

Magnetic Interactions in Molecules and an Analysis of Molecular Electronic Charge Distribution from Magnetic Parameters

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I. Introduction

In this paper we present a unified treatment of the important magnetic interactions in a molecule which has zero electronic spin and orbital angular momentum in the ground electronic state. We concentrate on a description of the magnetic interactions which are normally measured by microwave resonance techniques.

The necessary theory for a proper interpretation of the molecular Zeeman effect in diamagnetic molecules is developed in sections II to IV. This theory involves first a description of rotationally induced magnetic moments which arise from a coupling of the electronic and rotational motions. This analysis describes the molecular g -value tensor, \mathbf{g} . We also describe the magnetic field induced magnetic susceptibility tensor, χ , and we show the connection between the \mathbf{g} and χ tensors. The diagonal elements in the \mathbf{g} and χ tensors can also be combined with the moment of inertia tensor \mathbf{I} to give the molecular quadrupole moments in the principal inertial axis system. The molecular structure can be combined with the above information to yield the electric dipole moment (and sign), the diagonal elements in the paramagnetic susceptibility tensor, and the anisotropies in the second moments of the electronic charge distribution. Adding the bulk magnetic susceptibility to the above numbers yields the diagonal elements in the total and the diamagnetic susceptibility tensor elements.

In section V we describe in detail the measurement of the magnetic parameters described in section IV by the rotational molecular Zeeman effect. Data are given for a number of molecules in order to illustrate the methods, pitfalls, and accuracy of the results.

In section VI we describe the magnetic interactions which give rise to nuclear magnetic shielding, σ , and the nuclear spin-rotation interaction, \mathbf{M} . Nuclear magnetic shielding arises from an external magnetic field-molecule perturbation similar to the interaction leading to the field-induced moment and magnetic susceptibility. The spin-rotation interaction arises from a rotational-induced field at the nucleus in a way similar to the rotational-induced magnetic moment. The parallels between the \mathbf{g} and χ tensors with molecular center of mass (CM) origins and the σ and \mathbf{M} tensors with nuclear origins are very strong. For instance, the diagonal elements in the spin-rotation interaction tensor, \mathbf{M} , can be used to calculate the diagonal elements in the paramagnetic shielding tensor which is analogous to the relation between the molecular g values and the paramagnetic susceptibility. If the total nuclear shielding is known through magnetic resonance measurements, the spin-rotation interaction constants can be used to extract the diagonal elements in the diamagnetic shielding tensor. We then describe the rotational molecular Zeeman effect in the presence of strong nuclear-rotational coupling, and we demonstrate that the molecular Zeeman effect can be used to measure the magnetic shielding anisotropy.

The last section (VIII) in this paper describes a semiempirical atom dipole model which allows a reliable prediction of molecular electric dipole and quadrupole moments, diamagnetic susceptibilities, and diamagnetic nuclear shieldings. We also use the localized model to demonstrate the validity of Pascal's localized atom or bond values for magnetic susceptibilities which are transferrable from molecule to molecule. Finally we develop a set of localized bond and atom values for the individual diagonal elements in the molecular magnetic susceptibility tensor. Several tables of numbers comparing the above calculated and experimental values along with a variety of examples are given.

II. Intramolecular Electronic-Rotational Interactions

We will limit the discussion in this paper to molecules which have zero electronic spin and orbital angular momentum in the ground electronic state. This limitation is not severe as a great majority of molecules satisfy this criterion. We also ignore the effects of molecular vibrations.

Intramolecular electronic-rotational interactions arise from a breakdown in the separability of electronic and rotational coordinates. Consider a system of point electronic and nucle-

ar masses which compose a molecule. The velocity of the k th particle is given by

$$\mathbf{v}_k^0 = \dot{\mathbf{R}} + (\boldsymbol{\omega} \times \mathbf{r}_k) + \mathbf{v}_k \quad (1)$$

The super 0 represents the origin of the coordinate system which is fixed in the x , y , and z laboratory frame. \mathbf{R} is the vector from the arbitrary origin to the center of mass (CM) of the system of particles and $\dot{\mathbf{R}}$ is the velocity vector of the CM. $\boldsymbol{\omega}$ is the angular frequency of the coordinate system attached to the molecule with respect to the laboratory. \mathbf{r}_k is the vector from the center of mass to the k th particle, and \mathbf{v}_k is the velocity vector of the k th particle (from the CM) in the rotating coordinate system. The kinetic energy of the system of particles with mass m_k is

$$T = \frac{1}{2} \sum_k m_k \mathbf{v}_k^0 \cdot \mathbf{v}_k^0 \quad (2)$$

where the sum over k is over all electrons and nuclei. Substituting eq 1 into this equation gives

$$T = \frac{1}{2} \sum_k m_k (\dot{\mathbf{R}} + \boldsymbol{\omega} \times \mathbf{r}_k + \mathbf{v}_k) \cdot (\dot{\mathbf{R}} + \boldsymbol{\omega} \times \mathbf{r}_k + \mathbf{v}_k) = \frac{\dot{\mathbf{R}}^2}{2} \sum_k m_k + \frac{1}{2} \sum_k m_k (\boldsymbol{\omega} \times \mathbf{r}_k) \cdot (\boldsymbol{\omega} \times \mathbf{r}_k) + \frac{1}{2} \sum_k m_k v_k^2 + \dot{\mathbf{R}} \cdot \left(\sum_k m_k (\boldsymbol{\omega} \times \mathbf{r}_k) \right) + \dot{\mathbf{R}} \cdot \left(\sum_k m_k \mathbf{v}_k \right) + \sum_k m_k (\boldsymbol{\omega} \times \mathbf{r}_k) \cdot \mathbf{v}_k \quad (3)$$

Remembering that $\sum_k m_k = W$, which is the total molecular mass, and rearranging this equation gives

$$T = \frac{W}{2} \dot{\mathbf{R}}^2 + \frac{1}{2} \sum_k m_k (\boldsymbol{\omega} \times \mathbf{r}_k) \cdot (\boldsymbol{\omega} \times \mathbf{r}_k) + \frac{1}{2} \sum_k m_k v_k^2 + \dot{\mathbf{R}} \cdot \boldsymbol{\omega} \times \left(\sum_k m_k \mathbf{r}_k \right) + \dot{\mathbf{R}} \cdot \left(\sum_k m_k \mathbf{v}_k \right) + \boldsymbol{\omega} \cdot \left(\sum_k m_k \mathbf{r}_k \times \mathbf{v}_k \right) \quad (4)$$

We now note that in the rotating coordinate system the coordinates of the center of mass remain constant for all internal motions of the molecule. That is

$$\sum_k m_k \mathbf{r}_k = 0 \quad (5)$$

which also implies that

$$\sum_k m_k \mathbf{v}_k = 0 \quad (6)$$

Substituting eq 5 and 6 into eq 4 gives

$$T = \frac{W}{2} \dot{\mathbf{R}}^2 + \frac{1}{2} \sum_k m_k (\boldsymbol{\omega} \times \mathbf{r}_k) \cdot (\boldsymbol{\omega} \times \mathbf{r}_k) + \frac{1}{2} \sum_k m_k v_k^2 + \boldsymbol{\omega} \cdot \left(\sum_k m_k \mathbf{r}_k \times \mathbf{v}_k \right) \quad (7)$$

The first term in this equation is the pure translational term which will not enter the rotational electronic interaction; we drop this term. Dropping $(W/2)\dot{\mathbf{R}}^2$ and expanding the remaining sums over the nuclei, α , and electrons, i , gives¹

$$T = \frac{1}{2} \sum_{\alpha} M_{\alpha} (\boldsymbol{\omega} \times \mathbf{r}_{\alpha}) \cdot (\boldsymbol{\omega} \times \mathbf{r}_{\alpha}) + \frac{m}{2} \sum_i (\boldsymbol{\omega} \times \mathbf{r}_i) \cdot (\boldsymbol{\omega} \times \mathbf{r}_i) + \frac{1}{2} \sum_{\alpha} M_{\alpha} v_{\alpha}^2 + \frac{m}{2} \sum_i v_i^2 + \boldsymbol{\omega} \cdot \sum_{\alpha} M_{\alpha} \mathbf{r}_{\alpha} \times \mathbf{v}_{\alpha} + \boldsymbol{\omega} \cdot m \sum_i \mathbf{r}_i \times \mathbf{v}_i \quad (8)$$

m is the electron mass and M_{α} is the mass of the α th nucleus. We expand the first and second terms in this equation by standard techniques. The nuclear term gives

$$\frac{1}{2} \sum_{\alpha} M_{\alpha} (\boldsymbol{\omega} \times \mathbf{r}_{\alpha}) \cdot (\boldsymbol{\omega} \times \mathbf{r}_{\alpha}) = \frac{1}{2} \boldsymbol{\omega} \cdot \left\{ \sum_{\alpha} M_{\alpha} [(\mathbf{r}_{\alpha}^2 \mathbf{1} - \mathbf{r}_{\alpha} \mathbf{r}_{\alpha})] \right\} \cdot \boldsymbol{\omega} = \frac{1}{2} \boldsymbol{\omega} \cdot \mathbf{I}_n \cdot \boldsymbol{\omega} \quad (9)$$

The electronic term gives

$$\frac{1}{2} m \sum_i (\boldsymbol{\omega} \times \mathbf{r}_i) \cdot (\boldsymbol{\omega} \times \mathbf{r}_i) = \frac{1}{2} \boldsymbol{\omega} \cdot [m \sum_i \mathbf{r}_i^2 \mathbf{1} - \mathbf{r}_i \mathbf{r}_i] \cdot \boldsymbol{\omega} = \frac{1}{2} \boldsymbol{\omega} \cdot \mathbf{I}_e \cdot \boldsymbol{\omega} \quad (10)$$

\mathbf{I}_n is the nuclear moment of inertia from the nuclear center of mass (CM) with the sum in brackets above being over all nuclear mass points. \mathbf{I}_e is the corresponding moment for the electrons from the electronic center of mass. We assume here and in the following work that the nuclear CM is coincident with the electronic CM and also the molecular CM. The effects of making this approximation are of negligible importance.² We now drop the other terms involving only nuclear coordinates in eq 8. These interesting terms lead to the vibrational motion as well as the vibration-rotation interactions ($\boldsymbol{\omega} \cdot \sum_{\alpha} M_{\alpha} \mathbf{r}_{\alpha} \times \mathbf{v}_{\alpha}$) which we will not consider at this time. The terms which remain and depend only on the electronic and rotational motion are

$$T = \frac{1}{2} \boldsymbol{\omega} \cdot \mathbf{I}_n \cdot \boldsymbol{\omega} + \frac{m}{2} \sum_i \mathbf{v}_i \cdot \mathbf{v}_i + \frac{1}{2} \boldsymbol{\omega} \cdot \mathbf{I}_e \cdot \boldsymbol{\omega} + \boldsymbol{\omega} \cdot \sum_i m \mathbf{r}_i \times \mathbf{v}_i \quad (11)$$

The total angular momentum, \mathbf{J} , is obtained by Lagrangian mechanics by the first derivative of the kinetic energy (potential energy is zero) with respect to the angular velocity.¹

$$\mathbf{J} = \frac{\partial T}{\partial \boldsymbol{\omega}} = \boldsymbol{\omega} \cdot \mathbf{I}_n + m \sum_i \mathbf{r}_i \times \mathbf{v}_i + \boldsymbol{\omega} \cdot \mathbf{I}_e \quad (12)$$

The linear momentum of the i th electron, \mathbf{p}_i , is also obtained from eq 11 by the first derivative of T with respect to the velocity (remember that $\boldsymbol{\omega} \cdot \mathbf{r}_i \times \mathbf{v}_i = \mathbf{v}_i \cdot \boldsymbol{\omega} \times \mathbf{r}_i$).

$$\mathbf{p}_i = \frac{\partial T}{\partial \mathbf{v}_i} = m \mathbf{v}_i + m \boldsymbol{\omega} \times \mathbf{r}_i \quad (13)$$

We can now rewrite eq 11 for the kinetic energy to give

$$T = \frac{1}{2} \boldsymbol{\omega} \cdot \mathbf{J} + \frac{1}{2} \sum_i \mathbf{p}_i \cdot \mathbf{v}_i \quad (14)$$

where \mathbf{J} is given in eq 12 and \mathbf{p}_i is given in eq 13. We now use $m \mathbf{v}_i$ from eq 13

$$m \mathbf{v}_i = \mathbf{p}_i - m \boldsymbol{\omega} \times \mathbf{r}_i \quad (15)$$

in eq 14 to give

$$\begin{aligned} T &= \frac{1}{2} \boldsymbol{\omega} \cdot \mathbf{J} + \frac{1}{2m} \sum_i p_i^2 - \frac{1}{2} \sum_i \mathbf{p}_i \cdot \boldsymbol{\omega} \times \mathbf{r}_i \\ &= \frac{1}{2} \boldsymbol{\omega} \cdot \mathbf{J} - \frac{1}{2} \boldsymbol{\omega} \cdot \sum_i \mathbf{r}_i \times \mathbf{p}_i + \frac{1}{2m} \sum_i p_i^2 \\ &= \frac{1}{2} \boldsymbol{\omega} \cdot \mathbf{J} - \frac{1}{2} \boldsymbol{\omega} \cdot \mathbf{L} + \frac{1}{2m} \sum_i p_i^2 \\ &= \frac{1}{2} \boldsymbol{\omega} \cdot (\mathbf{J} - \mathbf{L}) + \frac{1}{2m} \sum_i p_i^2 \end{aligned} \quad (16)$$

We have also defined

$$\sum_i \mathbf{r}_i \times \mathbf{p}_i = \mathbf{L} \quad (17)$$

as the intrinsic electronic angular momentum or the electronic angular momentum in the rotating frame. The last term in eq 16, $(1/2m)\sum_i p_i^2$, is included in the electronic Hamiltonian to determine the ground-state electronic wave functions for the nonrotating molecule. These zero-order electronic states are discussed later in eq 37.

We now compare eq 11 and 16. Substituting eq 13 into eq 16 and comparing this result with eq 11 show that

$$\boldsymbol{\omega} \cdot (\mathbf{J} - \mathbf{L}) = \boldsymbol{\omega} \cdot \mathbf{I}_n \cdot \boldsymbol{\omega} \quad (18)$$

Evidently $(\mathbf{J} - \mathbf{L})$ can be expressed as

$$(\mathbf{J} - \mathbf{L}) = \mathbf{I}_n \cdot \boldsymbol{\omega} \quad (19)$$

\mathbf{I}_n is the moment of inertia for the point mass nuclei. In the principal inertial (nuclei only) axis system, \mathbf{I}_n is diagonal and we can write

$$\begin{aligned} (\mathbf{J} - \mathbf{L})_x &= (I_n)_{xx} \omega_x \\ (\mathbf{J} - \mathbf{L})_y &= (I_n)_{yy} \omega_y \\ (\mathbf{J} - \mathbf{L})_z &= (I_n)_{zz} \omega_z \end{aligned} \quad (20)$$

If we consider only the principal inertial axis system, \mathbf{I}_n is diagonal and we can define the inverse principal inertial tensor

$$\mathbf{I}_n^{-1} = \begin{bmatrix} 1 & 0 & 0 \\ (I_n)_{xx} & & \\ 0 & 1 & 0 \\ (I_n)_{yy} & & \\ 0 & 0 & 1 \\ (I_n)_{zz} & & \end{bmatrix} \quad (21)$$

where we require

$$\mathbf{I}_n^{-1} \cdot \mathbf{I}_n = \mathbf{I}_n \cdot \mathbf{I}_n^{-1} = \mathbf{1} \quad (22)$$

and we can rewrite eq 19 to give

$$\boldsymbol{\omega} = (\mathbf{J} - \mathbf{L}) \cdot \mathbf{I}_n^{-1} = \mathbf{I}_n^{-1} \cdot (\mathbf{J} - \mathbf{L}) \quad (23)$$

Substituting this result into eq 16, dropping the $(1/2m)\sum_i p_i^2$ term, and expanding gives

$$\begin{aligned} T &= \frac{1}{2}(\mathbf{J} - \mathbf{L}) \cdot \mathbf{I}_n^{-1} \cdot (\mathbf{J} - \mathbf{L}) = \frac{1}{2}\mathbf{J} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{J} - \mathbf{J} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{L} + \\ &\frac{1}{2}\mathbf{L} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{L} = \frac{1}{2} \sum_g \frac{J_g^2}{(I_n)_{gg}} - \sum_g \frac{J_g L_g}{(I_n)_{gg}} + \frac{1}{2} \sum_g \frac{L_g^2}{(I_n)_{gg}} \end{aligned} \quad (24)$$

The sums over g are over the three principal inertial axes. The first term leads to the rotational state eigenvalues for the square of the total angular momentum. The second term is the rotational-electronic coupling term which contributes to the rotational magnetic moment and the spin-rotation interaction. The last and smallest term depends only on the electronic angular momentum.

III. Magnetic Field Dependent Electronic Interactions and the Total Hamiltonian

Now we examine the nature of the magnetic field interactions on a distribution of electrons and nonvibrating nuclei. We start with a discussion of the electrons.

The corrections to the electronic kinetic energy in the presence of an external magnetic field are derived by starting with the Lorentz force for a charged particle in a field or alternately by defining the correct Lagrangian function and using standard classical equations of motion to give the Hamiltonian function as shown, for instance, by Slater.³ The resultant *electronic* kinetic energy in the presence of the magnetic field is given by

$$T_e = \frac{1}{2m} \sum_i (\mathbf{p}_i + \frac{e}{c} \mathbf{A})^2 \quad (25)$$

\mathbf{p}_i is the linear momentum of the i th electron and \mathbf{A} is the vector potential giving rise to the magnetic field. Expanding the square gives (remember that $\mathbf{p} = -\hbar \nabla$ is an operator and $\nabla \cdot \mathbf{A} = \mathbf{A} \cdot \nabla$)

$$T_e = \sum_i \frac{p_i^2}{2m} + \frac{e}{mc} \sum_i \mathbf{A} \cdot \mathbf{p}_i + \frac{e^2}{2mc^2} A^2 \quad (26)$$

where we have used the negative charge for the electrons in both eq 25 and 26. \mathbf{A} is the vector potential giving rise to the magnetic field, \mathbf{H} .

$$\mathbf{H} = \nabla \times \mathbf{A} \quad (27)$$

In the case of a planar magnetic field along the z axis, H_z , the field is given in terms of \mathbf{A} by

$$\begin{aligned} \mathbf{H} &= \nabla \times \mathbf{A} \\ H_z &= \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} \\ H_y = 0 &= \frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x} \\ H_x = 0 &= \frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z} \end{aligned} \quad (28)$$

Thus, in order to satisfy eq 28 for a magnetic field along the z axis we must require

$$\begin{aligned} A_x &= -\frac{1}{2}yH_z \\ A_y &= \frac{1}{2}xH_z \\ A_x &= 0 \\ \mathbf{A} &= -\frac{1}{2}\mathbf{r} \times \mathbf{H} \end{aligned} \quad (29)$$

Expanding the $\mathbf{A} \cdot \mathbf{p}_i$ dot product in eq 26 and substituting eq 29 for A_x , A_y , and A_z in both the $\mathbf{A} \cdot \mathbf{p}_i$ and A^2 terms gives

$$T_e = \sum_i \frac{p_i^2}{2m} + \frac{eH_z}{2mc} \sum_i (x_i p_{yi} - y_i p_{xi}) + \frac{e^2 H^2}{8mc^2} \sum_i (x_i^2 + y_i^2) \quad (30)$$

Remembering that $xp_y - yp_x = L_z$, the angular momentum (see eq 17), we can rewrite eq 30 more generally as

$$T_e = \sum_i \frac{p_i^2}{2m} + \frac{e}{2mc} \mathbf{H} \cdot \mathbf{L} + \frac{e^2}{8mc^2} \mathbf{H} \cdot \sum_i (r_i^2 \mathbf{1} - r_i r_i) \cdot \mathbf{H} \quad (31)$$

As mentioned previously, the $p_i/2m$ term enters the zero-order solution of the electronic Schrödinger equation for a nonrotating molecule in the absence of a magnetic field.

