3 \rangle_{Av} = 1.72 \times 10^{25} \text{ cm}^{-3},$$

or in a form convenient for comparison with Barnes and Smith¹⁶

$$\langle (a_0/r)^3 \rangle_{Av} = 2.51,$$

where a_0 is the Bohr radius. This is to be compared with

$$\langle (a_0/r)^3 \rangle_{Av} = 0.04$$

TABLE VII. Observed spectra and calculated molecular parameters of $Cl^{37}F$ and $Cl^{35}F$.^a

Transition J	Transition F	Observed transition frequencies	
		$Cl^{37}F$	$Cl^{35}F$
0→1	3/2→3/2	30 228.344±0.004 Mc	30 807.366±0.003 Mc
	3/2→5/2	30 257.135±0.003 Mc	30 843.875±0.004 Mc
	3/2→1/2	30 280.056±0.003 Mc	30 872.963±0.004 Mc

^a $(eqQ)_{Cl^{37}} = -114.977 \pm 0.025$ Mc, $(eqQ)_{Cl^{35}} = -145.837 \pm 0.028$ Mc, $C_i(Cl^{37}) = +18 \pm 3$ Kc, and $C_i(Cl^{35}) = +22 \pm 3$ Kc.

TABLE VIII. Observed spectrum of OCS^{33} compared with theoretical spectrum.^a

Transition $J=1 \rightarrow 2$	Frequencies (Mc)	
	Observed	Theoretical
$F=1/2 \rightarrow 3/2$	24 012.338±0.002	24 012.339
$5/2 \rightarrow 5/2$	24 012.959±0.003	24 012.960
$1/2 \rightarrow 1/2$	24 019.618±0.002	24 019.617
$3/2 \rightarrow 5/2$	24 020.249±0.002	24 020.247
$5/2 \rightarrow 7/2$	24 025.446±0.002	24 020.444
$3/2 \rightarrow 3/2$	24 032.719±0.015	24 032.724
$3/2 \rightarrow 1/2$		

^a Constants used in calculating the theoretical spectrum: $B_0 = 6004.905 \pm 0.001$ Mc, $(eqQ)_{S^{33}} = -29.130 \pm 0.008$ Mc, and $C_i = +2 \pm 1$ Kc.

TABLE IX. Observed spectrum of OCS^{79} compared to theoretical spectrum.^a

Transition $J=2 \rightarrow 3$	Frequencies (Mc)	
	Observed	Theoretical
$F=7/2 \rightarrow 7/2$	24 153.201±0.004	24 153.201
$9/2 \rightarrow 11/2$	24 159.928±0.004	24 159.932
$3/2 \rightarrow 1/2$	24 170.179±0.003	24 170.177
$11/2 \rightarrow 13/2$	24 190.772±0.004	24 190.776
$7/2 \rightarrow 9/2$	24 234.352±0.005	24 234.350
$5/2 \rightarrow 7/2$		

^a Constants used in calculating the theoretical spectrum: $B_0 = 4029.848 \pm 0.001$ Mc, $(eqQ)_{Se^{79}} = -752.210 \pm 0.020$ Mc, and $C_i = -3.2 \pm 1.5$ Kc.

TABLE X. Comparison of observed spectrum of $Cl^{35}CN^{14}$ with theoretical spectrum, showing determination of interaction constants for N^{14} .^a

F_i	Transition $J=1 \rightarrow 2$ $F_i \rightarrow F_i'$	F_i'	Frequencies (Mc)	
			Observed	Theoretical
5/2	3/2→5/2	5/2	23 863.416±0.002	23 863.416
5/2	7/2→5/2	5/2	23 863.724±0.003	23 863.724
5/2	3/2→5/2	3/2	23 863.959±0.003	23 863.958
5/2	7/2→5/2	7/2	23 864.138±0.003	23 864.138
5/2	5/2→5/2	5/2	23 864.479±0.003	23 864.478
5/2	5/2→5/2	7/2	23 864.888±0.003	23 864.887
5/2	5/2→5/2	3/2	23 865.015±0.003	23 865.015

^a Constants used in this calculation: $\nu_{5/2 \rightarrow 5/2} = 23 864.232$ Mc, $(eqQ)_{N^{14}} = -3.620 \pm 0.010$ Mc, and $C_N = +2.5 \pm 1.0$ Kc.

for a pure hydrogen $2p$ -orbital, indicating that certainly for hydrogen and probably for other light elements, representing the excited state as a p -electron is questionable.