We now add the terms corresponding to the nuclear contributions to T_e in eq 25 which include the rotational magnetic moment interacting with the external magnetic field and the nuclear contribution to the magnetic susceptibility. We write these terms for a nonvibrating molecule where all the velocity components are due to angular motion, $\mathbf{v}_\alpha = \boldsymbol{\omega} \times \mathbf{r}_\alpha$, by using methods developed above for the electrons. The new terms include

$$\begin{aligned} \mathcal{H} &= -\left(\frac{e}{2c} \sum_\alpha Z_\alpha \mathbf{r}_\alpha \times \boldsymbol{\omega} \times \mathbf{r}_\alpha\right) \cdot \mathbf{H} + \\ &\frac{e^2}{8c^2} \mathbf{H} \cdot \sum_\alpha \frac{Z_\alpha}{M_\alpha} (r_\alpha^2 \mathbf{1} - r_\alpha r_\alpha) \cdot \mathbf{H} \end{aligned} \quad (32)$$

where the sum over α is over all nuclei and \mathbf{r}_α is from the molecular center of mass. Expanding the first term in eq 32 gives

$$\begin{aligned} \mathcal{H} &= -\mathbf{H} \cdot \left\{ \frac{e}{2c} \sum_\alpha Z_\alpha (r_\alpha^2 \mathbf{1} - r_\alpha r_\alpha) \right\} \cdot \boldsymbol{\omega} + \\ &\frac{e^2}{8c^2} \mathbf{H} \cdot \sum_\alpha \frac{Z_\alpha^2}{M_\alpha} (r_\alpha^2 \mathbf{1} - r_\alpha r_\alpha) \cdot \mathbf{H} \end{aligned} \quad (33)$$

Substituting eq 23 gives an expression in \mathbf{J} and \mathbf{L} .

$$\mathcal{H} = -\mathbf{H} \cdot \left\{ \frac{e}{2c} \sum_{\alpha} Z_{\alpha} (r_{\alpha}^2 \mathbf{1} - r_{\alpha} r_{\alpha}) \right\} \mathbf{I}_n^{-1} \cdot (\mathbf{J} - \mathbf{L}) + \frac{e^2}{8c^2} \mathbf{H} \cdot \sum_{\alpha} \frac{Z_{\alpha}^2}{M_{\alpha}} (r_{\alpha}^2 \mathbf{1} - r_{\alpha} r_{\alpha}) \cdot \mathbf{H} \quad (34)$$

We will now combine the results in eq 34, 31, and 24 to give the complete Hamiltonian. Dropping the $p^2/2m$ term in eq 31 and adding the remaining terms to eq 24 along with the result in eq 34 give the Hamiltonian which describes the rotational motion of the molecule in the presence of rotational-electronic and magnetic field-electronic interactions.

$$\mathcal{H}' = \frac{1}{2} \mathbf{J} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{J} - \mathbf{J} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{L} + \frac{1}{2} \mathbf{L} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{L} + \frac{e}{2mc} \mathbf{H} \cdot \mathbf{L} + \frac{e^2}{8m^2 c^2} \mathbf{H} \cdot \sum_i (r_i^2 \mathbf{1} - r_i r_i) \cdot \mathbf{H} - \mathbf{H} \cdot \left\{ \frac{e}{2c} \sum_{\alpha} Z_{\alpha} (r_{\alpha}^2 \mathbf{1} - r_{\alpha} r_{\alpha}) \right\} \cdot \mathbf{I}_n^{-1} \cdot (\mathbf{J} - \mathbf{L}) + \frac{e^2}{8c^2} \mathbf{H} \cdot \sum_{\alpha} \frac{Z_{\alpha}^2}{M_{\alpha}} (r_{\alpha}^2 \mathbf{1} - r_{\alpha} r_{\alpha}) \cdot \mathbf{H} \quad (35)$$

We now rearrange eq 35 in a form more convenient for calculating the energy by perturbation theory.

$$\mathcal{H}' = \frac{1}{2} \mathbf{J} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{J} - \mathbf{L} \cdot \boldsymbol{\omega}' + \frac{1}{2} \mathbf{L} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{L} + \frac{e^2}{8c^2 m} \mathbf{H} \cdot \left[\sum_i (r_i^2 \mathbf{1} - r_i r_i) + m \sum_{\alpha} \frac{Z_{\alpha}^2}{M_{\alpha}} (r_{\alpha}^2 \mathbf{1} - r_{\alpha} r_{\alpha}) \right] \cdot \mathbf{H} - \frac{e}{2c} \sum_{\alpha} Z_{\alpha} \mathbf{H} \cdot (r_{\alpha}^2 \mathbf{1} - r_{\alpha} r_{\alpha}) \cdot \mathbf{I}_n^{-1} \cdot \mathbf{J}$$

$$\boldsymbol{\omega}' = \mathbf{I}_n^{-1} \cdot \mathbf{J} - \frac{e}{2mc} \mathbf{H} - \frac{e}{2c} \mathbf{I}_n^{-1} \cdot \sum_{\alpha} Z_{\alpha} (r_{\alpha}^2 \mathbf{1} - r_{\alpha} r_{\alpha}) \cdot \mathbf{H} \quad (36)$$

The $(e/2mc)\mathbf{H}$ contribution to $\boldsymbol{\omega}'$ is the well-known Larmour frequency.

IV. Electronic Average, Molecular g Values, and Magnetic Susceptibilities

We now examine the contributions to the energy arising from the Hamiltonian in eq 36. First we average over the electronic states and then we average over the rotational states.

The zero-order solution for the electronic Schrödinger equation in the absence of \mathcal{H}' in eq 36 yields a basis set of electronic states given by

$$\psi^0, \psi^1, \psi^2, \dots, \psi^k \quad (37)$$

where ψ^0 is the ground electronic state, and ψ^k are all the excited electronic states. We are assuming that the ground electronic state, ψ^0 , does not possess any electronic angular momentum. However, the excited states, ψ^k , may possess electronic angular momentum.

We now use standard perturbation theory to obtain the effect of the Hamiltonian in eq 36 on the zero-order electronic and rotational states. First we correct for the electronic effects by using eq 37 as the zero-order electronic wave functions. According to perturbation theory the corrections are easily obtained.

First order

$$E^{(1)} = \frac{1}{2} \mathbf{J} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{J} + \frac{1}{2} \mathbf{H} \cdot \left[\langle 0 | \frac{e^2}{4c^2 M} \sum_i (r_i^2 \mathbf{1} - r_i r_i) | 0 \rangle + \frac{e^2}{4c^2} \sum_{\alpha} \frac{Z_{\alpha}^2}{M_{\alpha}} (r_{\alpha}^2 \mathbf{1} - r_{\alpha} r_{\alpha}) \right] \cdot \mathbf{H} - \mathbf{H} \cdot \left[\frac{e}{2c} \sum_{\alpha} Z_{\alpha} (r_{\alpha}^2 \mathbf{1} - r_{\alpha} r_{\alpha}) \cdot \mathbf{I}_n^{-1} \cdot \mathbf{J} \right] + \frac{1}{2} \sum_{m>0} \langle 0 | \mathbf{L} | m \rangle \cdot \mathbf{I}_n^{-1} \cdot \langle m | \mathbf{L} | 0 \rangle \quad (38)$$

The last term in this expression does not depend on the rota-

tional state and cannot be measured by rotational spectroscopy. Thus, we will drop this term. The remaining terms in eq 38 all yield first-order rotational state dependence.

Second order

$$E^{(2)} = \sum_{k>0} \frac{\langle 0 | \mathbf{L} \cdot \boldsymbol{\omega}' | k \rangle \langle k | \mathbf{L} \cdot \boldsymbol{\omega}' | 0 \rangle}{E_0 - E_k} = \mathbf{J} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{A} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{J} + \frac{1}{2} \mathbf{H} \cdot \left\{ \frac{e^2}{2m^2 c^2} \mathbf{A} \right\} \cdot \mathbf{H} + \frac{e^2}{4c^2} \mathbf{H} \cdot \mathbf{I}_n^{-1} \cdot \sum_{\alpha} Z_{\alpha} (r_{\alpha}^2 \mathbf{1} - r_{\alpha} r_{\alpha}) \cdot \mathbf{A} \cdot \sum_{\alpha} Z_{\alpha} (r_{\alpha}^2 \mathbf{1} - r_{\alpha} r_{\alpha}) \cdot \mathbf{I}_n^{-1} \cdot \mathbf{H} - \frac{e}{mc} \mathbf{H} \cdot \mathbf{A} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{J} - \mathbf{H} \cdot \left\{ \frac{e}{c} \sum_{\alpha} Z_{\alpha} (r_{\alpha}^2 \mathbf{1} - r_{\alpha} r_{\alpha}) \cdot \mathbf{I}_n^{-1} \cdot \mathbf{A} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{J} \right\} + \frac{e^2}{2c^2 m} \mathbf{H} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{A} \cdot \sum_{\alpha} Z_{\alpha} (r_{\alpha}^2 \mathbf{1} - r_{\alpha} r_{\alpha}) \cdot \mathbf{H} \quad (39)$$

$$\mathbf{A} = \sum_{k>0} \frac{\langle 0 | \mathbf{L} | k \rangle \langle k | \mathbf{L} | 0 \rangle}{E_0 - E_k}$$

All terms in eq 39 will give rise to first-order corrections to the rotational state. There will be additional nonzero second-order corrections to the energy in $\frac{1}{2} \mathbf{L} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{L}$, but these terms are rotationally invariant and are not considered further. There will also be second-order corrections involving the cross terms between $\frac{1}{2} \mathbf{L} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{L}$ and $-\mathbf{L} \cdot \boldsymbol{\omega}'$ but these terms will give rise to only second-order corrections in J for linear and asymmetric top molecules. In the case of symmetric tops these cross terms will lead to first-order corrections in J . However, it is possible to show that in the case of a symmetric top with C_{3v} symmetry the second-order matrix elements in the $\frac{1}{2} \mathbf{L} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{L}$ and $-\mathbf{L} \cdot \boldsymbol{\omega}'$ cross term are identically zero.⁴ We therefore ignore these terms. There will, however, be nonzero third-order corrections involving products of $\frac{1}{2} \mathbf{L} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{L}$ with $(\mathbf{L} \cdot \boldsymbol{\omega}')^2$ which will give rise to first-order corrections to the rotational energy, J . These corrections are given by eq 40.

Third order

$$E^{(3)} = - \sum_{k>0} \frac{\langle 0 | \mathbf{L} \cdot \boldsymbol{\omega}' | k \rangle \langle k | \mathbf{L} \cdot \boldsymbol{\omega}' | 0 \rangle \sum_{m>0} \langle 0 | \mathbf{L} | m \rangle \cdot \mathbf{I}_n^{-1} \cdot \langle m | \mathbf{L} | 0 \rangle}{(E_0 - E_k)^2} + \sum_{\substack{k>0 \\ m>0 \\ l>0}} \frac{\langle 0 | \mathbf{L} \cdot \boldsymbol{\omega}' | k \rangle \langle k | \mathbf{L} \cdot \boldsymbol{\omega}' | m \rangle \langle m | \mathbf{L} | l \rangle \cdot \mathbf{I}_n^{-1} \cdot \langle l | \mathbf{L} | 0 \rangle}{(E_0 - E_k)(E_0 - E_m)} \quad (40)$$

Before examining these third-order corrections we will combine the first terms of eq 38 and 39 to give the zero-field or "pure" rotational contributions. We designate these terms as the rigid-rotor Hamiltonian, \mathcal{H}_{rr} .

$$\mathcal{H}_{rr} = \frac{1}{2} \mathbf{J} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{J} + \mathbf{J} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{A} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{J} = \frac{1}{2} \mathbf{J} \cdot [\mathbf{I}_n^{-1} \cdot (\mathbf{1} + 2\mathbf{A} \cdot \mathbf{I}_n^{-1})] \cdot \mathbf{J} = \frac{1}{2} \mathbf{J} \cdot \mathbf{I}_{eff}^{-1} \cdot \mathbf{J} \quad (41)$$

$$\mathbf{I}_{eff}^{-1} = \mathbf{I}_n^{-1} \cdot (\mathbf{1} + 2\mathbf{A} \cdot \mathbf{I}_n^{-1})$$

The $\mathbf{I}_{eff}^{-1} = \mathbf{I}_n^{-1} \cdot (\mathbf{1} + 2\mathbf{A} \cdot \mathbf{I}_n^{-1})$ is the measured inverse moment of inertia at zero magnetic field. As \mathbf{I}_{eff}^{-1} is measured at zero field, it is very convenient to express the other terms in the energy which depend on the inverse moments of inertia in terms of \mathbf{I}_{eff}^{-1} . Of course it is evident that $\mathbf{I} \gg +2|\mathbf{A}| \cdot \mathbf{I}_n^{-1}$ for all matrix elements; we will show later that $|\mathbf{A}| \cdot \mathbf{I}_n^{-1}$ is on the order of the electron-proton mass ratio.

Now, before evaluating the third-order corrections in eq 40, we sum the terms in eq 38 and 39 to give the rotational Ham-

iltonian up to second order in the electronic correction (eq 42). We use I_{eff}^{-1} whenever possible.

$$\begin{aligned} \mathcal{H} &= \frac{1}{2} \mathbf{J} \cdot I_{\text{eff}}^{-1} \cdot \mathbf{J} - \mathbf{H} \cdot \left\{ \frac{e}{2c} \sum_{\alpha} Z_{\alpha} (r_{\alpha}^2 \mathbf{1} - \right. \\ &\quad \left. r_{\alpha} r_{\alpha}) \cdot I_{\text{eff}}^{-1} \right\} \cdot \mathbf{J} - \mathbf{H} \cdot \left\{ \frac{e}{mc} \mathbf{A} \cdot I_n^{-1} \right\} \cdot \mathbf{J} - \frac{1}{2} \mathbf{H} \cdot \chi^d \cdot \mathbf{H} - \\ &\quad \frac{1}{2} \mathbf{H} \cdot \chi^p \cdot \mathbf{H} + \frac{1}{2} \mathbf{H} \cdot \gamma \cdot \mathbf{H} \\ \gamma &= \frac{e^2}{2c^2} I_n^{-1} \cdot \sum_{\alpha} Z_{\alpha} (r_{\alpha}^2 \mathbf{1} - r_{\alpha} r_{\alpha}) \cdot \mathbf{A} \cdot \sum_{\alpha} Z_{\alpha} (r_{\alpha}^2 \mathbf{1} - \\ &\quad r_{\alpha} r_{\alpha}) \cdot I_n^{-1} + \frac{e^2}{c^2 m} I_n^{-1} \cdot \mathbf{A} \cdot \sum_{\alpha} Z_{\alpha} (r_{\alpha}^2 \mathbf{1} - r_{\alpha} r_{\alpha}) + \\ &\quad \frac{e^2}{4c^2} \sum_{\alpha} \frac{Z_{\alpha}^2}{M_{\alpha}} (r_{\alpha}^2 \mathbf{1} - r_{\alpha} r_{\alpha}) \\ \chi^d &= - \frac{e^2}{4c^2 m} \langle 0 | \sum_i (r_i^2 \mathbf{1} - r_i r_i) | 0 \rangle \\ \chi^p &= - \frac{e^2}{2m^2 c^2} \mathbf{A} = - \frac{e^2}{2m^2 c^2} \sum_{k>0} \frac{\langle 0 | \mathbf{L} | k \rangle \langle k | \mathbf{L} | 0 \rangle}{E_0 - E_k} \\ \chi &= \chi^d + \chi^p \end{aligned} \quad (42)$$

χ^d , χ^p , and χ are the diamagnetic, paramagnetic, and total magnetic susceptibilities, respectively. γ is also a susceptibility term which has the same rotational dependence as χ^d and χ^p . Careful examination of γ will show that the elements in γ are smaller than the elements in χ^d and χ^p by the electron-proton mass ratio.