The experimental data available on the alkali halides is very much less satisfactory indeed than it is for hydrogen. The evidence is entirely from molecular beam experiments, but experiments using two different techniques, *viz.*, electric resonance and magnetic resonance. A salient difference in the two techniques for our purposes is that the electric resonance method selects a state of specific J and v whereas the magnetic resonance method averages properties over a Maxwellian distribution of J and v states. In several instances when the same molecule has been investigated by both techniques the results, specifically for c_i , are at considerable variance.

The full family of alkali fluorides has been investigated by the electric resonance method. The results of these measurements and the derived quantities obtained therefrom may be found in Table II. The electric resonance method does not give the sign of c_i , only its absolute value. Since, however, the measured magnitude of c_i greatly exceeds in each case the c_i which would be produced by the rotating rigid frame, exclusive of valence electrons, and since according to the theory presented in the aforementioned, the rigid frame c_i defines the maximum negative value possible, it must be assumed that the measured coupling constants are all positive, indicating domination of the electronic contribution to the c_i . Upon obtaining

TABLE XI. Comparison of observed spectrum of $\text{Cl}^{35}\text{CN}^{14}$ with theoretical spectrum, showing determination of interaction constants for Cl^{35} .^a

F_i, i	Transition $J=1 \rightarrow 2$ $F_i \rightarrow F_i'$	F_j	Theoretical relative intensity (Σ intensities = 100)	Observed transition frequency	Frequencies (Mc) Observed group frequency ^b $F_i' \rightarrow F_i''$	Theoretical group frequency		
1/2	3/2 \rightarrow 3/2	1/2	0.16	23 862.409 \pm 0.003	23 862.464 \pm 0.004	23 862.461		
1/2	3/2 \rightarrow 3/2	5/2	4.16					
1/2	1/2 \rightarrow 3/2	1/2	1.23					
1/2	3/2 \rightarrow 3/2	3/2	1.23					
1/2	1/2 \rightarrow 3/2	3/2	1.54	23 862.487 \pm 0.003				
5/2	3/2 \rightarrow 5/2	5/2	0.31	23 863.416 \pm 0.002	23 864.232 \pm 0.002	23 864.233		
5/2	7/2 \rightarrow 5/2	5/2	0.32	23 863.724 \pm 0.003				
5/2	3/2 \rightarrow 5/2	3/2	1.68	23 863.959 \pm 0.003				
5/2	7/2 \rightarrow 5/2	7/2	3.68	23 864.138 \pm 0.003				
5/2	5/2 \rightarrow 5/2	5/2	2.35	23 864.479 \pm 0.003				
5/2	5/2 \rightarrow 5/2	7/2	0.32	23 864.888 \pm 0.003				
5/2	5/2 \rightarrow 5/2	3/2	0.31	23 865.015 \pm 0.003				
5/2	3/2 \rightarrow 3/2	1/2	0.17	23 878.795 \pm 0.004			23 879.117 \pm 0.004	23 879.112
5/2	3/2 \rightarrow 3/2	3/2	0.18					
5/2	3/2 \rightarrow 3/2	5/2	0.02	c				
5/2	7/2 \rightarrow 3/2	5/2	0.44	23 878.930 \pm 0.003				
5/2	5/2 \rightarrow 3/2	3/2	0.28	c				
5/2	5/2 \rightarrow 3/2	5/2	0.53					
1/2	3/2 \rightarrow 1/2	3/2	3.08	group unresolved	23 883.270 \pm 0.006	23 833.265		
1/2	3/2 \rightarrow 1/2	1/2	2.46	lower half power point				
				23 883.210 \pm 0.003				
1/2	1/2 \rightarrow 1/2	3/2	2.46	peak				
1/2	1/2 \rightarrow 1/2	1/2	0.31	upper half power point				
				23 883.246 \pm 0.002				
				23 883.294 \pm 0.003				
5/2	7/2 \rightarrow 7/2	7/2	1.09	23 884.197 \pm 0.003	$\nu_{3/2 \ 5/2} = 23 885.055 \pm 0.004$	23 885.058		
3/2	3/2 \rightarrow 5/2	5/2	5.88					
3/2	3/2 \rightarrow 5/2	3/2	1.12	23 884.735 \pm 0.003				
3/2	5/2 \rightarrow 5/2	5/2	1.12	23 884.891 \pm 0.002				
5/2	5/2 \rightarrow 7/2	7/2	12.23	23 885.142 \pm 0.002			$\nu_{5/2 \ 7/2} = 23 885.058 \pm 0.004$	
5/2	7/2 \rightarrow 7/2	9/2	16.70					
5/2	3/2 \rightarrow 7/2	5/2	8.90	23 885.298 \pm 0.002				
3/2	5/2 \rightarrow 5/2	7/2	9.33	23 885.988 \pm 0.002				
3/2	1/2 \rightarrow 5/2	3/2	3.48	23 886.210 \pm 0.002				
5/2	5/2 \rightarrow 7/2	5/2	1.08					
3/2	3/2 \rightarrow 3/2	1/2	0.79	maxima at:	23 899.938 \pm 0.003	23 899.937		
3/2	3/2 \rightarrow 3/2	5/2	0.86	minor				
				23 899.362 \pm 0.003				
3/2	3/2 \rightarrow 3/2	3/2	1.92	major				
3/2	5/2 \rightarrow 3/2	5/2	4.50	23 899.421 \pm 0.003				
3/2	5/2 \rightarrow 3/2	3/2	0.86	23 900.090 \pm 0.002				
3/2	1/2 \rightarrow 3/2	1/2	1.00	23 900.624 \pm 0.002				
3/2	1/2 \rightarrow 3/2	3/2	0.79	23 900.695 \pm 0.002				
3/2	3/2 \rightarrow 1/2	3/2	0.25	23 920.233 \pm 0.003			23 920.742 \pm 0.003	23 920.742
3/2	3/2 \rightarrow 1/2	1/2	0.31					
3/2	5/2 \rightarrow 1/2	3/2	0.84	23 920.912 \pm 0.002				
3/2	1/2 \rightarrow 1/2	3/2	0.02					
3/2	1/2 \rightarrow 1/2	1/2	0.25	23 921.520 \pm 0.004				