We now return to the third-order terms and note that the first term in eq 40 produces terms which appear as in eq 42 times a further reducing factor on the order of $2\mathbf{A} \cdot I_n^{-1} \cong m/M_p$ (the ratio of electron to proton masses). Thus, we will rewrite eq 42 by assuming that the third-order corrections will convert I_n^{-1} in eq 42 to I_{eff}^{-1} , giving

$$\mathcal{H} = \frac{1}{2} \mathbf{J} \cdot I_{\text{eff}}^{-1} \cdot \mathbf{J} - \mathbf{H} \cdot \left\{ \frac{e}{2c} \sum_{\alpha} Z_{\alpha} (r_{\alpha}^2 \mathbf{1} - r_{\alpha} r_{\alpha}) \cdot I_{\text{eff}}^{-1} + \frac{e}{mc} \mathbf{A} \cdot I_{\text{eff}}^{-1} \right\} \cdot \mathbf{J} + \frac{1}{2} \mathbf{H} \cdot \chi \cdot \mathbf{H} \quad (43)$$

Further terms in the perturbation series including other third-order terms and fourth-order terms will refine the values of I_{eff}^{-1} and add increasingly smaller terms to γ . We drop the γ terms and we assume that the perturbation theory converges to the experimental value of I_{eff}^{-1} obtained from the first term in eq 43 at zero field.^{4,5}

We now define the molecular g values from eq 43 as

$$\begin{aligned} \mathcal{H} &= \frac{1}{2} \mathbf{J} \cdot I_{\text{eff}}^{-1} \cdot \mathbf{J} - \frac{\mu_0}{\hbar} \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{J} - \frac{1}{2} \mathbf{H} \cdot \chi \cdot \mathbf{H} \\ \mathbf{g} &= \mathbf{g}_n + \mathbf{g}_e \\ \mathbf{g}_n &= M_p \sum_{\alpha} Z_{\alpha} (r_{\alpha}^2 \mathbf{1} - r_{\alpha} r_{\alpha}) \cdot I_{\text{eff}}^{-1} \\ \mathbf{g}_e &= \frac{2M_p}{m} I_{\text{eff}}^{-1} \cdot \sum_{k>0} \frac{\langle 0 | \mathbf{L} | k \rangle \langle k | \mathbf{L} | 0 \rangle}{E_0 - E_k} \end{aligned} \quad (44)$$

$\mu_0 = \hbar e/2M_p c$ is the nuclear magneton and m and M_p are the electron and proton masses; $\frac{1}{2} \mathbf{J} \cdot I_{\text{eff}}^{-1} \cdot \mathbf{J}$ is the rigid rotor term and I_{eff}^{-1} is measured at zero field. \mathbf{g}_n and \mathbf{g}_e are the nuclear and electronic contributions to the molecular g -value tensor, \mathbf{g} , defined similar to the results of Eshbach and Strandberg⁶ following earlier theoretical work by Condon,⁷ Wick,⁸ and Ramsey⁹ and early experimental work on H_2 by Stern and coworkers.¹⁰ It is evident that the molecular moment, $(\mu_0/\hbar) \mathbf{g} \cdot \mathbf{J}$ is a sum of positive nuclear and negative ($E_0 < E_k$) electronic terms. The individual diagonal elements in the g -value tensor are given by

$$g_{xx} = \frac{M_p}{J_{xx}} \sum_{\alpha} Z_{\alpha} (r_{\alpha}^2 - x_{\alpha}^2) + \frac{2M_p}{m I_{xx}} \sum_{k>0} \frac{|\langle 0 | L_x | k \rangle|^2}{E_0 - E_k} \quad (45)$$

and cyclic permutations for g_{yy} and g_{zz} .

We can also give a phenomenological description of a molecular magnetic moment which is suggested by the above equations.¹¹ In the absence of rotation ($J = 0$) there is no rotational magnetic moment. In a rotating molecule the nuclear current contribution leads to a magnetic moment given by the first term in eq 45. The electrons in the molecule which are localized to a single atom will rotate in a direction opposite to the nuclear motion like the seats on a ferris wheel which to maintain their orientation with respect to the laboratory framework as the wheel (overall nuclear framework) rotates. This electronic counter rotation cancels the nuclear contribution to the moment. However, if the electrons on one atom are coupled to another atom in a molecular bond, the electrons will rotate with the molecular framework destroying the cancellation effect described above for uncoupled electrons. The result is a nonzero total magnetic moment.

The individual elements in the magnetic susceptibility tensor are given from eq 42 by¹²

$$\begin{aligned} \chi_{xx} &= \chi_{xx}^d + \chi_{xx}^p \\ \chi_{xx} &= - \frac{e^2}{4c^2 m} \langle 0 | \sum_i (y_i^2 + z_i^2) | 0 \rangle - \\ &\quad \frac{e^2}{2c^2 m} \sum_{k>0} \frac{|\langle 0 | L_x | k \rangle|^2}{E_0 - E_k} \end{aligned} \quad (46)$$

and cyclic permutations for χ_{yy} and χ_{zz} . χ_{xx}^d and χ_{xx}^p are the diamagnetic and paramagnetic components of the susceptibility, respectively. χ_{xx}^d is always negative and depends only on the ground-state distribution of electrons. χ_{xx}^p is generally positive as $E_k > E_0$ and depends on a sum over all excited electronic states.

Equation 46 shows that the magnetic field induced electronic moment, $\frac{1}{2} \mathbf{H} \cdot \chi$, is a sum of negative and positive terms. The negative terms arise through the diamagnetic response of the molecule's electrons which gives a moment which opposes the field. The second and positive contribution to the electronic magnetic moment arises through a paramagnetic response of the molecule's electrons; the paramagnetic moment complements the applied magnetic field.

It is clear that the second terms in g_{xx} (eq 45) and χ_{xx} (eq 46) have the same dependence on the sum over all excited molecular electronic states. Therefore, if the total g_{xx} can be measured and if the nuclear component of g_{xx} can be computed from the known molecular structure, the numerical value for the paramagnetic dependence in the susceptibility can be obtained. Substituting the $\sum_{k>0} |\langle 0 | L_x | k \rangle|^2 / (E_0 - E_k)$ dependence in g_{xx} into χ_{xx} gives¹³

$$\begin{aligned} \chi_{xx} &= \chi_{xx}^d + \chi_{xx}^p \\ &= - \frac{e^2}{4c^2 m} \langle 0 | \sum_i (y_i^2 + z_i^2) | 0 \rangle - \frac{e^2}{4c^2 m} \left\{ \frac{g_{xx}/xx}{M_p} - \sum_{\alpha} Z_{\alpha} (y_{\alpha}^2 + z_{\alpha}^2) \right\} \end{aligned} \quad (47)$$

and cyclic permutations for χ_{yy} and χ_{zz} .

Now, if the elements in the total magnetic susceptibility tensor can also be measured, the numerical value of χ_{xx}^d can be extracted. χ_{xx}^d depends only on the ground electronic state electron distribution and gives some notion of the outer electronic shape of the molecule.

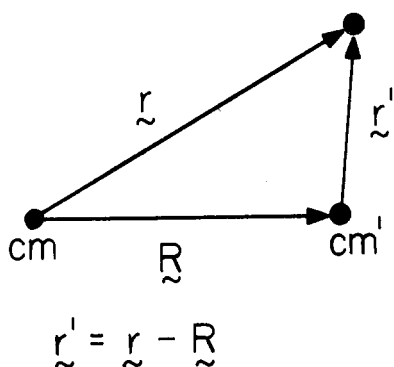


Figure 1. The vectors r , and r' from two different origins in a molecule which are directed toward an electron or nuclear charge as needed in the molecular g values.

A. Electric Dipole Moments

It is evident that molecular g values, as in eq 45, are dependent on the moments of inertia and the location of the molecular center of mass. We will now show that the magnitude and *sign* of the molecular electric dipole moment can be determined by measuring the molecular g value for two different isotopic species of the same molecule.¹⁴

Let eq 45 represent the molecular g value for one isotopic species of a linear molecule. Let $g_{xx'}$ stand for the g value in the same molecule for a different isotopic species with a different CM. The perpendicular g values are

$$g_{xx} = \frac{M_p}{I_{xx}} \sum_{\alpha} Z_{\alpha} z_{\alpha}^2 + \frac{2M_p}{mI_{xx}} \sum_{k>0} \frac{|\langle 0|L_x|k\rangle|^2}{E_0 - E_k}$$

$$g_{xx'} = \frac{M_p}{I_{xx'}} \sum_{\alpha} Z_{\alpha} (z_{\alpha}')^2 + \frac{2M_p}{mI_{xx'}} \sum_{k>0} \frac{|\langle 0|L_x'|k\rangle|^2}{E_0 - E_k} \quad (48)$$

z is the internuclear axis. z_{α} , I_{xx} , and L_x will be different in the two different isotopic species. However, $(g_{xx'}I_{xx'}/M_p)$ can be related to $(g_{xx}I_{xx}/M_p)$ by a linear transformation of coordinates. The vectors from the two centers are shown in Figure 1. The transformations from the unprimed origin to the primed origin for a shift in origin along the z axis of magnitude Z are given by

$$\begin{aligned} r' &= r - R \\ x' &= x \\ y' &= y \\ z' &= z - Z \\ \rho_{x'} &= \rho_x \\ \rho_{y'} &= \rho_y \\ \rho_{z'} &= \rho_z - p_z \end{aligned} \quad (49)$$

and

$$\begin{aligned} L_x' &= (r' \times p')_x = y'p_z' - z'p_y' = y(\rho_z - p_z) - \\ &(z - Z)\rho_y = y\rho_z - zp_y - y\rho_z + Z\rho_y = L_x - y\rho_z + Z\rho_y \end{aligned} \quad (50)$$

Making the appropriate substitutions into $g_{xx'}$ in eq 48 gives eq 51. p_z and Z are independent of electrons and, therefore,

$$\begin{aligned} \frac{g_{xx'}I_{xx'}}{M_p} &= \sum_{\alpha} Z_{\alpha} (z_{\alpha}')^2 - 2z_{\alpha}Z + Z^2 + \frac{1}{m} \times \\ &\sum_{k>0} \frac{\langle 0|L_x - y\rho_z + Z\rho_y|k\rangle \langle k|L_x - y\rho_z + Z\rho_y|0\rangle + \\ &\langle 0|L_x - y\rho_z + Z\rho_y|k\rangle \langle k|L_x - y\rho_z + Z\rho_y|0\rangle}{E_0 - E_k} \end{aligned} \quad (51)$$

do not operate on the electronic functions. p_y does, however, operate on the electronic functions. Using

$$\begin{aligned} \langle 0|p_y|k\rangle &= \frac{im}{\hbar} (E_0 - E_k) \langle 0|y|k\rangle \\ \langle k|p_y|0\rangle &= \frac{im}{\hbar} (E_k - E_0) \langle k|y|0\rangle \end{aligned} \quad (52)$$

where $p_y = -i\hbar(d/dy)$ and y are electronic operators, in eq 51 gives eq 53. Cancelling the $(E_0 - E_k)$ factors, we can now

$$\begin{aligned} \frac{g_{xx'}I_{xx'}}{M_p} &= \sum_{\alpha} Z_{\alpha} (z_{\alpha}')^2 - 2z_{\alpha}Z + Z^2 + \\ &\frac{2}{m} \sum_{k>0} \left[\frac{|\langle 0|L_x|k\rangle|^2}{E_0 - E_k} \right] + 2\frac{im}{\hbar} \left(\frac{1}{m}\right) \sum_{k>0} [(E_0 - E_k)] \times \\ &\left[\frac{\langle 0|Zy|k\rangle \langle k|L_x|0\rangle - \langle 0|L_x|k\rangle \langle k|Zy|0\rangle}{(E_0 - E_k)} \right] - \\ &\frac{im}{\hbar} \left(\frac{1}{m}\right) \sum_{k>0} [(E_0 - E_k)] \times \\ &\left[\frac{\langle 0|Zp_y|k\rangle \langle k|Zy|0\rangle - \langle 0|Zy|k\rangle \langle k|Zp_y|0\rangle}{(E_0 - E_k)} \right] \end{aligned} \quad (53)$$

close the summations over k in the last two terms to yield ground-state terms. Thus, eq 53 reduces to

$$\begin{aligned} \frac{g_{xx'}I_{xx'}}{M} &= \frac{g_{xx}I_{xx}}{M} + \sum_{\alpha} Z_{\alpha} (-2z_{\alpha}Z + Z^2) + \\ &\frac{1}{\hbar} \{ 2\langle 0|ZyL_x - L_xZy|0\rangle - \langle 0|Zp_yZy - ZyZp_y|0\rangle \} \end{aligned} \quad (54)$$

The quantities averaged over the ground-state function can be further reduced. The first two operators in the average value give

$$\begin{aligned} ZyL_x - L_xZy &= -i\hbar \{ Zy(y \frac{d}{dz} - z \frac{d}{dy}) - \\ &(y \frac{d}{dz} - z \frac{d}{dy})Zy \} = -i\hbar(Zz) \end{aligned} \quad (55)$$

The second term gives

$$Zp_yZy - ZyZp_y = -i\hbar \{ Z \frac{d}{dy} Zy - ZyZ \frac{d}{dy} \} = -i\hbar(Z^2) \quad (56)$$

Substituting eq 55 and 56 into eq 54 shows that the Z^2 terms cancel, giving

$$\begin{aligned} \frac{g_{xx'}I_{xx'}}{M_p} - \frac{g_{xx}I_{xx}}{M_p} &= -2Z \sum_{\alpha} z_{\alpha} + 2Z\langle 0|z|0\rangle = \\ &-2Z \{ \sum_{\alpha} z_{\alpha} - \langle 0|z|0\rangle \} \end{aligned} \quad (57)$$

Multiplying this equation by e , the charge on an electron (or proton), we recognize the expression for the molecular electric dipole moment along the z axis, D_z .

$$\begin{aligned} (g_{xx'}I_{xx'} - g_{xx}I_{xx}) \left(\frac{e}{2M_p} \right) &= \\ -Z \{ e \sum_{\alpha} z_{\alpha} - e\langle 0|z|0\rangle \} &= -ZD_z \end{aligned} \quad (58)$$

Z is the distance from the unprimed to the primed CM. Thus, by measuring the moments I_{xx} and $I_{xx'}$ and g values in two different isotopic species, the sign of D_z can be obtained. Equation-58 is valid for linear molecules where the z axis contains the nuclei. It is easy to generalize this equation to nonlinear molecules.

$$(g_{xx'}I_{xx'} - g_{xx}I_{xx}) \left(\frac{e}{2M_p} \right) = -ZD_z - YD_z \quad (59)$$

In summary we note that the sign and magnitude of the electric dipole moment can be obtained by measuring the molecular g values in two different isotopic species.

B. Molecular Quadrupole Moments and Second Moments of the Electronic Charge Distribution

It is evident that the diagonal elements of the molecular quadrupole moment tensor \mathbf{Q} are related to the diagonal elements of the magnetic susceptibility tensor in eq 46. The $(2x^2 - y^2 - z^2) = (3r^2 - x^2)$ operators appear in Q_{xx} and the $(y^2 + z^2)$ operators appear in χ_{zz} . Thus, the value of Q_{xx} is easily written in terms of the magnetic susceptibility anisotropy $(\chi_{zz} + \chi_{yy} - 2\chi_{xx})$, g values, and moments of inertia. The appropriate relation is¹⁵

$$Q_{zz} = \frac{e}{2} \sum_{\alpha} Z_{\alpha} (3z_{\alpha}^2 - r_{\alpha}^2) - \frac{e}{2} \langle 0 | \sum_i (3z_i^2 - r_i^2) | 0 \rangle = \frac{2mc^2}{e} (\chi_{xx} + \chi_{yy} - 2\chi_{zz}) + \frac{e}{2M_p} (g_{xx/xx} + g_{yy/yy} - 2g_{zz/zz}) \quad (60)$$

and cyclic permutations for Q_{yy} and Q_{zz} . The values of χ_{xx} , χ_{yy} , and χ_{zz} are in units of cm^3 per molecule. If molar χ_{xx} values are used in eq 60, they must be divided by N , Avogadro's number. It is easy to check eq 60 by substituting χ_{xx} , χ_{yy} , and χ_{zz} from eq 47. The molecular quadrupole moments of several molecules have been determined by measuring the diagonal elements in the \mathbf{g} and \mathbf{I} tensors and the magnetic susceptibility anisotropies $(\chi_{xx} + \chi_{yy} - 2\chi_{zz})$, and the results will be discussed in section V. Equation 60 simplifies for a linear molecule to¹⁶

$$Q_{zz} = e \sum_{\alpha} Z_{\alpha} z_{\alpha}^2 - e \langle 0 | \sum_i (z_i^2 - x_i^2) | 0 \rangle = \frac{e}{M_p} g_{xx/xx} + \frac{4mc^2}{e} (\chi_{xx} - \chi_{zz}) \quad (61)$$

A similar equation is evident for symmetric tops.¹⁷

$$Q_{zz} = \frac{e}{M_p} (g_{zz/zz} - g_{xx/xx}) + \frac{4mc^2}{e} (\chi_{xx} - \chi_{zz}) \quad (62)$$

z is the symmetry axis for both eq 61 and 62.

We now recall that only the value of the first nonzero electric multipole moment is independent of the origin. All higher order moments depend on the origin. Consider a molecular quadrupole moment along the internuclear z axis in a linear molecule at two different origins along the z axis separated by Z . According to eq 61

$$Q_{zz}' = e \sum_{\alpha} Z_{\alpha} (z_{\alpha}')^2 - e \langle 0 | \sum_i [(z_i')^2 - (x_i')^2] | 0 \rangle \quad (63)$$

Now, according to our previous discussion, $z' = z - Z$ and $x' = x$ for the linear molecule giving

$$Q_{zz}' = e \sum_{\alpha} Z_{\alpha} (z_{\alpha} - Z)^2 - e \langle 0 | \sum_i [(z_i - Z)^2 - x_i^2] | 0 \rangle = Q_{zz} - 2ZD_z + Z^2M_0 \quad (64)$$

D_z is the electric dipole moment and M_0 is the molecular monopole moment. If $M_0 = 0$ (neutral molecule) and $D_z = 0$, $Q_{zz} = Q_{zz}'$. If the molecule is neutral and if the molecule has a nonzero electric dipole moment

$$Q_{zz}' - Q_{zz} = -2ZD_z \quad (65)$$

Substituting the functions for Q_{zz}' and Q_{zz} from eq 61 in terms of $g_{xx/xx}$ and $\chi_{xx} - \chi_{zz}$ leads to eq 59 when we note that the magnetic susceptibility anisotropy $(\chi_{xx} - \chi_{zz})$ is independent of the origin of the measurement. These equations are easily generalized to nonlinear molecules.

The anisotropies in second moment of the electronic

charge distributions are also available from the above information.

$$\langle y^2 \rangle - \langle x^2 \rangle = \langle 0 | \sum_i y_i^2 | 0 \rangle - \langle 0 | \sum_i x_i^2 | 0 \rangle = \sum_{\alpha} Z_{\alpha} (y_{\alpha}^2 - x_{\alpha}^2) + \frac{1}{M_p} [g_{yy/yy} - g_{xx/xx}] + \frac{4mc^2}{e^2} [\chi_{yy} - \chi_{xx}] \quad (66)$$

Finally, if the bulk magnetic susceptibility is known, the individual tensor elements in χ^d and χ can be determined. The bulk or average magnetic susceptibility is given by

$$\chi = \frac{1}{3} (\chi_{xx} + \chi_{yy} + \chi_{zz}) \quad (67)$$

The individual second moments of the electronic charge distributions can also be determined by

$$\langle x^2 \rangle = - \frac{2mc^2}{e^2} [\chi_{yy}^d + \chi_{zz}^d - \chi_{xx}^d] = - \frac{2mc^2}{e^2} [(\chi_{yy} + \chi_{zz} - \chi_{xx}) - (\chi_{yy}^p + \chi_{zz}^p - \chi_{xx}^p)] \quad (68)$$

A summary of the interconnections between the magnetic parameters is shown in Figure 2.⁵ The top line of parameters are measured directly by the molecular Zeeman effect as outlined in the next section.

V. Rotational Molecular Zeeman Effect

The molecular Zeeman effect as described here is the observation of the effects of high magnetic fields on the rotational energy levels of a freely rotating diamagnetic molecule. If the magnetic field perturbations on the rigid rotor energy levels are small relative to the zero-field rotational energies, a power series in the field can be employed to describe the total energy. Expanding about zero field gives eq 69. E_0 is the

$$E = E_0 - \sum_{i=x,y,z} \left(\frac{\partial E}{\partial H_i} \right)_{H_i=0} H_i + \frac{1}{2} \sum_{i,j=x,y,z} \left(\frac{\partial^2 E}{\partial H_i \partial H_j} \right)_{H_i=0, H_j=0} H_i H_j + \frac{1}{6} \sum_{i,j,k=x,y,z} \left(\frac{\partial^3 E}{\partial H_i \partial H_j \partial H_k} \right)_{0,0,0} H_i H_j H_k + \dots \quad (69)$$

zero-field rotational energy, and the sums are over the three Cartesian axes in the laboratory fixed axis system (x, y, z) . H_i is the component of the external field \mathbf{H} which is projected along the i th laboratory axis. The derivatives of the energy with respect to the field are all evaluated at zero field. We now define the derivatives in terms of the magnetic parameters described in the last section (see eq 44).

Rotational magnetic dipole moment

$$\frac{\mu_0}{h} (\mathbf{g} \cdot \mathbf{J})_i = (\mu_J)_i = - \left(\frac{\partial E}{\partial H_i} \right)_0 \quad (70)$$

Molecular magnetic susceptibility

$$\chi_{ij} = - \left(\frac{\partial^2 E}{\partial H_i \partial H_j} \right)_{0,0} \quad (71)$$

The cubic and quartic magnetic susceptibilities are defined in terms of the third and fourth derivatives of the energy with respect to the field by Flygare and Benson.⁵ It appears evident that eq 69 converges rapidly at least in fields up to about 25,000 G. In the case of higher fields, which are available in superconducting solenoid systems, these cubic and quartic terms should be included. Flygare and Benson⁵ have given more details on the nature of these higher order terms and the corresponding order of magnitude values. In this paper we

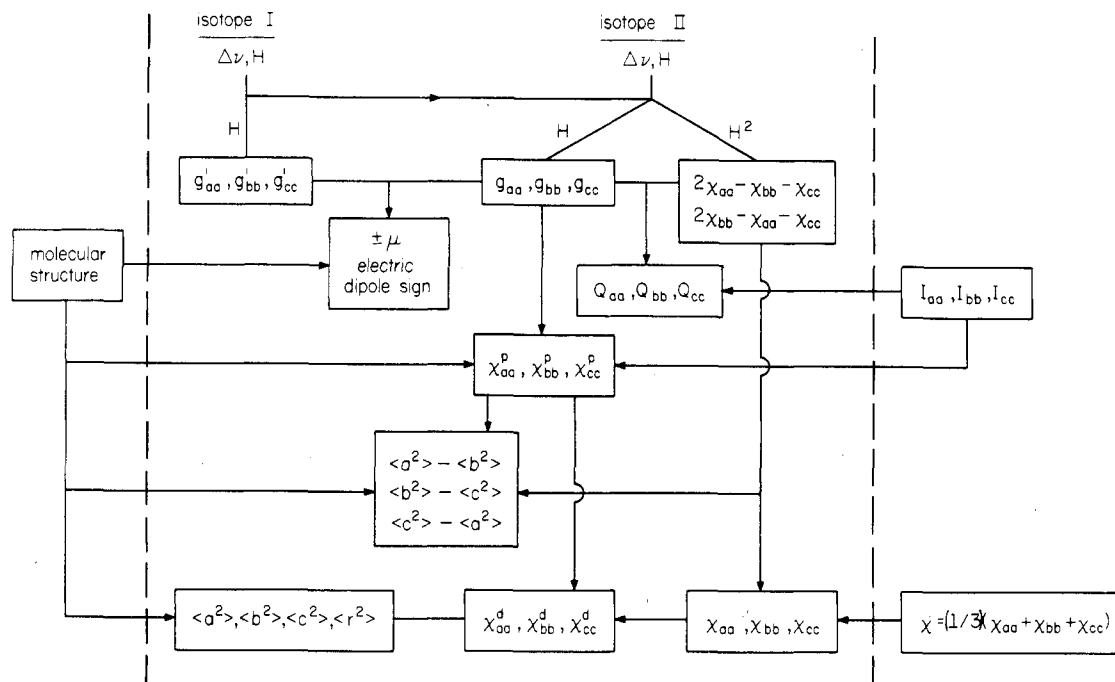


Figure 2. Summary of data available from the measurement of the magnetic field (H) giving rise to the frequency shifts ($\Delta\nu$) in the molecular Zeeman effect. The information between the dotted lines must be added to the non-Zeeman information outside of the dotted lines when indicated.

will make the assumption that eq 69 converges rapidly and we include only terms through the square of the field. Truncating and substituting eq 70 and 71 into eq 69 gives

$$\mathcal{H} = \mathcal{H}_{rr} - \mu_J \cdot H - \frac{1}{2} H \cdot \chi \cdot H \quad (72)$$

where \mathcal{H}_{rr} is the rigid-rotor Hamiltonian and μ_J is now the vector rotational magnetic moment as defined in eq 70 and 44; $-\frac{1}{2} H \cdot \chi$ is the field induced magnetic moment. We also recall that all vectors in eq 72 are defined in the space-fixed (laboratory) axis system. In analyzing the errors inherent in truncating eq 72 at the H^2 term, we return again to Flygare and Benson⁵ and quote their result: "In summary, at fields below about 25,000 gauss it is safe to truncate at the χ terms and the resultant g values are accurate to about 0.1 percent and the χ anisotropies to better than 1 percent." For more details and a documentation of earlier work the reader is referred to the earlier paper.⁵

We return to eq 44 to rewrite eq 72 giving

$$\mathcal{H} = \mathcal{H}_{rr} - \frac{\mu_0}{h} H \cdot g \cdot J - \frac{1}{2} H \cdot \chi \cdot H \quad (73)$$

We can now write g and χ in the principal inertial axis system (molecular fixed) with the direction cosine transformation, Φ , leading to

$$\mathcal{H} = \mathcal{H}_{rr} - \frac{\mu_0}{h} H \cdot [\Phi g] \cdot J - \frac{1}{2} H \cdot [\Phi \chi \Phi] \cdot H \quad (74)$$

We now use the a , b , and c axes to denote the principal inertial axis system.

Hüttner and Flygare¹⁸ have discussed in detail the rotational average of this Hamiltonian in both the nuclear coupled and uncoupled cases. We will discuss the effects of nuclear coupling in section VII. In the absence of nuclear spin the rotational energy for a molecule is computed by first obtaining the eigenfunctions of $\mathcal{H}_{rr} = \frac{1}{2} J \cdot I_{\text{eff}}^{-1} \cdot J$ from eq 44 at zero field. These rigid-rotor and J^2 eigenfunctions are then used to evaluate the first-order corrections to the rotational energy due to the g and χ terms in eq 74. The rotational energy for a general molecule in a static unidirectional magnetic field, H , in the uncoupled basis first-order in J is given in the absence of

nuclear spin as¹⁸ shown in eq 75. $\chi = \frac{1}{3}(\chi_{aa} + \chi_{bb} + \chi_{cc})$ is the average magnetic susceptibility, $E^0(J, \tau, M)$ is the zero-

$$E(J, \tau, M) = E^0(J, \tau, M) - \frac{\mu_0 M H}{J(J+1)} \sum_{\alpha} g_{\alpha} \langle J\tau || J_{\alpha}^2 || J\tau \rangle - \frac{1}{2} H^2 \chi - \frac{H^2}{J(J+1)} \left[\frac{3M^2 - J(J+1)}{(2J-1)(2J+3)} \right] \times \sum_{\alpha} (\chi_{\alpha\alpha} - \chi) \langle J\tau || J_{\alpha}^2 || J\tau \rangle \quad (75)$$

field rotational energy, M is the projection of J on the space-fixed field axis, and $\langle J\tau || J_{\alpha}^2 || J\tau \rangle$ is the reduced matrix element of J_{α}^2 in the general asymmetric top basis indicated by quantum number τ . The $\langle J\tau || J_{\alpha}^2 || J\tau \rangle$ matrix elements are easily computed from the experimental principal moments of inertia by transforming the symmetric top $\langle JK || J_{\alpha}^2 || J'K' \rangle$ matrix to the asymmetric top basis.¹⁸ The sums over α are over the three principal inertial axes a , b , and c . Thus, we note that in general the three independent diagonal elements in the molecular g -value tensor (g_{aa} , g_{bb} , and g_{cc}) can be measured.

However, the sign of M cannot be determined experimentally with the normal plane-polarized electromagnetic field, so only the relative signs of the three g values are determined. The sign of the M transition and resulting g value signs can be obtained by using circularly polarized microwave radiation. χ cannot be measured because the $-\frac{1}{2} H^2 \chi$ term is independent of J and M . Only two independent magnetic susceptibility anisotropies can be determined because

$$\sum_{\alpha} (\chi_{\alpha\alpha} - \chi) = 0$$

We take these two independent anisotropies to be

$$\chi_{aa} - \chi = \frac{1}{3}(2\chi_{aa} - \chi_{bb} - \chi_{cc})$$

$$\chi_{bb} - \chi = \frac{1}{3}(2\chi_{bb} - \chi_{aa} - \chi_{cc})$$

$\chi_{cc} - \chi$ is the negative value of the sum of $\chi_{aa} - \chi$ and $\chi_{bb} - \chi$. Thus in general, the Zeeman perturbation provides five parameters. In a symmetric top there are only two inde-

pendent g values and a single independent anisotropy. In a linear molecule there is a single independent g value and a single anisotropy.

Equation 75 reduces to a simpler form for symmetric top and linear molecules where for a prolate top with the symmetry axis along a , we write

$$\langle J_c^2 \rangle = \frac{1}{2}[J(J+1) - K^2] = \langle J_b^2 \rangle$$

$$\langle J_a^2 \rangle = K^2 \quad (76)$$

Substituting into eq 75 gives (a is the rotational symmetry axis)

$$E(JKM) = E^0(JKM) - \mu_0 MH[g_{bb} + (g_{aa} - g_{bb}) \frac{K^2}{J(J+1)}] - \frac{1}{2}H^2\chi - \frac{H^2}{3} \left[\frac{3M^2 - J(J+1)}{(2J-1)(2J+3)} \right] \times \left\{ (\chi_{bb} - \chi_{aa}) - \frac{3K^2}{J(J+1)} (\chi_{bb} - \chi_{aa}) \right\} \quad (77)$$

In the case of a linear molecule, $K = 0$, giving (a is the internuclear axis)

$$E(JM) = E^0(JM) - H\mu_0 Mg_{bb} - \frac{H^2}{3} \left[\frac{3M^2 - J(J+1)}{(2J-1)(2J+3)} \right] (\chi_{bb} - \chi_{aa}) - \frac{1}{2}H^2\chi \quad (78)$$

Equations 75, 77, and 78 have been used extensively for the determination of the g values and magnetic susceptibility anisotropies in rotating molecules in the absence of nuclear spin.⁵ Molecular beam techniques have been employed to extract g_{bb} and $\chi_{bb} - \chi_{aa}$ values from several linear molecules.¹⁹ It is difficult to extend the molecular beam method to more complex molecules, however, and most of the recent work has been generated by using high-resolution microwave spectroscopy with high magnetic fields.⁵

Figure 3 shows a schematic of the $J = 1 \rightarrow 2$ energy levels and transitions in a linear molecule in a magnetic field according to eq 78. Both $\Delta M = \pm 1$ and $\Delta M = 0$ transitions are shown. The $J = 1 \rightarrow 2$, $\Delta M = 0$ transition is independent of the linear Zeeman effect, and a study of this transition will illustrate the accuracy of the measurement of the magnetic susceptibility anisotropy $\chi_{\perp} - \chi_{\parallel}$. Figure 4 shows the experimental trace of the $J = 1 \rightarrow 2$, $\Delta M = 0$ transition in OCS.²⁰ The frequency markers in this transition are every 10 kHz. This figure gives a good impression of the accuracy (on the order of 1%) in measuring the magnetic susceptibility anisotropy by microwave spectroscopy with fields up to 30 kG. Molecular g values can normally be measured more accurately. However, this depends also on the type of molecule. The molecular g values parallel to the methyl group in symmetric top molecules such as $\text{CH}_3\text{C}\equiv\text{CH}$ and CH_3X (where X is an atom) are difficult to measure because $K \neq 0$ transitions must be observed.¹⁷ These transitions have broad line widths due to the first-order Stark effects in the $K \neq 0$ levels of a symmetric top. In addition the translational Stark effect which is caused by the velocity induced electric field of a molecule moving with velocity v in a magnetic field ($E \approx vH/c$) also causes broadening in transitions which have first-order Stark effects.⁵

Figure 5 illustrates three cases of relative H -dependent and H^2 -dependent spectra in asymmetric top molecules. In light- or medium-sized molecules the linear Zeeman effect dominates the spectra leading to symmetric looking spectra and very accurate measurements of the molecular g values. In heavy molecules the field-induced magnetic moments, $\frac{1}{2}H \cdot \chi$, are larger than the rotationally induced moments, leading to more accurate measurements of $2\chi_{aa} - \chi_{bb} - \chi_{cc}$ and $2\chi_{bb} - \chi_{aa} - \chi_{cc}$ than the molecular g values. The progression as described above is shown in Figure 5 starting with

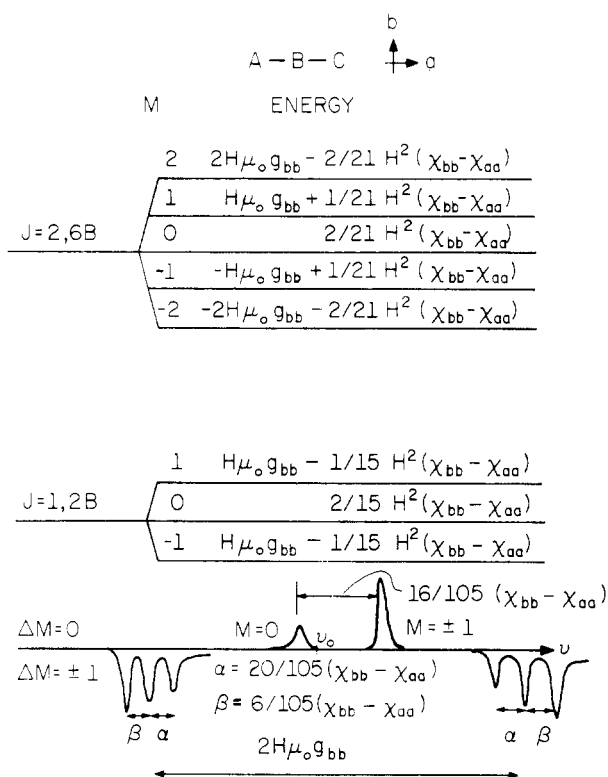


Figure 3. Schematic of the $J = 1$ and $J = 2$ rotational energy levels of a linear molecule in the presence of a magnetic field. The $J = 1 \rightarrow 2$, $\Delta M = 0$ and $\Delta M = \pm 1$ transitions are shown with the corresponding splittings leading to the measurement of g_{bb} and $\chi_{bb} - \chi_{aa}$. Figure 4 shows an experimental trace of the $J = 1 \rightarrow 2$, $\Delta M = 0$ transition in OCS.

$Hg > H^2\chi$ in sulfur dioxide to $Hg \approx H^2\chi$ in ethylene sulfide to $Hg < H^2\chi$ in fluorobenzene. The same transition is shown in all cases where the increasing asymmetry is evident. An extreme case in the $Hg < H^2\chi$ region is found in tropone where the magnetic susceptibility anisotropies were obtained from the Zeeman splittings, in spite of the fact that the g values could not be determined.²¹

Tables I through VI list some typical molecular g values, magnetic susceptibility anisotropies, and molecular quadrupole moments for linear, symmetric top, planar nonring asymmetric top, three-membered ring, four-membered ring, and other planar ring molecules. The numbers presented in these tables were obtained by least-squares fitting the observed splittings on 40–100 transitions for each molecule to the energy expressions in eq 75, 77, or 78. The uncertainties are standard deviations. The uncertainties in the molecular quadrupole moments calculated with eq 60, 61, or 62 depend in most cases on the uncertainties in the magnetic susceptibility anisotropies as the g values are normally the more accurate Zeeman parameter. It is evident from Tables I and II that the determination of the sign of the electric dipole moment is a marginal experiment as the standard deviations are normally as large as the measured moments. Nevertheless most of the dipoles are in agreement with the more accurately determined magnitudes as obtained by the Stark effect, and in most cases the signs are the expected values.

We refer again to Figure 2 which shows the relation between the measurements, which are the field-dependent frequency shifts and the corresponding magnetic fields, and the remaining magnetic parameters. g_{aa} , g_{bb} , g_{cc} , $2\chi_{aa} - \chi_{bb} - \chi_{cc}$, and $2\chi_{bb} - \chi_{aa} - \chi_{cc}$ are measured directly and all other parameters are determined from these numbers, the moments of inertia, the molecular structure, and the value of the bulk magnetic susceptibility. The sources of error in these measurements are in frequencies and fields. Of course for

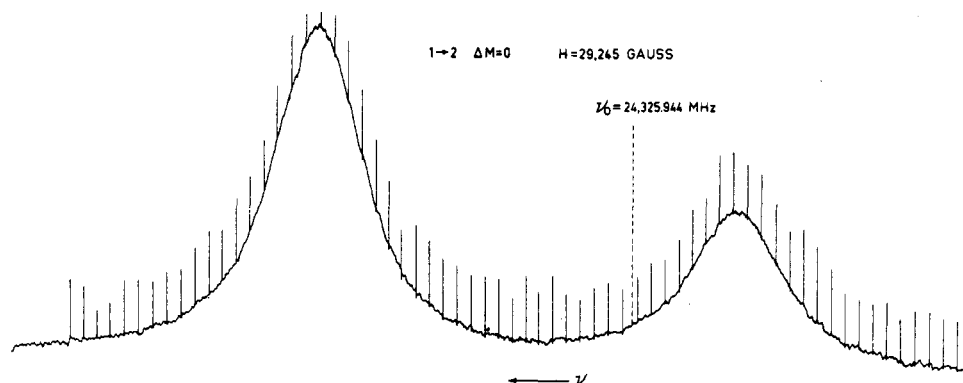


Figure 4. The $J = 1 \rightarrow 2$, $\Delta M = 0$ transition in OCS at $H = 29,245$ G. The frequency markers are every 10 kHz. The splitting is 303×10^3 Hz which according to Figure 3 leads to $\chi_{bb} - \chi_{aa} = (1.54 \pm 0.02) \times 10^{-29}$ erg/G². The spectrum is from ref 20.