^a Constants used in calculating the theoretical spectrum: $\nu_0 = 23 883.275 \pm 0.003$ Mc, $(eQq)_{\text{Cl}^{35}} = -83.285 \pm 0.020$ Mc, $(eQq)_{\text{N}^{14}} = -3.620 \pm 0.010$ Mc, $C_{\text{Cl}} = +3 \pm 1.5$ Kc, and $C_{\text{N}} = +2.5 \pm 1.0$ Kc.

^b By observed group frequency is meant the observed frequency with nitrogen-interaction subtracted out (see text).

^c Not measured.

c_i (electronic) from c_i by subtracting out the readily calculable and usually small c_i (rigid frame), one can calculate $\langle 1/r^3 \rangle_{\text{Av}} \sum_n (L_n)$. This latter quantity is observed to increase monotonically from LiF through CsF, i.e., with molecular size. One would expect $\langle 1/r^3 \rangle_{\text{Av}} \sum_n (L_n)$ to increase roughly as r_e^2 , where r_e is

the equilibrium internuclear distance of the molecule, since $\sum_n (L_n)$ contains in its denominator $E_n - E_0$, the spacing between ground and lowest excited energy levels. On a simple particle-in-a-box model one calculates energy levels spaced as the inverse square of the linear dimensions of the box. Though insufficient points

TABLE XII. Observed spectrum of $\text{Cl}^{35}\text{CN}^{15}$ compared with theoretical spectrum.^{a, b}

Comp. No.	Transition $J=1 \rightarrow 2$	Frequencies (Mc)	
		Observed	Theoretical
1	$F=5/2 \rightarrow 5/2$	$22\,973.205 \pm 0.003$	22 973.208
2	$1/2 \rightarrow 1/2$	$22\,992.235 \pm 0.003$	22 992.235
3	$3/2 \rightarrow 5/2$	$22\,994.038 \pm 0.002$	22 994.038
	$5/2 \rightarrow 7/2$		
4	$3/2 \rightarrow 3/2$	$23\,008.896 \pm 0.003$	23 008.899
5	$3/2 \rightarrow 1/2$	$23\,029.709 \pm 0.003$	23 029.709

^a Interval 2→3, which is the most critical in determining C_{Cl} was measured to be 1.793 ± 0.002 Mc.

^b Constants used in calculating the theoretical spectrum: $v_0 = 22\,992.242 \pm 0.005$ Mc, $(eqQ)_{\text{Cl}^{35}} = -83.280 \pm 0.020$ Mc, and $C_{Cl} = +3.5 \pm 0.6$ Kc.