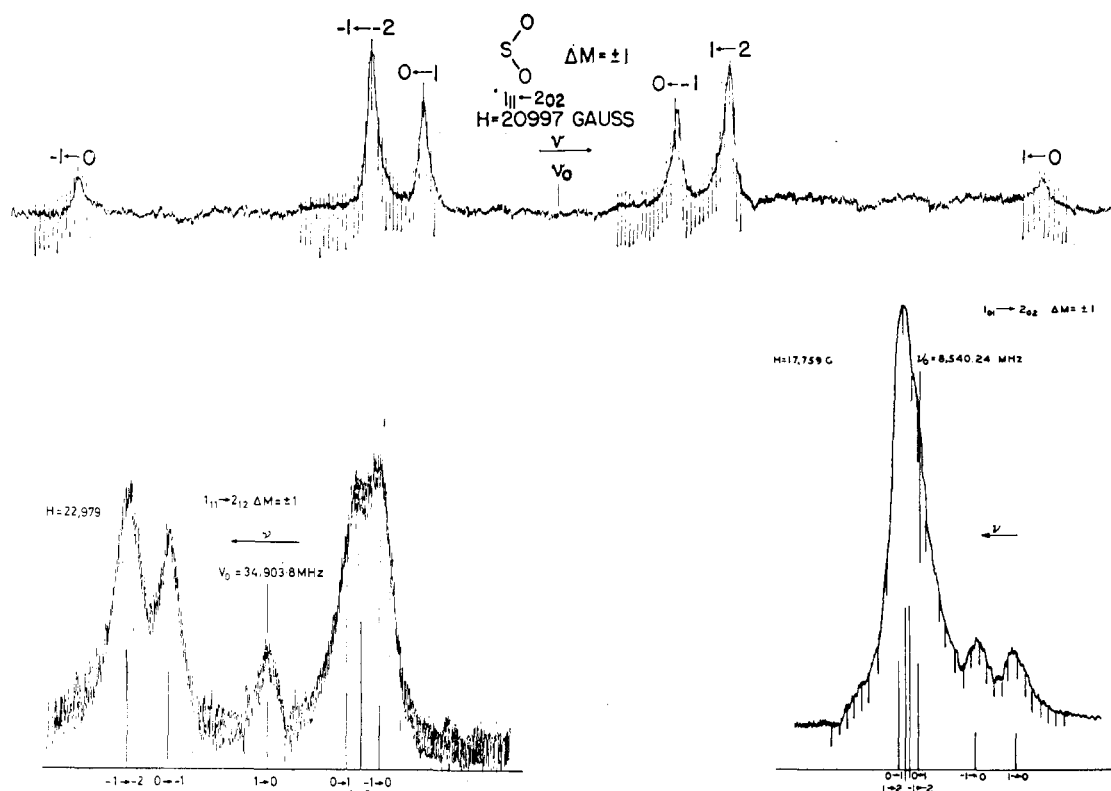


Figure 5. A series of spectra showing different relative contributions to the linear and quadratic Zeeman effect in the same $J = 1_{11} \rightarrow 2_{02}$ transitions in different molecules. The top spectra for SO_2 shows a nearly symmetric linear field Zeeman effect, $Hg > H^2\chi$ [J. M. Pochan, R. G. Stone, and W. H. Flygare, *J. Chem. Phys.*, **51**, 4278 (1969)]. The lower left shows an intermediate, $Hg \approx H^2\chi$, spectra for the same $1_{11} \rightarrow 2_{02}$ transition in ethylene sulfide [D. H. Sutter and W. H. Flygare, *Mol. Phys.*, **16**, 153 (1969)]. The lower right diagram shows the $1_{11} \rightarrow 2_{02}$ transition in fluorobenzene where $Hg < H^2\chi$ [W. Hüttner and W. H. Flygare, *J. Chem. Phys.*, **50**, 2863 (1969)].

very large Zeeman splittings, the accuracy of the magnetic field becomes critical. The complete molecular Zeeman results are listed, for example, in Table VII for pyridine, ethylene oxide, and formic acid. The corresponding complete sets of values for the other molecules listed in Tables I-VI can be found in the original references.

We will describe some of the interpretations of molecular Zeeman parameters in section VIII.

VI. Nuclear Magnetic Shielding and Nuclear Spin-Rotation Interactions

In section II we examined the rotational-electronic interactions which lead to the rotational Hamiltonian in eq 24. We also examined the external field-electronic interactions in section III with the resultant perturbation Hamiltonian in eq 31. Adding the nuclear rotation term in eq 34 gave the complete Hamiltonian in eq 35 and 36. Equation 35 is valid in the ab-

sence of nuclear-electronic interactions. In this section we will add in the effects of the nuclear-electronic interactions which give rise to the spin-rotation interaction and nuclear magnetic shielding.

The spin-rotation interaction arises, in the absence of any external fields, from the interaction of a nuclear magnetic moment with the intramolecular magnetic field at the nucleus due to the intrinsic electronic and rotational motion of the molecule. The internal field at the k th nucleus is given by a sum of electronic, H_e^k , and nuclear, H_n^k , terms

$$H^k = H_e^k + H_n^k = -\frac{e}{c} \sum_i \frac{\mathbf{r}_{ki} \times \mathbf{v}_{ki}}{r_{ki}^3} + \frac{e}{c} \sum_{\alpha} Z_{\alpha} \frac{\mathbf{r}_{k\alpha} \times \mathbf{v}_{k\alpha}}{r_{k\alpha}^3} \quad (79)$$

where all vectors originate at the k th nucleus which is indicated by \mathbf{r}_{ki} and $\mathbf{r}_{k\alpha}$. The sum over i is over all electrons in the

TABLE I. Molecular g Values, Electric Dipole Moments (and Signs), Magnetic Susceptibility Anisotropies, and Molecular Quadrupole Moments of a Number of Linear Molecules as Measured by Microwave Spectroscopy

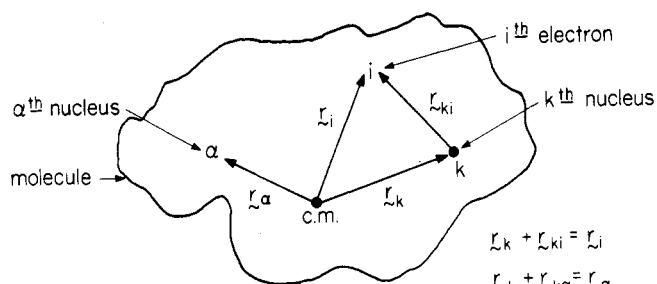
| | g_{\perp} | μ^a | $\chi_{\perp} - \chi_{\parallel}^b$ | Q_{\parallel}^c | Ref |
|---|-------------------------|------------------|-------------------------------------|-------------------|-----|
| $^{-10}\text{O}^{12}\text{C}^{32}\text{S}^+$ | -0.028711 ± 0.00004 | $+0.75 \pm 0.30$ | 9.27 ± 0.10 | -0.88 ± 0.15 | d |
| $^{15}\text{N}^{15}\text{N}^{16}\text{O}$ | -0.07606 ± 0.0001 | ... | 10.15 ± 0.15 | -3.65 ± 0.25 | d |
| $^{-16}\text{O}^{12}\text{C}^{80}\text{Se}^+$ | -0.01952 ± 0.0002 | $+0.9 \pm 1.9$ | 10.06 ± 0.18 | -0.32 ± 0.24 | d |
| $^{-12}\text{C}^{32}\text{S}^+$ | -0.2702 ± 0.0004 | $+2.7 \pm 1.0$ | 24.2 ± 1.2 | 0.8 ± 1.4 | e |
| $^{12}\text{C}^{80}\text{Se}$ | -0.2431 ± 0.0016 | ... | 27.8 ± 1.4 | -2.6 ± 1.6 | e |
| HC^{15}N | -0.0904 ± 0.0003 | ... | 7.2 ± 0.4 | 3.1 ± 0.6 | f |
| FC^{15}N | -0.0504 ± 0.0008 | ... | 7.2 ± 0.8 | -3.7 ± 1.0 | g |
| $^{35}\text{Cl}^{15}\text{N}^-$ | -0.0384 ± 0.0003 | -2.4 ± 3.6 | 10.8 ± 0.8 | -3.9 ± 1.0 | h |
| $^{79}\text{Br}^{15}\text{N}$ | -0.0325 ± 0.0010 | ... | 11.8 ± 1.0 | -6.0 ± 1.1 | h |
| FCCH | -0.0077 ± 0.0002 | ... | 5.2 ± 0.2 | 4.0 ± 0.2 | d |
| $^{-35}\text{Cl}^{12}\text{C}^+\text{H}$ | -0.00630 ± 0.00014 | -0.3 ± 0.2 | 9.3 ± 0.5 | 8.8 ± 0.4 | i |
| $^{79}\text{Br}^{12}\text{C}^+\text{H}$ | -0.00395 ± 0.00032 | ... | 9.5 ± 0.9 | 8.5 ± 1.1 | f |
| HCP | -0.0430 ± 0.0010 | ... | 8.4 ± 0.9 | 4.4 ± 1.2 | f |
| $^+\text{H}^{11}\text{B}^{32}\text{S}^-$ | -0.0414 ± 0.0002 | -2.7 ± 0.6 | 7.2 ± 0.5 | 2.7 ± 0.6 | j |

^a Units of 10^{-18} esu cm. These dipole moments and signs were obtained from Zeeman measurements according to eq 58. Of course, the magnitudes of these dipole moments can be determined very accurately by Stark or dielectric constant measurements. ^b Units in 10^{-6} erg/(G² mol). ^c Units in 10^{-26} esu cm². ^d See ref 5 for original literature references. ^e J. McGurk, H. L. Tigelaar, S. L. Rock, C. L. Norris, and W. H. Flygare, *J. Chem. Phys.*, **58**, 1420 (1973). ^f S. L. Hartford, W. C. Allen, C. L. Norris, E. F. Pearson, and W. H. Flygare, *Chem. Phys. Lett.*, **18**, 153 (1973). ^g S. L. Rock, J. C. McGurk, and W. H. Flygare, *ibid.*, **19**, 153 (1973). ^h J. J. Ewing, H. L. Tigelaar, and W. H. Flygare, *J. Chem. Phys.*, **56**, 1957 (1972). ⁱ W. C. Allen and W. H. Flygare, *Chem. Phys. Lett.*, **15**, 461 (1972). ^j E. F. Pearson, C. L. Norris, and W. H. Flygare, *J. Chem. Phys.*, **60**, 1761 (1974).

TABLE II. Molecular g Values, Electric Dipole Moments (and Signs), Magnetic Susceptibility Anisotropies, and Molecular Quadrupole Moments of a Number of Symmetric Tops

| | g_{\perp} | μ^a | g_{\parallel} | $\chi_{\perp} - \chi_{\parallel}^b$ | Q_{\parallel}^c | Ref |
|--|-----------------------|-----------------|----------------------|-------------------------------------|-------------------|-----|
| $^+\text{CH}_3\text{CCH}^-$ | $+0.0035 \pm 0.0002$ | -0.7 ± 0.2 | $+0.312 \pm 0.0002$ | 7.7 ± 0.2 | 4.8 ± 0.3 | e |
| CH_3CCCH | 0 ± 0.0005 | ... | $(0.310)^d$ | 13.1 ± 0.2 | 9.9 ± 0.8 | e |
| $\text{CH}_3^{14}\text{NC}$ | -0.0317 ± 0.003 | ... | $(0.310)^d$ | 13.5 ± 1.7 | -2.7 ± 1.6 | e |
| $^+\text{CH}_3\text{C}^{15}\text{N}^-$ | -0.0338 ± 0.0008 | $+3.5 \pm 1.5$ | $(0.310)^d$ | 10.2 ± 1.0 | -1.8 ± 1.2 | e |
| CH_3F | -0.062 ± 0.002 | ... | $+0.265 \pm 0.008$ | 8.5 ± 0.6 | -0.4 ± 1.0 | f |
| $^+\text{CH}_3^{35}\text{Cl}^-$ | -0.0165 ± 0.0003 | $+2.3 \pm 2.0$ | $(0.305)^d$ | 8.0 ± 0.5 | 1.2 ± 0.8 | e |
| $\text{CH}_3^{79}\text{Br}$ | -0.0057 ± 0.0003 | ... | $+0.294 \pm 0.016$ | 8.5 ± 0.4 | 3.6 ± 0.8 | e |
| $\text{CH}_3^{127}\text{I}$ | -0.0068 ± 0.0004 | ... | $+0.310 \pm 0.016$ | 11.0 ± 0.5 | 5.4 ± 0.9 | e |
| $^-\text{SiH}_3\text{CH}_3^+$ | -0.03583 ± 0.0001 | 0.96 ± 0.40 | $+0.0182 \pm 0.0069$ | 2.4 ± 0.2 | -6.3 ± 0.5 | g |

^a Units of 10^{-18} esu cm. ^b Units of 10^{-6} erg/(G² mol). ^c Units of 10^{-26} esu cm². ^d Assumed. ^e See ref 5 for original literature references. ^f C. L. Norris, E. F. Pearson, and W. H. Flygare, *J. Chem. Phys.*, **60**, 1758 (1974). ^g R. L. Shoemaker and W. H. Flygare, *J. Amer. Chem. Soc.*, **94**, 684 (1972).

**Figure 6.** The molecular coordinate system showing the vectors from the CM to the k th and α th nuclei and i th electron.

molecule, and the sum over α is over all nuclei (excluding k) with atomic number Z_{α} . A coordinate system showing these vectors in a molecule is given in Figure 6. In the presence of an external field \mathbf{H} we write the total field at the k th nucleus as

$$\mathbf{H}^k = \mathbf{H} + \mathbf{H}_e^k + \mathbf{H}_n^k = \mathbf{H} - \frac{e}{c} \sum_i \frac{\mathbf{r}_{ki} \times \mathbf{v}_{ki}}{r_{ki}^3} + \frac{e}{c} \sum_{\alpha} Z_{\alpha} \frac{\mathbf{r}_{k\alpha} \times \mathbf{v}_{k\alpha}}{r_{k\alpha}^3} \quad (80)$$

The pure nuclear term in eq 80 can be rewritten by remembering that $\mathbf{v}_{k\alpha}$ and $\mathbf{r}_{k\alpha}$ depend only on the nuclear coordinates in a nonvibrating molecule, giving

$$\mathbf{v}_{k\alpha} = \boldsymbol{\omega} \times \mathbf{r}_{k\alpha}$$

Substituting into \mathbf{H}_n^k in eq 80 gives

$$\begin{aligned} \mathbf{H}_n^k &= \frac{e}{c} \sum_{\alpha} Z_{\alpha} \frac{\mathbf{r}_{k\alpha} \times \mathbf{v}_{k\alpha}}{r_{k\alpha}^3} = \frac{e}{c} \sum_{\alpha} Z_{\alpha} \frac{\mathbf{r}_{k\alpha} \times (\boldsymbol{\omega} \times \mathbf{r}_{k\alpha})}{r_{k\alpha}^3} = \\ &= \frac{e}{c} \sum_{\alpha} Z_{\alpha} (\mathbf{r}_{k\alpha}^2 \boldsymbol{\omega} - \mathbf{r}_{k\alpha} \mathbf{r}_{k\alpha}) \cdot \boldsymbol{\omega} = \\ &= \frac{e}{c} \sum_{\alpha} Z_{\alpha} (\mathbf{r}_{k\alpha}^2 \mathbf{1} - \mathbf{r}_{k\alpha} \mathbf{r}_{k\alpha}) \cdot \mathbf{I}_n^{-1} \cdot (\mathbf{J} - \mathbf{L}) \quad (81) \end{aligned}$$

where $\boldsymbol{\omega} = \mathbf{I}_n^{-1} \cdot (\mathbf{J} - \mathbf{L})$ from eq 23 has also been used.

The electronic term can also be rewritten to reflect the influences of the magnetic field. The electronic velocity vector of an electron in the presence of a magnetic field is given in eq 25. Substituting $\mathbf{v}_i = \mathbf{p}_i + (e/c)\mathbf{A}$ in eq 25 into \mathbf{H}_e^k in eq 80 gives

$$\mathbf{H}_e^k = -\frac{e}{mc} \sum_i \frac{\mathbf{r}_{ki}}{r_{ki}^3} \times (\mathbf{p}_{ki} + \frac{e}{2c} \mathbf{H} \times \mathbf{r}_i) \quad (82)$$

where \mathbf{p}_{ki} is the i th electron's linear momentum in the absence of the field, and we have also used $\mathbf{A} = \frac{1}{2}\mathbf{H} \times \mathbf{r}$ from eq 29. Expanding and using $\mathbf{A} \times \mathbf{B} \times \mathbf{C} = \mathbf{B}(\mathbf{A} \cdot \mathbf{C}) - \mathbf{A}(\mathbf{B} \cdot \mathbf{C})$ gives

$$\mathbf{H}_e^k = -\frac{e}{mc} \sum_i \frac{\mathbf{L}_{ki}}{r_{ki}^3} - \frac{e^2}{2mc^2} \sum_i \frac{(\mathbf{r}_{ki}^2 \mathbf{1} - \mathbf{r}_{ki} \mathbf{r}_{ki}) \cdot \mathbf{H}}{r_{ki}^3} \quad (83)$$

where $\mathbf{L}_{ki} = \mathbf{r}_{ki} \times \mathbf{p}_{ki}$. Combining eq 83 and 81 into eq 80 gives the field at the nucleus.