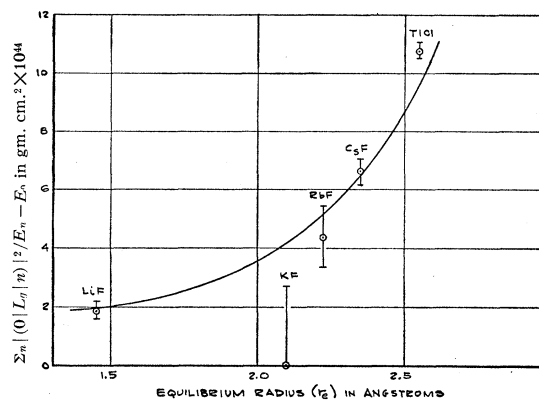
are available to establish any curve unambiguously, the graph in Fig. 1 shows that $\sum_n(L_n)$ does indeed increase at least as fast as r_e^2 for the diatomic halides. In obtaining $\sum_n(L_n)$ approximation (26) was made for $\langle 1/r^3 \rangle_{Av}$.

The zero value for c_i reported for KF need not be considered an important exception in view of the large experimental error involved. Furthermore KCl¹⁷ and KBr¹⁸ have also been investigated by the same technique, and the $\mathbf{I} \cdot \mathbf{J}$ energy reported as too small to be detected. This is not surprising since these molecules have a larger moment of inertia than KF, and since the nuclei Cl and Br both have smaller g_I than does F.

The c_i measured in a number of alkali halides by the magnetic resonance molecular beams method are listed in Table III. In the interests of completeness, all available literature values have been included. Before an interpretation of these values is made, however, some inspection of their probable validity is in order.

The difficulty in obtaining reliable values of c_i from magnetic resonance molecular beams data has several sources.

First, the resonance is observed in molecules having a Maxwellian distribution of excited rotational and

FIG. 1. Plot of $\sum_n [(0|L_n|n)|^2 / (E_n - E_0)] / E_n$ vs r_e for the alkali halides.

vibrational states determined by the source oven temperature. A most probable J of 50 is, for instance, typical. In calculating the theoretical line shape of the resultant absorption, an average of the electric and magnetic interactions over the populated states must be made. This calculation is not simple and does not lead to strictly unambiguous determination of the interaction constants. In particular, when a nucleus has both an electric quadrupole interaction and a magnetic dipole interaction, the latter, being much smaller in $1/\sum$ molecules, will be poorly determined. Of all the atoms involved in Table III, only fluorine has no quadrupole moment and is free from this trouble. Furthermore, the assumption is made in averaging over excited rotational and vibrational states that the interaction constants are not functions of J or v . Fabricand, Carlson, and Lee¹⁹ detect a considerable change of electric quadrupole interaction energy, with v in KBr, and the same variation probably occurs to some extent in all the molecules observed.

Second, the equilibrium interatomic spacing enters

TABLE XIII. Observed spectrum of O^{17}CS compared with theoretical spectrum.

Line No.	Transition $J=1 \rightarrow 2$	Frequencies (Mc)				
		Observed ^a	Theoretical (A)	Δ	Theoretical (B)	Δ
1	$F=3/2 \rightarrow 5/2$	$23\,534.101 \pm 0.014$	23 534.106	-0.005	23 534.102	-0.001
2	$7/2 \rightarrow 7/2$	$23\,534.164 \pm 0.012$	23 534.159	+0.005	23 534.163	+0.001
3	$3/2 \rightarrow 3/2$	$23\,534.308 \pm 0.012$	23 534.295	+0.013	23 534.305	+0.003
4	$7/2 \rightarrow 9/2$	$23\,534.422$	23 534.422	0	23 534.421	+0.001
	$5/2 \rightarrow 7/2$					
5	$3/2 \rightarrow 1/2$	$23\,534.481 \pm 0.014$	23 534.489	-0.008	23 534.493	-0.011
	$5/2 \rightarrow 5/2$					
		Intervals in Kc				
		1→2	2→3	3→4	4→5	
Experimental		63 ± 9	144 ± 6	114 ± 12	59 ± 14	
Theoretical (A)		53	136	127	67	
Theoretical (B)		61	142	116	72	
		Theoretical (A) = constants of reference a: $eqQ = -1.32$ Mc and $C_i = 0$ Kc.				
		Theoretical (B) = constants as follows: $eqQ = 1.38$ Mc and $C_i = 4.0$ Kc.				

^a Geschwind, Gunther-Mohr, and Silvey, Phys. Rev. **85**, 474 (1952).

¹⁸ Lee, Fabricand, Carlson, and Rabi, Phys. Rev. **91**, 1395 (1953).

¹⁹ Fabricand, Carlson, Lee, and Rabi, Phys. Rev. **91**, 1403 (1953).