TABLE III. Molecular g Values, Magnetic Susceptibility Anisotropies, and Molecular Quadrupole Moments in Some Nonring Planar Asymmetric Tops^a


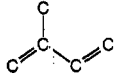
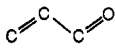

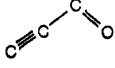






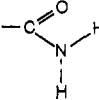
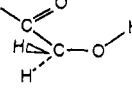
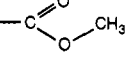
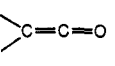



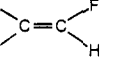
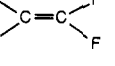
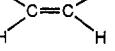
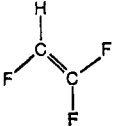
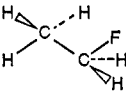






|  | g_{zz} g_{yy} g_{zz} | $2\chi_{yy} - \chi_{yy} - \chi_{zz}$ $-\chi_{zz} + 2\chi_{yy} - \chi_{zz}$ | Q_{zz} Q_{yy} Q_{zz} |
|---|--|---|--|
|  | -0.0621 ± 0.0013 -0.0339 ± 0.0016 +0.0080 ± 0.0016 | +16.7 ± 1.2 +19.2 ± 1.0 | +1.7 ± 2.2 +3.3 ± 2.3 -5.0 ± 3.2 |
|  | -0.5512 ± 0.0019 -0.0567 ± 0.0010 -0.0080 ± 0.0010 | +24.1 ± 0.9 +17.1 ± 1.5 | -2.5 ± 1.1 +3.3 ± 1.7 -0.8 ± 2.2 |
|  | -0.0789 ± 0.0006 -0.0424 ± 0.0004 +0.0107 ± 0.0005 | -0.7 ± 0.3 +13.4 ± 0.5 | +0.6 ± 0.3 +2.9 ± 0.5 -3.5 ± 0.7 |
|  | -0.553 ± 0.002 -0.040 ± 0.002 -0.015 ± 0.001 | +4.4 ± 0.8 +9.0 ± 1.6 | +3.1 ± 1.3 +1.1 ± 2.2 -4.2 ± 2.4 |
|  | -0.0214 ± 0.0006 -0.0093 ± 0.0004 -0.0210 ± 0.0006 | -10.4 ± 0.7 +1.2 ± 0.6 | +3.3 ± 0.6 -2.0 ± 0.5 -1.3 ± 1.0 |
|  | -0.0193 ± 0.0007 0.0000 ± 0.0003 -0.0083 ± 0.0003 | -4.2 ± 0.5 -2.8 ± 0.5 | +3.2 ± 0.5 -1.5 ± 0.5 -1.7 ± 0.8 |
|  | -0.3609 ± 0.0021 -0.0731 ± 0.0003 -0.0245 ± 0.0006 | +8.1 ± 2.5 +9.6 ± 1.4 | -1.2 ± 1.5 +1.0 ± 0.9 +0.2 ± 1.8 |
|  | -2.9017 ± 0.0008 -0.2243 ± 0.0001 -0.0994 ± 0.0001 | +25.5 ± 0.5 -3.9 ± 0.3 | -0.1 ± 0.3 +0.2 ± 0.2 -0.1 ± 0.5 |
|  | -5.6202 ± 0.0068 -0.1337 ± 0.0004 -0.0239 ± 0.0004 | +52.3 ± 1.1 -5.1 ± 0.7 | +3.0 ± 0.7 -2.4 ± 0.5 -0.6 ± 1.1 |
|  | -0.0903 ± 0.0006 -0.2797 ± 0.0060 -0.0270 ± 0.0006 | +9.4 ± 0.3 +3.4 ± 0.5 | +5.2 ± 0.6 -5.3 ± 0.6 +0.1 ± 0.6 |
|  | -0.0649 ± 0.0004 -0.2843 ± 0.0011 -0.0117 ± 0.0004 | +8.0 ± 0.5 +2.2 ± 0.7 | +3.4 ± 0.4 -0.3 ± 0.5 -3.1 ± 0.8 |
|  | -0.0726 ± 0.0010 -0.1239 ± 0.0013 -0.0178 ± 0.0010 | +18.8 ± 2.0 +7.1 ± 2.5 | +3.8 ± 1.9 -5.6 ± 2.0 +1.8 ± 3.3 |
|  | -0.0391 ± 0.0009 -0.1267 ± 0.0010 -0.0167 ± 0.0016 | +3.1 ± 0.9 +11.0 ± 0.9 | 0.4 ± 0.9 -1.6 ± 0.8 1.2 ± 1.3 |
|  | -0.4182 ± 0.0009 -0.0356 ± 0.0013 -0.0238 ± 0.0006 | -5.0 ± 0.7 -0.2 ± 0.6 | -0.7 ± 0.3 +3.8 ± 0.4 -3.1 ± 0.4 |
|  | -0.0411 ± 0.0004 -0.0725 ± 0.0006 -0.0398 ± 0.0004 | +0.8 ± 0.4 -3.9 ± 0.5 | +1.9 ± 0.3 -4.1 ± 0.4 +2.2 ± 0.6 |
|  | -0.0568 ± 0.0006 -0.0747 ± 0.0004 -0.0328 ± 0.0006 | -1.6 ± 0.9 -5.3 ± 0.6 | -3.7 ± 0.7 -0.2 ± 0.5 +3.9 ± 1.1 |
|  | -0.4227 ± 0.0007 -0.0771 ± 0.0002 -0.0371 ± 0.0002 | +6.1 ± 0.3 +5.9 ± 0.3 | -4.5 ± 0.2 +2.6 ± 0.2 +1.9 ± 0.4 |
|  | -0.1533 ± 0.0008 -0.0526 ± 0.0001 -0.0037 ± 0.0001 | -0.8 ± 0.2 +9.6 ± 0.2 | -0.2 ± 0.2 +3.1 ± 0.2 -2.9 ± 0.3 |
|  | -0.0421 ± 0.0005 -0.0466 ± 0.0004 -0.0119 ± 0.0004 | -2.3 ± 0.6 +7.7 ± 0.5 | +2.4 ± 0.5 -0.9 ± 0.4 -1.5 ± 0.8 |
|  | -0.1015 ± 0.0009 -0.0296 ± 0.0003 -0.0158 ± 0.0002 | +5.7 ± 0.4 -1.6 ± 0.3 | -1.7 ± 0.4 +3.0 ± 0.3 -1.3 ± 0.5 |

TABLE III (Continued)

| | | | |
|---|--|----------------------------------|--|
|  | -0.0503 ± 0.0002 -0.0321 ± 0.0002 -0.0170 ± 0.0002 | -4.2 ± 0.2 +7.7 ± 0.3 | -3.5 ± 0.3 +2.7 ± 0.4 +0.8 ± 0.5 |
|  | +0.0185 ± 0.0006 -0.0124 ± 0.0003 -0.0197 ± 0.0004 | -6.6 ± 0.4 -0.7 ± 0.5 | -2.0 ± 0.4 +1.3 ± 0.4 +0.7 ± 0.7 |
|  | -2.968 ± 0.035 -0.228 ± 0.007 -0.081 ± 0.006 | +98.0 ± 5.6 -17.4 ± 4.4 | -17.1 ± 5.2 +9.2 ± 4.7 +7.9 ± 7.9 |
|  | -0.6037 ± 0.0005 -0.1161 ± 0.0002 -0.0882 ± 0.0004 | +6.4 ± 0.5 +3.1 ± 0.3 | -5.3 ± 0.4 +1.3 ± 0.3 +4.0 ± 0.6 |
|  | -0.213 ± 0.005 -0.058 ± 0.002 -0.068 ± 0.002 | -8.8 ± 1.4 -4.4 ± 0.7 | -1.6 ± 1.4 +2.1 ± 1.1 -0.5 ± 1.9 |
|  | +0.642 ± 0.001 -0.119 ± 0.001 -0.061 ± 0.001 | -19.6 ± 0.6 +12.8 ± 1.2 | 0.2 ± 0.4 1.9 ± 0.8 -2.1 ± 1.1 |
|  | +0.718 ± 0.007 +0.657 ± 0.001 +0.645 ± 0.006 | -0.199 ± 0.048 +0.464 ± 0.024 | -0.13 ± 0.03 +2.63 ± 0.02 -2.50 ± 0.02 |
|  | 0.355 ± 0.008 0.195 ± 0.008 0.209 ± 0.008 | | |

^a The dipole moment signs are also listed when appropriate. The units are the same as in Tables I and II. References are from ref 5 unless indicated. ^b S. L. Rock and W. H. Flygare, *J. Chem. Phys.*, **56**, 4723 (1972). ^c S. L. Rock, E. F. Pearson, E. Appleman, C. L. Norris, and W. H. Flygare, *J. Chem. Phys.*, **59**, 3940 (1973).

$$\mathbf{H}^k = \mathbf{H} - \frac{e}{mc} \sum_i \frac{\mathbf{L}_{ki}}{r_{ki}^3} - \frac{e^2}{2mc^2} \sum_i \left[\frac{r_{ki}^2 \mathbf{1} - r_{ki} r_{ki}}{r_{ki}^3} \right] \cdot \mathbf{H} + \frac{e}{c} \sum_{\alpha} \frac{Z_{\alpha}}{r_{k\alpha}^3} (r_{k\alpha}^2 \mathbf{1} - r_{k\alpha} r_{k\alpha}) \cdot \mathbf{I}_n^{-1} \cdot (\mathbf{J} - \mathbf{L}) \quad (84)$$









The energy of the interaction of the magnetic dipole moment of the k th nucleus, μ^k , with the field at the k th nucleus, \mathbf{H}^k in eq 84, is given by eq 85. $\gamma_k = (\mu_0/\hbar) g_k$ is the gyromagnetic

$$\mathcal{H}_n = -\mu^k \cdot \mathbf{H}^k = -\gamma_k \mathbf{I}_k \cdot \mathbf{H}^k = -\frac{\mu_0}{\hbar} g_k \mathbf{I}_k \cdot \mathbf{H}^k = -\gamma_k \mathbf{I}_k \cdot \mathbf{H} + \frac{e}{mc} \gamma_k \mathbf{I}_k \cdot \sum_i \frac{\mathbf{L}_{ki}}{r_{ki}^3} + \frac{e^2}{2mc^2} \gamma_k \mathbf{I}_k \cdot \sum_i \left(\frac{r_{ki}^2 \mathbf{1} - r_{ki} r_{ki}}{r_{ki}^3} \right) \cdot \mathbf{H} - \frac{e}{c} \gamma_k \mathbf{I}_k \cdot \sum_{\alpha} \frac{Z_{\alpha}}{r_{k\alpha}^3} (r_{k\alpha}^2 \mathbf{1} - r_{k\alpha} r_{k\alpha}) \cdot \mathbf{I}_n^{-1} \cdot \mathbf{J} + \frac{e}{c} \gamma_k \mathbf{I}_k \cdot \sum_{\alpha} \frac{Z_{\alpha}}{r_{k\alpha}^3} (r_{k\alpha}^2 \mathbf{1} - r_{k\alpha} r_{k\alpha}) \cdot \mathbf{I}_n^{-1} \cdot \mathbf{L} \quad (85)$$

ratio of the k th nucleus, $\mu_0 = \hbar e/2M_p c = 0.50508 \times 10^{-23}$ erg/G is the nuclear magneton, g_k is the nuclear g value, and \mathbf{I}_k is the nuclear angular momentum of the k th nucleus. We now combine the results in eq 36 and 85 to give the complete Hamiltonian including the nuclear terms (eq 86). ω' is defined

$$\mathcal{H} = \mathcal{H}' + \mathcal{H}_n = \frac{1}{2} \mathbf{J} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{J} - \mathbf{L} \cdot \omega' + \frac{1}{2} \mathbf{L} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{L} + \frac{e^2}{8c^2 m} \mathbf{H} \cdot \sum_i (r_i^2 \mathbf{1} - r_i r_i) \cdot \mathbf{H} - \frac{e}{2c} \sum_{\alpha} Z_{\alpha} \mathbf{H} \cdot (r_{\alpha}^2 \mathbf{1} - r_{\alpha} r_{\alpha}) \cdot \mathbf{I}_n^{-1} \cdot \mathbf{J} - \gamma_k \mathbf{I}_k \cdot \mathbf{H} + \frac{e}{mc} \gamma_k \mathbf{I}_k \cdot \sum_i \frac{\mathbf{L}_{ki}}{r_{ki}^3} + \frac{e^2}{2mc^2} \gamma_k \mathbf{I}_k \cdot \sum_i \left(\frac{r_{ki}^2 \mathbf{1} - r_{ki} r_{ki}}{r_{ki}^3} \right) \cdot \mathbf{H} - \frac{e}{c} \gamma_k \mathbf{I}_k \cdot \sum_{\alpha} \frac{Z_{\alpha}}{r_{k\alpha}^3} (r_{k\alpha}^2 \mathbf{1} - r_{k\alpha} r_{k\alpha}) \cdot \mathbf{I}_n^{-1} \cdot (\mathbf{J} - \mathbf{L}) \quad (86)$$












TABLE IV. Molecular g Values, Magnetic Susceptibility Anisotropies, and Molecular Quadrupole Moments for a Series of Three-Membered Rings^a

|  | g_{xx} g_{yy} g_{zz} | $2\chi_{xx} - \chi_{yy} - \chi_{zz}$ $-\chi_{xx} + 2\chi_{yy} + \chi_{zz}$ | Q_{xx} Q_{yy} Q_{zz} |
|---|--|---|--|
|  | -0.0672 ± 0.0007 -0.0231 ± 0.0004 +0.0244 ± 0.0004 | 18.3 ± 0.5 14.9 ± 0.6 | -0.7 ± 0.5 +0.9 ± 0.6 -0.2 ± 0.9 |
|  | -0.0897 ± 0.0009 -0.1492 ± 0.0002 +0.0536 ± 0.0002 | 7.1 ± 0.6 26.8 ± 0.4 | -0.4 ± 0.4 +2.4 ± 0.3 -2.0 ± 0.6 |
|  | +0.0229 ± 0.0009 -0.0422 ± 0.0008 +0.0539 ± 0.0010 | 4.6 ± 0.8 16.5 ± 0.7 | -2.6 ± 0.6 +1.3 ± 0.6 +1.3 ± 0.6 |
|  | +0.0189 ± 0.0004 -0.0946 ± 0.0003 0.0318 ± 0.0006 | 0.8 ± 1.0 18.1 ± 0.6 | -4.3 ± 0.5 +2.5 ± 0.4 +1.8 ± 0.8 |
|  | -0.0159 ± 0.0021 -0.0242 ± 0.0003 +0.0487 ± 0.0004 | 12.1 ± 0.9 18.7 ± 0.6 | -0.5 ± 0.7 +1.2 ± 0.8 -0.7 ± 0.7 |
|  | -0.2900 ± 0.0013 -0.0963 ± 0.0004 -0.0121 ± 0.0004 | 13.5 ± 0.1 22.0 ± 0.8 | -3.0 ± 0.9 4.0 ± 0.7 -1.0 ± 1.3 |
|  | -0.0813 ± 0.007 -0.0261 ± 0.004 +0.0166 ± 0.003 | 13.9 ± 0.3 16.4 ± 0.6 | +0.6 ± 0.4 -0.3 ± 0.6 -0.3 ± 0.8 |

^a The units are the same as in Tables I and II. References are from ref 5 unless indicated. ^b R. C. Benson, W. H. Flygare, M. Oda, and R. Breslow, *J. Amer. Chem. Soc.*, **95**, 2772 (1973). ^c R. C. Benson and W. H. Flygare, *J. Chem. Phys.*, **58**, 2651 (1973).

in eq 36. We now use perturbation theory to examine the contributions to the energy. We have examined in detail the contribution due to \mathcal{H}' (eq 36) in section IV. We now examine

TABLE V. Molecular g Values, Magnetic Susceptibility Anisotropies, and Molecular Quadrupole Moments for a Series of Planar Four-Membered Rings^a

|  | g_{zz} g_{yy} g_{zz} | $2\chi_{zz} - \chi_{yy} - \chi_{zz}$ $-2\chi_{yy} - \chi_{zz} - \chi_{zz}$ | Q_{zz} Q_{yy} Q_{zz} | Ref |
|---|--|---|--|-----|
|  | -0.0516 ± 0.0007 -0.0663 ± 0.0007 -0.0219 ± 0.0006 | -0.9 ± 0.5 +5.0 ± 0.7 | -0.3 ± 0.6 +1.6 ± 0.7 -1.3 ± 1.0 | 5 |
|  | -0.0532 ± 0.0007 -0.0703 ± 0.0007 +0.0023 ± 0.0007 | 21.2 ± 0.6 22.1 ± 0.7 | +4.0 ± 1.2 +4.0 ± 1.2 -8.0 ± 1.8 | b |
|  | -0.0073 ± 0.0005 -0.0429 ± 0.0007 -0.0747 ± 0.0005 | -20.1 ± 0.5 -13.5 ± 0.8 | -4.9 ± 0.5 +2.3 ± 0.7 +2.6 ± 1.0 | 5 |
|  | -0.0148 ± 0.0010 -0.0169 ± 0.0006 -0.0554 ± 0.0005 | -20.9 ± 1.0 -24.6 ± 1.0 | -2.7 ± 1.0 +3.2 ± 1.0 -0.5 ± 1.6 | 5 |
|  | -0.0320 ± 0.0008 -0.0218 ± 0.0010 -0.0184 ± 0.0011 | -6.4 ± 0.5 +4.3 ± 1.7 | -1.2 ± 1.1 -1.1 ± 2.0 +2.3 ± 2.4 | 5 |
|  | -0.0740 ± 0.0020 -0.0325 ± 0.0004 -0.0279 ± 0.0004 | 14.8 ± 0.9 -10.6 ± 1.0 | -9.4 ± 1.2 +4.6 ± 1.1 +4.8 ± 1.7 | 5 |
|  | -0.1059 ± 0.0008 -0.0581 ± 0.0004 -0.0437 ± 0.0004 | 9.6 ± 0.5 -7.8 ± 0.6 | -12.8 ± 0.8 7.9 ± 0.8 4.9 ± 0.8 | c |
|  | -0.0510 ± 0.002 -0.0435 ± 0.001 -0.0313 ± 0.001 | -10.9 ± 4.7 2.3 ± 0.9 | -5.4 ± 1.0 5.1 ± 1.2 0.2 ± 1.5 | c |
|  | -0.0758 ± 0.0005 -0.0356 ± 0.0004 -0.0319 ± 0.0004 | -0.5 ± 0.3 1.7 ± 0.4 | -3.1 ± 0.4 -1.9 ± 0.5 5.0 ± 0.5 | d |
|  | -0.1091 ± 0.0004 -0.0324 ± 0.0004 -0.0169 ± 0.0004 | 2.3 ± 0.9 12.1 ± 0.4 | -2.5 ± 0.9 1.5 ± 0.8 1.0 ± 1.3 | d |

^a The units are the same as in Tables I and II. ^b R. C. Benson and W. H. Flygare, Flygare, *J. Chem. Phys.*, **58**, 2366 (1973). ^c C. L. Norris, H. L. Tigelaar, and W. H. Flygare, *Chem. Phys.*, **1**, 1 (1973). ^d H. L. Tigelaar, T. D. Gierke, and W. H. Flygare, *J. Chem. Phys.*, **56**, 1966 (1972).

only the additional effects due to the addition of \mathcal{H}_n (eq 85) above to give the complete Hamiltonian. Using the zero-order electronic basis in eq 37, we have in eq 87 and 88 additional