TABLE XIV. Observed spectrum of CH_3Cl compared with theoretical spectrum.^a

Isotopic species	Transition $J=0 \rightarrow 1$	Frequencies (Mc)	
		Observed	Theoretical
$\text{CH}_3\text{Cl}^{37}$	$F=3/2 \rightarrow 1/2$	26 191.004±0.002	26 191.002
	$3/2 \rightarrow 5/2$	26 179.219±0.002	26 179.220
	$3/2 \rightarrow 3/2$	26 164.490±0.002	26 164.489
$\text{CH}_3\text{Cl}^{35}$	$3/2 \rightarrow 1/2$	26 604.365±0.002	26 604.366
	$3/2 \rightarrow 5/2$	26 589.421±0.002	26 589.420
	$3/2 \rightarrow 3/2$	26 570.734±0.002	26 570.735

^a The following are constants used in calculating the theoretical spectra. For $\text{CH}_3\text{Cl}^{37}$: $\nu_0 = 26\,176.273 \pm 0.002$ Mc, $(eqQ)_{\text{Cl}} = -58.921 \pm 0.006$ Mc, and $C_{\text{Cl}} = +1.2 \pm 1.0$ Kc. For $\text{CH}_3\text{Cl}^{35}$: $\nu_0 = 26\,585.679 \pm 0.008$ Mc, $(eqQ)_{\text{Cl}} = -74.740 \pm 0.006$ Mc, and $C_{\text{Cl}} = +1.4 \pm 1.2$ Kc.

TABLE XV. Observed spectrum of $\text{SiH}_3\text{Cl}^{37}$ compared with theoretical spectrum.^a

Comp. No.	Transition $J=1 \rightarrow 2$	Frequencies (Mc)	
		Observed	Theoretical
1	$F=1/2 \rightarrow 3/2$	26 041.590±0.005	26 041.588
2	$5/2 \rightarrow 5/2$	26 042.257±0.005	26 042.255
3	$1/2 \rightarrow 1/2$	26 049.414±0.010	26 049.414
4	$3/2 \rightarrow 5/2$ $5/2 \rightarrow 7/2$	26 050.091±0.010	26 050.091
		26 055.681±0.007	26 055.682
6	$3/2 \rightarrow 1/2$	26 063.513±0.010	26 063.508

Interval in Mc			
	1→2	2→3	3→4
Experimental	0.667±0.002	13.424±0.004	0.677±0.004
Theoretical	0.667	13.424	0.679

^a Constants used in calculating theoretical spectrum: $\nu_0 = 26\,049.419 \pm 0.010$ Mc, $(eqQ)_{\text{Cl}} = -31.323 \pm 0.010$ Mc, $C_{\text{Cl}} = +2.5 \pm 1.0$ Kc.

explicitly into the calculation of c_i , and the radius is in some cases uncertain by about 10%.

Third, the presence of dimers in the beam might be expected to alter the absorption line.²⁰ Since the magnetic interaction constants are inferred from line shapes, the determination of c_i might therefore be strongly affected by dimerization.

The aforementioned difficulties pertain to all magnetic resonance molecular beam experiments quoted in Table III. In addition, the measurements of a low-frequency transition ($J = \pm \frac{1}{2} \rightarrow J \mp \frac{1}{2}$) reported by Coté and Kusch²¹ suffer from difficulties peculiar to it. A satisfactory quantitative theory of the low-frequency transition cannot be said to exist, and the values of c_i from reference 21 might more properly be considered suggested values rather than measured values. Since these suggested values are in two instances considerably more negative than the negative lower bound set for c_i (total) by c_i (rigid frame), it is not likely that they are correct.

In view of the foregoing set of vitiating factors, it seems unprofitable to attempt a detailed interpretation of the results quoted in Table III. Though some of the determinations are probably valid, sufficient doubt surrounds the c_i values obtained from the magnetic

resonance molecular beams experiments to make detailed analysis of them unprofitable.

There remain four diatomic molecules other than hydrogen and the alkali halides for which c_i has been measured by either electric resonance molecular beam or microwave techniques. One of them, TlCl , is chemically very like an alkali halide. For this molecule c_i has been measured for both nuclei, and $\sum_n (L_n)$ can be calculated from either using the approximation for $\langle 1/r^3 \rangle_{\text{av}}$ discussed earlier in this section. As one sees from Table IV, $\sum_n (L_n)$ as calculated from the Tl interaction is nearly six times as large as that calculated from the Cl interaction. Furthermore $\sum_n (L_n)$ as calculated from the Cl data fits well the variation in $\sum_n (L_n)$ with r_e as calculated from the fluorine interaction in the alkali fluorides and plotted in Fig. 1, whereas $\sum_n (L_n)$ as calculated from the Tl data would be far off scale. The conclusion is that $\langle 1/r^3 \rangle_{\text{av}}$ depends strongly on the chemical environment of the nucleus in question. The approximation (26) is useful for comparing the magnetic interaction of different nuclei in similar chemical circumstances, but may generate discrepancies of as large as a factor of five if used to com-

TABLE XVI. Observed intervals in spectrum of $\text{SiD}_3\text{Cl}^{35}$ compared with theoretical intervals.^a

Interval	Frequency (Mc)	
	Measured	Theoretical
$(1/2 \rightarrow 3/2)$	16.969 ± 0.004	16.969
$(5/2 \rightarrow 5/2)$	0.8472 ± 0.0012	0.8472

^a Constants used in calculating theoretical intervals: $(eqQ)_{\text{Cl}} = 39.595 \pm 0.010$ Mc and $C_{\text{Cl}} = +1.0 \pm 0.7$ Kc.

TABLE XVII. Observed spectrum of $\text{GeH}_3\text{Cl}^{35}$ compared with theoretical spectrum.^a

Transition $J=2 \rightarrow 3$	Frequencies (Mc)	
	Observed	Theoretical
$F=7/2 \rightarrow 7/2$	25 988.908±0.002	25 988.908
$3/2 \rightarrow 5/2$ $1/2 \rightarrow 3/2$	25 997.749±0.002	25 997.749
	26 000.658±0.002	26 000.658
$7/2 \rightarrow 9/2$	26 006.145±0.002	26 006.145

^a Constants used in calculating the theoretical spectrum: $\nu_0 = 26\,000.099 \pm 0.002$ Mc, $(eqQ)_{\text{Cl}} = -47.013 \pm 0.004$ Mc, and $C_{\text{Cl}} = 0.5 \pm 0.7$ Kc.

TABLE XVIII. Comparison of observed spectrum and theoretical spectrum for ClCN^{35} in the excited bending vibration state $\nu_2=1$. All lines listed belong to the lower frequency l -doublet group.^a

Transition $K=1$ $J=1 \rightarrow 2$	Frequencies (Mc)	
	Observed	Theoretical
$F=3/2 \rightarrow 5/2$	23 026.264±0.003	23 026.268
$3/2 \rightarrow 3/2$	23 033.745±0.002	23 033.744
$5/2 \rightarrow 7/2$	23 046.962±0.003	23 046.963
$1/2 \rightarrow 3/2$	23 052.177±0.004	23 052.173
$1/2 \rightarrow 1/2$	23 062.643±0.002	23 062.644

^a Constants used in calculating theoretical spectrum: $\nu_0 = 23\,041.917 \pm 0.003$ Mc, $(eqQ)_{\text{Cl}} = 482 \pm 30$ Kc, $(eqQ)_{\text{C}} = -82.825 \pm 0.015$ Mc, $q_1 = 6.966 \pm 0.004$ Mc, $(C_{zz})_{\text{Cl}} = +3.5 \pm 0.6$ Kc, and $(C_{zz})_{\text{C}} = +8 \pm 5$ Kc.

²⁰ Ochs, Coté, and Kusch, J. Chem. Phys. 21, 459 (1953).

²¹ R. L. Coté and P. Kusch, Phys. Rev. 90, 103 (1953).

pare nuclei in distinctly different chemical situations. In the present instance we have no molecular g -factor from which to calculate $\sum_n (L_n)$ more directly. For the linear polyatomic molecules to which we will proceed very shortly, both c_i and g_J are available in some instances, and more insight into the validity of approximation (26) will be gained.

Both CS and ClF are covalent molecules of similar dimensions. One would expect the $\langle 1/r^3 \rangle_{Av}$ approximation to have about the same validity in each case, and the resultant $\sum_n (L_n)$ to be nearly equal, as is indeed the case. The $\sum_n (L_n)$ for DI is considerably smaller than for the other molecules of Table IV, but even so is surprisingly large. The total molecular electronic wave function closely resembles that of an iodine ion, that is to say, may be represented by spherically symmetric shells about the iodine nucleus. Since the molecular center of mass nearly coincides with the iodine nucleus, the electronic wave function should be little perturbed by molecular rotation. Large electron slippage and small $\sum_n (L_n)$ would be expected to result. Possibly the $\langle 1/r^3 \rangle_{Av}$ approximation is poor for very heavy atoms (*cf.* Tl in TlCl), leading to a spuriously large $\sum_n (L_n)$. It is interesting to note that DBr,²² for which a similarly sized interaction might be expected, has been investigated by virtually identical techniques and no magnetic interaction detected.