First order

$$E^{(1)} = -\gamma_{kl} \mathbf{k} \cdot \mathbf{H} + \frac{e^2}{2mc^2} \gamma_{kl} \mathbf{k} \cdot \left\langle 0 \left| \sum_i \frac{r_{ki}^2 \mathbf{1} - r_{ki} r_{ki}}{r_{ki}^3} \right| 0 \right\rangle \cdot \mathbf{H} - \frac{e}{c} \gamma_{kl} \mathbf{k} \cdot \sum_{\alpha} \frac{Z_{\alpha}}{r_{k\alpha}^3} (r_{k\alpha}^2 \mathbf{1} - r_{k\alpha} r_{k\alpha}) \cdot \mathbf{I}_n^{-1} \cdot \mathbf{J} \quad (87)$$

Second order

$$E^{(2)} = \frac{e^2}{2m^2 c^2} \gamma_{kl} \mathbf{k} \cdot \left\{ \sum_{k>0} \frac{\langle 0 | \sum_i \frac{\mathbf{L}_{ki}}{r_{ki}^3} | k \rangle \langle k | \mathbf{L} | 0 \rangle + \text{CC}}{E_0 - E_k} \right\} \cdot \mathbf{H} - 2 \frac{e}{c} \gamma_{kl} \mathbf{k} \cdot \sum_{\alpha} \frac{Z_{\alpha}}{r_{k\alpha}^3} (r_{k\alpha}^2 \mathbf{1} - r_{k\alpha} r_{k\alpha}) \cdot \mathbf{I}_n^{-1} \cdot \mathbf{A} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{J} - \frac{e}{mc} \gamma_{kl} \mathbf{k} \cdot \left\{ \sum_{k>0} \frac{\langle 0 | \sum_i \frac{\mathbf{L}_{ki}}{r_{ki}^3} | k \rangle \langle k | \mathbf{L} | 0 \rangle + \text{CC}}{E_0 - E_k} \right\} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{J} + \text{higher order terms} \quad (88)$$

contributions to the results considered previously in eq 38 and 39. CC means the complex conjugate of the preceding term. Combining the first- and second-order terms and dropping the higher order terms give the energy which still depends on the rotational state J (eq 89). $\mathbf{I}_{\text{eff}}^{-1}$ is defined in eq

$$\mathcal{H} = -\gamma_{kl} \mathbf{k} \cdot (1 - \sigma) \cdot \mathbf{H} - \frac{e}{c} \gamma_{kl} \mathbf{k} \cdot \sum_{\alpha} \frac{Z_{\alpha}}{r_{k\alpha}^3} (r_{k\alpha}^2 \mathbf{1} - r_{k\alpha} r_{k\alpha}) \cdot \mathbf{I}_n^{-1} \cdot \mathbf{J} - \frac{e}{mc} \gamma_{kl} \mathbf{k} \cdot \left\{ \sum_{k>0} \frac{\langle 0 | \sum_i \frac{\mathbf{L}_{ki}}{r_{ki}^3} | k \rangle \langle k | \mathbf{L} | 0 \rangle + \text{CC}}{E_0 - E_k} \right\} \cdot \mathbf{I}_n^{-1} \cdot \mathbf{J}$$

$$\sigma = \sigma^d + \sigma^p$$



















$$\sigma^d = \frac{e^2}{2mc^2} \langle 0 | \sum_i \frac{r_{ki}^2 \mathbf{1} - r_{ki} r_{ki}}{r_{ki}^3} | 0 \rangle$$

$$\sigma^p = \frac{e^2}{2m^2 c^2} \sum_{k>0} \frac{\langle 0 | \sum_i \frac{\mathbf{L}_{ki}}{r_{ki}^3} | k \rangle \langle k | \mathbf{L} | 0 \rangle + \text{CC}}{E_0 - E_k} \quad (89)$$

41. σ^d and σ^p are the diamagnetic and paramagnetic nuclear magnetic shielding tensors with individual diagonal elements given by²² eq 90 and cyclic permutations for σ_{yy} and σ_{zz} .

$$\sigma_{xx} = \sigma_{xx}^d + \sigma_{xx}^p = \frac{e^2}{2mc^2} \langle 0 | \sum_i \frac{(y_{ki}^2 + z_{ki}^2)}{r_{ki}^3} | 0 \rangle + \frac{e^2}{2m^2 c^2} \sum_{k>0} \times \left[\frac{\langle 0 | \sum_i \frac{(\mathbf{L}_{ki})_x}{r_{ki}^3} | k \rangle \langle k | L_x | 0 \rangle + \langle 0 | L_x | k \rangle \langle k | \sum_i \frac{(\mathbf{L}_{ki})_x}{r_{ki}^3} | 0 \rangle}{E_0 - E_k} \right] \quad (90)$$

TABLE VI. Molecular g Values, Magnetic Susceptibility Anisotropies, and Molecular Quadrupole Moments of a Number of Planar Ring Compounds^a

|  | g_{xx} g_{yy} g_{zz} | $2\chi_{xx} - \chi_{yy} - \chi_{zz}$ $-\chi_{xx} + 2\chi_{yy} - \chi_{zz}$ | Q_{xx} Q_{yy} Q_{zz} | Ref |
|---|--|---|--|-----|
|  | -0.0670 ± 0.0008 -0.0397 ± 0.0015 $+0.0266 \pm 0.0017$ | 52.9 ± 0.8 63.6 ± 1.5 | -1.9 ± 0.8 $+5.1 \pm 1.0$ -3.2 ± 1.0 | 5 |
|  | -0.0770 ± 0.0005 -0.1010 ± 0.0008 $+0.0428 \pm 0.0004$ | 54.3 ± 0.6 60.5 ± 0.8 | -3.5 ± 0.9 $+9.7 \pm 1.1$ -6.2 ± 1.5 | 5 |
|  | -0.0880 ± 0.0007 -0.0405 ± 0.0006 $+0.0233 \pm 0.0006$ | 50.5 ± 1.6 53.7 ± 1.1 | 4.6 ± 1.8 2.8 ± 1.7 -7.4 ± 2.7 | b |
|  | -0.0433 ± 0.0011 -0.0400 ± 0.0024 -0.0062 ± 0.0009 | 9.1 ± 2.2 5.7 ± 1.6 | $+3.2 \pm 2.8$ $+2.7 \pm 2.8$ -5.9 ± 3.8 | 5 |
|  | -0.0827 ± 0.0003 -0.0700 ± 0.0003 $+0.0385 \pm 0.0002$ | 37.8 ± 0.3 30.7 ± 0.3 | $+3.7 \pm 0.4$ $+1.4 \pm 0.4$ -5.1 ± 0.5 | 5 |
|  | -0.0895 ± 0.0010 -0.0643 ± 0.0010 $+0.0752 \pm 0.0010$ | 50.2 ± 1.0 34.6 ± 1.8 | $+6.6 \pm 1.2$ $+5.8 \pm 1.6$ -12.4 ± 2.5 | 5 |
|  | -0.0911 ± 0.0007 -0.0913 ± 0.0002 $+0.0511 \pm 0.0001$ | 43.0 ± 0.2 34.4 ± 0.2 | $+0.2 \pm 0.4$ $+5.9 \pm 0.3$ -6.1 ± 0.4 | 5 |
|  | -0.0862 ± 0.0023 -0.0662 ± 0.0006 $+0.0501 \pm 0.0005$ | 49.6 ± 1.1 50.6 ± 1.3 | $+1.7 \pm 1.6$ $+6.6 \pm 1.5$ -8.3 ± 2.2 | 5 |
|  | -0.0849 ± 0.0012 -0.0428 ± 0.0011 $+0.3650 \pm 0.0010$ | 50.2 ± 0.8 51.8 ± 1.3 | 2.1 ± 1.7 6.5 ± 2.2 -8.6 ± 2.8 | c |
|  | -0.0856 ± 0.0016 -0.0502 ± 0.0009 -0.0112 ± 0.0010 | 7.2 ± 1.2 21.7 ± 1.4 | -1.1 ± 1.8 $+0.9 \pm 1.9$ $+0.2 \pm 2.8$ | 5 |
|  | -0.0499 ± 0.0014 -0.1131 ± 0.0010 -0.0150 ± 0.0012 | 22.9 ± 1.5 30.3 ± 2.0 | $+5.9 \pm 3.2$ -11.6 ± 3.0 $+5.7 \pm 4.4$ | d |
|  | -0.0914 ± 0.001 -0.0503 ± 0.001 -0.0122 ± 0.001 | 25.3 ± 1.0 8.3 ± 1.1 | -7.1 ± 1.6 8.1 ± 1.8 -1.0 ± 2.4 | e |
|  | -0.0868 ± 0.002 -0.0501 ± 0.001 -0.0048 ± 0.001 | 28.7 ± 1.4 9.3 ± 1.5 | -7.2 ± 2.0 12.0 ± 2.1 -4.8 ± 3.0 | e |
|  | -0.1059 ± 0.0014 -0.0482 ± 0.0007 $+0.0219 \pm 0.0007$ | 35.9 ± 0.7 38.1 ± 1.1 | 5.8 ± 1.4 3.6 ± 1.6 -9.4 ± 2.1 | c |
|  | -0.0771 ± 0.0021 -0.0542 ± 0.001 -0.0093 ± 0.001 | 23.9 ± 1.4 21.9 ± 2.0 | -11.2 ± 2.7 $+13.8 \pm 3.0$ -1.9 ± 4.0 | f |
|  | -0.0753 ± 0.0016 -0.0488 ± 0.0011 -0.0059 ± 0.0010 | 22.1 ± 1.2 27.4 ± 1.4 | -4.7 ± 2.7 $+5.6 \pm 2.6$ -0.9 ± 3.4 | f |
|  | | 32.1 ± 3.9 39.8 ± 5.6 | | f |


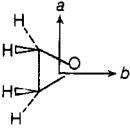
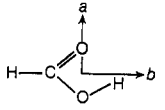
^a Units are the same as in Tables I and II. ^b D. Sutter, *Z. Naturforsch. A*, **26**, 1644 (1971). ^c W. Gzieslik, D. Sutter, H. Dreizler, C. L. Norris, S. L. Rock, and W. H. Flygare, *ibid.*, **27**, 1692 (1972). ^d R. C. Benson and W. H. Flygare, *J. Chem. Phys.*, **58**, 2366 (1973). ^e C. L. Norris, R. C. Benson, and W. H. Flygare, *Chem. Phys. Lett.*, **10**, 75 (1971). ^f Reference 21.

It is evident that σ_{xx}^d is the diamagnetic and σ_{xx}^p is the paramagnetic shielding. The diamagnetic shielding is always positive and decreases the net field at the nucleus. σ_{xx}^p is normally negative, as $E_0 < E_k$, leading to an enhanced magnetic field at the nucleus. Therefore, we see from eq 90 that the average field at the nucleus is equal to the laboratory field

plus a paramagnetic and minus a diamagnetic field, both of these later effects (fields) being caused by the electrons. In atoms, the paramagnetic term in eq 89 goes to zero as $\langle k | L | 0 \rangle = (L)_{av} \langle k | 0 \rangle = 0$.

Most measurements of magnetic shielding in molecules are done in the liquid or gas phases, which gives only the average

TABLE VII. Molecular Zeeman Parameters in Pyridine, Ethylene Oxide, and Formic Acid Which Include the Molecular Quadrupole Moments, Second Moment of the Charge Distributions, and the Magnetic Susceptibility^a

| |  |  |  |
|---|---|--|---|
| g_{aa} | -0.0770 ± 0.0005 | -0.0946 ± 0.0003 | -0.2797 ± 0.006 |
| g_{bb} | -0.1010 ± 0.0008 | 0.0189 ± 0.0004 | -0.0903 ± 0.0006 |
| g_{cc} | 0.0428 ± 0.0004 | 0.0318 ± 0.0006 | -0.0270 ± 0.0006 |
| $2\chi_{aa} - \chi_{bb} - \chi_{cc}$ | 54.3 ± 0.6 | 18.06 ± 0.57 | 3.4 ± 0.5 |
| $2\chi_{bb} - \chi_{aa} - \chi_{cc}$ | 60.5 ± 0.8 | 0.78 ± 0.97 | 9.4 ± 0.3 |
| Q_{aa} | -3.5 ± 0.9 | 2.5 ± 0.4 | -5.3 ± 0.4 |
| Q_{bb} | 9.7 ± 1.1 | -4.3 ± 0.5 | 5.2 ± 0.4 |
| Q_{cc} | -6.2 ± 1.5 | 1.8 ± 0.8 | 0.1 ± 0.4 |
| χ_{aa}^P | 241.5 ± 1.5 | 60.7 ± 0.8 | 28.8 ± 0.1 |
| χ_{bb}^P | 247.4 ± 2.0 | 67.3 ± 1.5 | 106.5 ± 0.1 |
| χ_{cc}^P | 393.9 ± 2.0 | 88.4 ± 2.0 | 117.2 ± 0.1 |
| $\langle a^2 \rangle - \langle b^2 \rangle$ | 0.92 ± 0.80 | 7.6 ± 0.3 | 17.8 ± 0.3 |
| $\langle b^2 \rangle - \langle c^2 \rangle$ | 48.28 ± 0.60 | 15.5 ± 0.3 | -4.3 ± 0.3 |
| $\langle c^2 \rangle - \langle a^2 \rangle$ | -49.19 ± 0.60 | -23.1 ± 0.3 | -22.1 ± 0.3 |
| $\chi = \frac{1}{3}(\chi_{aa} + \chi_{bb} + \chi_{cc})$ | -48.4 ± 0.1 | -30.7 | -19.9 ± 0.3 |
| χ_{aa} | -30.4 ± 0.5 | -24.7 ± 0.7 | -18.8 ± 0.8 |
| χ_{bb} | -28.3 ± 0.6 | -30.4 ± 0.7 | -16.8 ± 0.8 |
| χ_{cc} | -86.8 ± 0.8 | -37.0 ± 0.8 | -24.2 ± 0.8 |
| χ_{aa}^d | -217.9 ± 1.6 | -85.4 ± 0.9 | -47.6 ± 0.8 |
| χ_{bb}^d | -275.7 ± 2.0 | -27.7 ± 1.1 | -123.3 ± 0.8 |
| χ_{cc}^d | -480.6 ± 2.2 | -125.4 ± 2.0 | -141.4 ± 0.8 |
| $\langle a^2 \rangle$ | 57.1 ± 0.8 | 16.3 ± 0.4 | 25.6 ± 0.3 |
| $\langle b^2 \rangle$ | 56.2 ± 0.8 | 13.3 ± 0.4 | 7.7 ± 0.3 |
| $\langle c^2 \rangle$ | 7.9 ± 0.8 | 6.8 ± 0.4 | 3.5 ± 0.3 |

^a χ values are in units of 10^{-6} erg/(G², mol), Q values are in units of 10^{-26} esu cm², and $\langle a^2 \rangle$ values are in units of 10^{-16} cm². See ref 5 for the original references for these molecules.

magnetic shielding, $\sigma = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$. In the liquid or gas phase the nuclear magnetic resonance measurement is at considerably lower frequency than the rotational frequencies which effectively averages out the J dependence in eq 90 leading to a measurement of the trace of the σ matrix, $\sigma = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$. However, we will show below how measurements of the rotational dependence in eq 89 by rotational spectroscopy can measure the anisotropy in the nuclear magnetic shielding tensor. In addition there are several relatively new techniques in nuclear magnetic resonance involving pulsed and orientated molecule techniques which allow the measurement of the magnetic shielding anisotropy.²³

The effect of third-order corrections to the result in eq 89 will be to add a term which will convert the remaining I_n^{-1} to I_{eff}^{-1} . Further higher order corrections will continue to add corrections to the effective inverse moment of inertia tensor, I_{eff}^{-1} . As these inverse moments are measured at zero field, we return to the discussion following eq 41 and rewrite eq 89 including these higher order terms to give

$$\mathcal{H} = -\gamma_k I_k \cdot (1 - \sigma) \cdot \mathbf{H} - (1/\hbar^2) I_k \cdot \mathbf{M} \cdot \mathbf{J}$$

$$\mathbf{M} = \mathbf{M}_n + \mathbf{M}_e = \frac{e}{c} \gamma_k \hbar^2 \sum_{\alpha} \frac{Z_{\alpha}}{r_{k\alpha}^3} (r_{k\alpha}^2 \mathbf{1} - r_{k\alpha} r_{k\alpha}) \cdot I_{\text{eff}}^{-1} +$$

$$2 \frac{e}{mc} \gamma_k \hbar^2 \left[\sum_{k>0} \frac{\langle 0 | \sum_i (\mathbf{L}_{ki} / r_{ki}^3) | k \rangle \langle k | \mathbf{L} | 0 \rangle}{E_0 - E_k} \right] \cdot I_{\text{eff}}^{-1} \quad (91)$$

\mathbf{M} is the spin-rotation constant with individual diagonal elements given by eq 92 and cyclic permutations for M_{yy}^k and M_{zz}^k .

It is evident that I_{eff}^{-1} in eq 91 is the zero-field experimental inverse moment tensor as discussed in detail in section IV.

$$M_{xx}^k = \frac{\hbar e g_k \mu_0}{c I_{xx}} \sum_{\alpha} \frac{Z_{\alpha}}{r_{k\alpha}^3} (r_{k\alpha}^2 - x_{k\alpha}^2) + \frac{\hbar e g_k \mu_0}{m c I_{xx}} \sum_{k>0} \frac{\langle 0 | \sum_i (\mathbf{L}_{ki} / r_{ki}^3) | k \rangle \langle k | L_x | 0 \rangle + \langle 0 | L_x | k \rangle \langle k | \sum_i (\mathbf{L}_{ki} / r_{ki}^3) | 0 \rangle}{E_0 - E_k} \quad (92)$$

Realizing that the second term in eq 91 represents the interaction of a nuclear magnetic moment, $\mu_k = (g_k/\hbar)\mu_0 I_k$ with an internal magnetic field, we rewrite this term as

$$-\frac{1}{\hbar^2} I_k \cdot \mathbf{M} \cdot \mathbf{J} = -\frac{1}{\hbar} \mu_k \cdot \mathbf{R} \cdot \mathbf{J}$$

$$\mathbf{R} = \frac{1}{g_k \mu_0} \mathbf{M} \quad (93)$$

where the \mathbf{R} tensor has units of magnetic field and the J/\hbar multiplier shows that the magnitude of the internal field is weighted by the rotational angular momentum. The spin-rotation tensor constants given in eq 92 are a sum of a positive pure nuclear term and a negative ($E_0 < E_k$) electronic term. We note the similarities in concept between the rotationally induced molecular-magnetic moments (g values in eq 44 and 45) and the corresponding rotationally induced magnetic field at the k th nucleus in eq 92 and 93. In both cases, the bare nuclei contribute and the ground-state electronic distribution of electrons do not contribute. In both constants, the electronic states which possess electronic orbital angular momentum contribute to the electronic term. The ferris wheel discussion at the end of section IV in the CM framework is also appropriate here with the k th nucleus as a framework of reference.