Two groups of related linear triatomic molecules have been investigated as can be seen from inspection of Table V. For OCS and OCS_e both c_i and g_J are available; furthermore c_i has been measured at more than one nucleus in the molecules OCS and ClCN. Looking first at the carbonyls one sees that $\sum_n (L_n)$ is larger for the heavier molecules, both as calculated from c_i and from g_J . The oxygen and the sulfur of OCS are in similar chemical situations, so we may use approximation (26) to reduce $\langle 1/r^3 \rangle_{Av} \sum_n (L_n)$ to $\sum_n (L_n)$ for comparison. In this instance we find $\sum_n (L_n)$ as derived from the two interactions nearly the same, in fact equal within the fairly large experimental error. Moreover the values of $\sum_n (L_n)$ calculated from the two c_i agree well with the values calculated from g_J , indicating that here the approximation to $\langle 1/r^3 \rangle_{Av}$ has considerable validity. Again for OCS there is reasonably good agreement between $\sum_n (L_n)$ as calculated from g_J and as calculated from c_i using approximation (26).

We find in the data on the various isotopic forms of HCN and ClCN continued manifestation of the trends which we have seen to characterize the interaction. Nitrogen occupies a similar chemical position in HCN and ClCN and $\sum_n (L_n)$ calculated from its magnetic interaction nearly doubles in going from the light to the heavy molecule; chlorine and nitrogen occupy chemically different sites, and $\sum_n (L_n)$ calculated from the two c_i of the same molecule using approximation (26) differ by a factor of over two.

A linear polyatomic molecule in a bending vibrational mode may be treated to a good approximation as a very prolate slightly asymmetric top. As such it is capable of acquiring rotational angular momentum parallel to the symmetry axis, and the nuclear magnetic moments will couple to this angular momentum. The theoretical expression for the interaction energy for a nucleus on the axis of a symmetric top molecule is the sum of expressions (12) and (17) of the theory section, and may be written

$$W = \left[C_{xx} + (C_{zz} - C_{xx}) \frac{K^2}{J(J+1)} \right] \mathbf{I} \cdot \mathbf{J}, \quad (27)$$

where

$$C_{xx} = \frac{\mu_0 N g_I}{A_x} \left[4\mu_0 B \langle 1/r^3 \rangle_{Av} \sum_n \frac{|(0|L_x|n)|^2}{E_n - E_0} - \sum_i \frac{q_i' (r_{ij})^2 - (r_{ij})_x^2}{c (r_{ij})^3} \right] \quad (28)$$

and

$$C_{zz} = \frac{\mu_0 N g_I}{A_z} \left[4\mu_0 B \langle 1/r^3 \rangle_{Av} \sum_n \frac{|(0|L_z|n)|^2}{E_n - E_0} - \sum_i \frac{q_i' (r_{ij})^2 - (r_{ij})_z^2}{c (r_{ij})^3} \right]. \quad (29)$$

If A_z is small, as is the case for the bent linear molecule, one might expect a large c_{zz} . Actually the measured c_{zz} for ClCN in the bending vibrational mode proved to be quite small, leading to a very small value of $\sum_n |(0|L_z|n)|^2 / E_n - E_0$. The inference is that the amplitude of bending is so small that the nuclear frame acquires angular momentum about the z -axis without very much affecting the electronic wave functions.

Ammonia, on the other hand, offers an instance where A_x and A_z are nearly equal. We are fortunate in this case in having good experimental data both on the magnetic interaction and on the molecular g -factor. The agreement in $\sum_n (L_n)$ as calculated from the two sources is good. Furthermore $\sum_n |(0|L_z|n)|^2 / E_n - E_0$ is predicted to be slightly larger than $\sum_n |(0|L_x|n)|^2 / E_n - E_0$ by both sources, and the magnitudes in each instance are in reasonably good agreement, indicating that here again the approximation to $\langle 1/r^3 \rangle$ is justified and more than just a proportionality factor. The coupling constants of the off-axial protons have also been measured,⁸ and as pointed out previously at least one component of the magnetic field at their site is dominated by the nuclear frame rather than the electrons. However, both since the interpretation of the off-axial interaction is complicated and since the constants are not very precisely known, no analysis of them further than the comments already made in the hydrogen section will be attempted. Ammonia also affords a case where the functional form of the magnetic interaction

²² W. Gordy and C. A. Burrus, Phys. Rev. **93**, 419 (1954).

has been tested over a range of values of J and K from 1 to 6. Good agreement with expression (27) was obtained.

An intermediate type of symmetric top molecule, one with A_z considerably smaller than A_x but not as much smaller as is the case for a bent linear molecule, is provided by methyl chloride, chloro-silane, or chloro-germane. Unfortunately only c_{xx} has been determined for these molecules, and the experimental error, especially for chloro-germane is relatively large. It can be seen, however, that the approximate magnitude of $\sum_n (L_n)$ is the same as it has been for other molecules of similar dimension, and that the progression toward larger $\sum_n (L_n)$ with increasing molecular size also appears to occur.

SUMMARY AND CONCLUSIONS

A number of conclusions can be drawn from the foregoing experimental evidence.

1. The theory of magnetic interactions in $^1\Sigma$ molecules, as summarized in the theory section of this paper, is consonant with all existing experimental evidence on magnetic coupling constants except that obtained from measurement of line shapes in magnetic resonance molecular beam experiments. However, there appears to be convincing evidence that the values of c_i so far obtained from these line shapes are unreliable. Eliminating the suspect data and introducing additional data obtained specifically for the purposes of this paper allows a considerable degree of order to be recognized in magnetic interactions of the type discussed.

2. For all nuclei in $^1\Sigma$ molecules except hydrogen the contribution of the valence electrons to the magnetic field at any given nucleus exceeds considerably that due to the rotating rigid frame composed of the nuclei plus firmly bound closed-shell electrons. This result is undoubtedly a consequence of the fact that the valence electrons may penetrate near to the nucleus in question and thus produce a large effective $\langle 1/r^3 \rangle_{Av}$.

3. The magnetic interaction constants of a molecule can be approximately predicted if the molecular parameters $\sum_n |(0|L_g|n)|^2/E_n - E_0$ and $\langle 1/r^3 \rangle_{Av}$ for the valence electrons are known. Also, $\sum_n |(0|L_g|n)|/E_n - E_0$ can be calculated from the molecular g -factor if known, or can be estimated in many cases by interpolation or extrapolation from the data on known similar molecules when g_J is not available. For a given series of structurally similar molecules, this quantity increases with molecular size. An approximation to $\langle 1/r^3 \rangle_{Av}$ has been presented and discussed. The available evidence indicates that for medium weight atoms, $6 < Z < 30$, the approximation will not be in error by more than a factor of two for any chemical environment. A more

detailed application of the theory than has been presented, or a more thorough understanding of the approximations allowable in applying it, must await the arrival of a considerable quantity of more precise experimental data on this type of interaction.

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APPENDIX

The microwave spectra presented in this appendix (Tables XIV–XVIII) were all measured or remeasured in order to determine the nuclear magnetic interaction with the fields due to molecular rotation. All measurements except those on ClF were performed on a high-resolution, bridge-type, K -band spectrometer. The energy expression from which the theoretical spectrum was calculated for molecules containing only one nucleus possessing an electric quadrupole moment was^{23,24}

$$W = B(J)(J+1) + (eqQ) \left\{ \frac{3K^2}{J(J+1)} - 1 \right\} \\ \times \left[\frac{\frac{3}{4}C(C+1) - I(I+1)J(J+1)}{2(2J+3)(2J-1)I(2I-1)} \right] + W(\text{mag}),$$

where

$$C = F(F+1) - I(I+1) - J(J+1) \\ F = J+I, \quad J+I-1 \dots |J-I|.$$

Here (eqQ) is the electric quadrupole coupling as defined by Townes and Bardeen,²⁵ and $W(\text{mag})$ is the expression for the magnetic energy appropriate to the molecular type under consideration obtained from the theory section of this paper. For $\text{Cl}^{35}\text{CN}^{14}$, in which two nuclei have electric quadrupole moments, the theory of Townes and Bardeen²⁵ derived for this case was used. The relatively complex nature of the theory prevents its being presented here, and the reader is referred for such information to the article cited.

²³ H. B. G. Casimir, *On the Interaction between Atomic Nuclei and Electrons* (DeErven F. Bohn, Haarlem, 1936).

²⁴ J. H. Van Vleck, *Phys. Rev.* **71**, 468 (1947).

²⁵ C. H. Townes and J. Bardeen, *Phys. Rev.* **73**, 97 (1948).