The nuclear spin-rotation constants can be measured by observing the perturbation on either the rotational energy levels or the nuclear energy levels at zero magnetic field. Consider the \mathbf{M} tensor for a nucleus in a linear molecule which is given by

$$\mathbf{M}_{(\text{linear})} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & M_{\perp} & 0 \\ 0 & 0 & M_{\perp} \end{bmatrix}$$

The diagonal element along the internuclear axis is zero by using the same arguments that demonstrate that the entire tensor is zero in an atom. The \mathbf{M} tensor for a nucleus on the C_3 axis of a symmetric top such as F in FCH_3 is written as

$$\mathbf{M}_{(\text{symmetric top})} = \begin{bmatrix} M_{\parallel} & 0 & 0 \\ 0 & M_{\perp} & 0 \\ 0 & 0 & M_{\perp} \end{bmatrix}$$

Returning to the linear molecule we write the zero-field Hamiltonian in eq 91 as

$$\mathcal{H} = -(M_{\perp}/\hbar^2)\mathbf{J}\cdot\mathbf{l}$$

In the absence of an external magnetic field, the coupled basis is appropriate. The function is

$$\psi_{J,I,F,M_F}$$

which is an eigenfunction of \mathcal{J}^2 , \mathcal{I}^2 , F^2 , and F_z . The development of the energy from these equations is straightforward for the simple scalar coupling. The total angular momentum is \mathbf{F} .

$$\mathbf{F} = \mathbf{I} + \mathbf{J}$$

$$\mathbf{I}\cdot\mathbf{J} = \frac{1}{2}(F^2 - I^2 - J^2)$$

The perturbation energy is

$$E(I,J,F) = \langle JIFM_F | \mathcal{H} | JIFM_F \rangle$$

$$= -(M_{\perp}/2)[F(F+1) - I(I+1) - J(J+1)]$$

The total energy of the linear molecule includes the rigid rotor energy. Thus

$$E = hBJ(J+1) - (M_{\perp}/2)[F(F+1) - I(I+1) - J(J+1)] \quad (94)$$

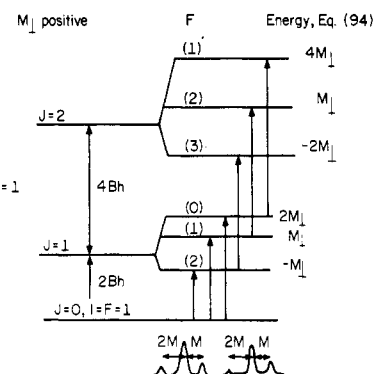


Figure 7. The zero external field energy levels in a linear molecule showing the nonzero spin-rotation interaction described in eq 94. The example is for a $l = 1$ nucleus, and the $J = 0, 1$, and 2 rotational levels are shown. The predicted spectra is also shown.

An energy level diagram demonstrating eq 94 in a linear molecule is shown in Figure 7. In the absence of other interactions, the spin-rotation interaction constant for a linear molecule can be measured directly from the splittings in a rotational transition as shown in Figure 7. Beam maser microwave spectroscopy has been very useful in resolving spin-rotation spectra in molecules. In addition, molecular beam measurements of both rotational and nuclear energy levels have been employed in these necessarily high-resolution studies.¹⁹

The spin-rotation constants for several linear molecules have been determined and some of the results are listed in Table VIII. Also listed are the nuclear magnetic g values and the corresponding rotational field constant, R_{\perp} . The magnetic field at the nucleus due to rotation depends on the rotational state according to eq 83. Thus the net field is the average given by

$$H_{\text{av}}^k = \sqrt{J(J+1)}R_{\perp} \xrightarrow{\text{high } J} JR_{\perp}$$

The field for any J state is easily obtained from this equation and the experimental values of R_{\perp} in Table VIII.

It is quite easy to generalize the above linear molecule results to the general asymmetric top by first writing the \mathbf{M} tensor in terms of the molecular fixed principal inertial values by using the direction cosines (start with the field-independent term in eq 91)

$$\mathcal{H} = -\frac{1}{\hbar^2} \mathbf{J}\cdot[\mathbf{M}\Phi]\cdot\mathbf{l}$$

TABLE VIII. Spin-Rotation, M_{\perp} , and the Rotational Field, R_{\perp} , Constants for Several Linear Molecules^a

| Molecule | Nucleus | g_k | M_{\perp}/\hbar , Hz | $\frac{M_{\perp}/\mu_0 g_k}{R_{\perp}, \text{G}} = r \times 10^{-8}$ | $r \times 10^{-8}$ cm | $I_{\perp} \times 10^{-40}$ g cm ² | $\sigma_{\text{av}}^{\text{p}} \times 10^6$ (eq 98) | $\sigma_{\text{av}}^{\text{d}} \times 10^6$ (eq 99) | $\sigma_{\text{av}} \times 10^6$ |
|----------------------------------|-----------------|---------|-------------------------------------|--|--|--|--|--|----------------------------------|
| H-H | H | 5.854 | $+112.734 \times 10^3$ ^a | 25.2 | 0.7416 | 0.467 | -6 | 32 | 26 |
| H- ¹⁹ F | H | 5.854 | $+71 \times 10^3$ ^a | 16.1 | 0.917 | 1.34 | -80 | 110 | 30 |
| H- ¹⁹ F | ¹⁹ F | 5.2546 | -284 ± 10^3 ^b | -71.0 | 0.917 | 1.34 | -63 | 483 | 420 (410) ^b |
| ⁶ Li- ¹⁹ F | ¹⁹ F | 5.2546 | -37.3 ± 10^3 ^c | -9.3 | 1.525 | 10.61 | -73 | 489 | 416 |
| ⁷ Li- ¹⁹ F | ¹⁹ F | 5.2546 | -32.9×10^3 ^c | -8.2 | 1.525 | 11.91 | -73 | 489 | 416 |
| ¹⁹ F- ¹⁹ F | ¹⁹ F | 5.2546 | -157×10^3 ^d | -39.0 | 1.418 | 32.0 | -750 | 530 | -220 |
| ¹⁵ N- ¹⁵ N | ¹⁵ N | -0.5660 | $+22 \times 10^3$ ^e | -51.0 | 1.094 | 15.0 | -485 | 386 | -99 |
| ¹³ C- ¹⁶ O | ¹³ C | 1.4042 | -32.6×10^3 ^f | -30.5 | 1.128 | 15.16 | -323 | 327 | +4 |
| ¹³ C- ¹⁷ O | ¹⁷ O | -0.7572 | $+29 \times 10^3$ ^g | -50.3 | 1.128 | 14.9 | -460 | 445 | -15 |
| H ¹² C=CH | H | 5.854 | 3.58×10^3 ^a | 0.80 | $d_{\text{HC}} = 1.060$ $d_{\text{CC}} = 1.207$ | 23.8 | -70 | 98 | 28 |

^a N. F. Ramsey, *Amer. Sci.*, **49**, 509 (1961). ^b Corrected for vibrational effects; see D. K. Hinderman and C. D. Cornwell, *J. Chem. Phys.*, **48**, 4148 (1968). ^c See C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill, New York, N.Y., 1955. ^d M. R. Baker, C. H. Anderson, and N. F. Ramsey, *Phys. Rev. A*, **133**, 1533 (1964). ^e C. W. Kern and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 260 (1962). ^f I. Ozier, L. N. Crapo, and N. F. Ramsey *ibid.*, **49**, 2315 (1968). ^g W. H. Flygare and V. W. Weiss, *ibid.*, **45**, 2785 (1966). ^h g_k is the nuclear g value, and I_{\perp} is the moment of inertia. $\sigma_{\text{av}}^{\text{d}}$ for H₂ is an accurate calculation. $\sigma_{\text{av}}^{\text{d}}$ for the remaining molecules is estimated from eq 99 and Table XIV. $\sigma_{\text{av}}^{\text{p}}$ is computed with I_{\perp} , r , and eq 98. $\sigma_{\text{av}} = \sigma_{\text{av}}^{\text{d}} + \sigma_{\text{av}}^{\text{p}}$.

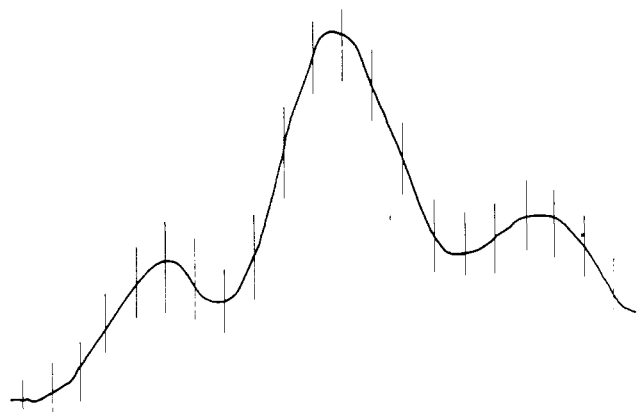


Figure 8. The $1_{11} \rightarrow 1_{10}$ transition in OCF_2 at $\nu_0 = 5872.37$ MHz showing the ^{19}F spin-rotation interaction. The markers are every 5 kc/sec. The spin-rotation constants were obtained from the spectra, and the results are listed in Table IX [W. H. Flygare and V. W. Weiss, *J. Chem. Phys.*, **45**, 2785 (1966)]. The energy levels for this $1_{11} \rightarrow 1_{10}$ can be constructed from those in Figure 7 in the $I_1 + I_2 = I, I + J = F$ coupling case.

This Hamiltonian is similar to the linear field term in eq 74, and Hüttner and Flygare¹⁸ have developed the equations necessary for solution. The resultant energy is given (in the coupled basis) by

$$E(I, J, \tau, F) = - \frac{[E(E+1) - J(J+1) - I(I+1)]}{2J(J+1)} \times \sum_{\alpha} M_{\alpha\alpha} \langle J\tau || J_{\alpha}^2 || J\tau \rangle \quad (95)$$

where the reduced matrix elements over J_{α}^2 are defined following eq 75; see, for instance, eq 76 for a symmetric top. It is evident from eq 95 that the diagonal elements in the spin-rotation interaction tensor, \mathbf{M} , are measured by the rotational perturbation. A typical asymmetric top spectra microwave is shown in Figure 8 for $\text{F}_2\text{C}=\text{O}$. The spin-rotation constants for F_2CO as well as some symmetric top and other asymmetric top molecules are given in Table IX. It is evident from Tables VIII and IX that the rotationally induced fields are normally less than conveniently available laboratory fields.

A. Relation between the Shielding and Spin-Rotation Tensors and Scales for Absolute Nuclear Shielding

We can now relate either the values of R_{xx} or M_{xx} to the magnetic shielding, σ_{xx} . All three constants have identical dependence on the sum over the excited electronic states. We will relate the magnetic-induced shielding to the rotationally induced field given by R_{xx} . Returning to eq 90, 92, and 93 gives the magnetic shielding at any nucleus in terms of the value of $R_{xx} = M_{xx}/\mu_0 g_k$.²⁴

$$\sigma_{xx} = \sigma_{xx}^d + \sigma_{xx}^p = \frac{e^2}{2mc^2} \langle 0 | \sum_i \frac{(y_i^2 + z_i^2)}{r_i^3} | 0 \rangle + \frac{e^2}{2mc^2} \left\{ \frac{M_{xx}/xxC}{e\hbar\mu_0 g_k} - \sum_{\alpha} \frac{Z_{\alpha}}{r_{\alpha}^3} (y_{\alpha}^2 + z_{\alpha}^2) \right\} \quad (96)$$

All distances are from the nucleus in question, and the sum over α omits this nucleus. We have mentioned previously that, normally, only the average magnetic shielding is measured by nuclear magnetic resonance experiments. The average shielding is given by eq 97. This expression further simplifies for high symmetry molecules. The value of σ_{av} for diatomic molecules is given by eq 98. R_{\perp} is the single induced magnetic-field constant (see eq 93). Z is the atomic number of the other nucleus in the diatomic, and r is the internuclear

$$\sigma_{av} = \sigma_{av}^d + \sigma_{av}^p = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) = \frac{e^2}{3mc^2} \langle 0 | \sum_i \frac{1}{r_i} | 0 \rangle + \frac{e^2}{6mc^2} \left[\frac{M_{xx}/xxC}{e\hbar\mu_0 g_k} + \frac{M_{yy}/yyC}{e\hbar\mu_0 g_k} + \frac{M_{zz}/zzC}{e\hbar} - 2 \sum_{\alpha} \frac{Z_{\alpha}}{r_{\alpha}} \right] \quad (97)$$

$$\sigma_{av}(\text{diatomic}) = \sigma_{av}^d + \sigma_{av}^p = \frac{e^2}{3mc^2} \langle 0 | \sum_i \frac{1}{r_i} | 0 \rangle + \frac{e^2}{3mc^2} \left[\frac{R_{\perp}/C}{e\hbar} - \frac{Z}{r} \right] \quad (98)$$

distance. The paramagnetic shielding (σ_{xx}^p in eq 96 or σ_{av}^p in eq 97) can be computed directly from the molecular spin-rotation constants (or magnetic-field constants) and the molecular structure. The results for several diatomics are listed in Table XIII under σ_{av}^p .

The average magnetic shielding at a nucleus cannot be measured directly by nuclear magnetic resonance. Only the chemical shift, which is the difference in the magnetic shielding for a nucleus in two different chemical environments, is measured by nuclear magnetic resonance methods.

$$\Delta\sigma_{av} = \sigma_{av}(A) - \sigma_{av}(B) = \sigma_{av}^p(A) + \sigma_{av}^d(A) - \sigma_{av}^p(B) - \sigma_{av}^d(B)$$

Now, in principle, $\sigma_{av}^p(A)$ and $\sigma_{av}^p(B)$ can be determined from eq (97) by using the spin-rotation constants and the molecular structure. If we can determine $\sigma_{av}^d(A)$ for the nucleus in molecule A by an independent method, then $\sigma_{av}^d(B)$ can be extracted from the above equation and the measured values of $\Delta\sigma_{av}$, $\sigma_{av}^p(B)$, and $\sigma_{av}^p(A)$. The value of $\sigma_{av}^d(A)$ need only be determined once for each nucleus in any given molecule, and all other $\sigma^d(B)$ can be extracted from the chemical shifts. Values of $\sigma_{av}^d(A)$ can be determined from *ab initio* calculations on the ground-state electronic wave functions in simple molecules which are convenient for chemical shift measurements. For instance, the diamagnetic shielding at the proton in H_2 has been calculated to high accuracy. The result is²⁵

$$\frac{e^2}{3mc^2} \langle 0 | \sum_i \frac{1}{r_i} | 0 \rangle_{\text{H in H}_2} = 32.0 \times 10^{-6}$$

Some of the wave functions and calculated σ_{av}^d are available for the other molecules. However, as σ_{av}^d is a local atomic property which weights most heavily the inner electrons, we can approximate σ_{av}^d in molecules by a sum over atomic properties (as we show in detail in the next section).²⁶



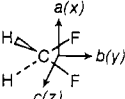

$$\sigma_{av}^d(\text{nucleus } k \text{ in a molecule}) = \sigma_{av}^d(\text{free } k \text{ atom}) + \frac{e^2}{3mc^2} \sum_{\alpha} \frac{Z_{\alpha}}{r_{\alpha}} \quad (99)$$

The free atom diamagnetic shieldings are discussed in the next section (see Table XIII). Equation 99 implies that other atom corrections may be added by assuming the other atom's charges are distributed at the nuclear points throughout the molecule. The values of σ_{av}^d from eq 99 in several molecules are listed in Table VIII. The values of σ_{av}^d in Table VIII are all within 1% of the values calculated with the best available molecule wave functions as we will show in the next section. Thus, eq 99 is an extremely good approximation. If eq 99 is valid, we can further simplify eq 97. Substituting eq 99 into eq 97 shows that the pure nuclear term vanishes giving²⁶

$$\sigma_{av}^d = \sigma_{av}^d(\text{atom}) + \frac{e}{6m\hbar c} [R_{xx}/xx + R_{yy}/yy + R_{zz}/zz] \quad (100)$$

where $\sigma_{av}^d(\text{atom})$ is the free atom diamagnetic shielding as in Table XIII. In a linear molecule, eq 100 reduces to

TABLE IX. Nuclear Spin-Rotation Constants M_{zz}/h in Units of kHz for Several Molecules

| | Nucleus | M_{xx}/h | M_{yy}/h | M_{zz}/h | Ref |
|---|------------------|------------------|-------------------|-------------------|-----|
| $^{37}\text{Cl}-\text{F}$ | ^{19}F | 0 | 22.6 ± 0.2 | 22.6 ± 0.2 | a |
| | ^{35}Cl | 0 | -21.60 ± 0.05 | -21.60 ± 0.05 | a |
| $\text{O}=\text{C}=\text{S}$ | ^{17}O | 0 | -4.0 ± 1.5 | -4.0 ± 1.5 | c |
| | ^{13}C | 0 | 3.1 ± 0.2 | 3.1 ± 0.2 | |
| | ^{32}S | 0 | 2.0 ± 1.0 | 2.0 ± 1.0 | |
| CH_4 | H | 10.4 ± 0.4 | 10.4 ± 0.4 | 10.4 ± 0.4 | d |
| SiH_4 | H | 3.9 ± 0.2 | 3.9 ± 0.2 | 3.9 ± 0.2 | d |
| CF_4 | ^{19}F | -6.9 ± 0.4 | -6.9 ± 0.4 | -6.9 ± 0.4 | d |
| SiF_4 | ^{19}F | -2.42 ± 0.08 | -2.42 ± 0.08 | -2.42 ± 0.08 | d |
| GeF_4 | ^{19}F | -1.88 ± 0.08 | -1.88 ± 0.08 | -1.88 ± 0.08 | d |
| CH_3F | ^{19}F | -51.1 ± 1.3 | 4.0 ± 1.9 | 4.0 ± 1.9 | |
| | H | 14.7 ± 0.7 | 0.8 ± 1.5 | 0.8 ± 1.5 | e |
|  | ^{17}O | 371 ± 10 | 25 ± 10 | -2 ± 10 | f |
|  | ^{19}F | -19 ± 3 | -13 ± 3 | -5 ± 3 | g |
| | | -19.8 ± 0.2 | -13.5 ± 0.1 | -7.8 ± 0.3 | h |
|  | ^{19}F | -20.4 ± 1.0 | -4.9 ± 0.5 | -13.1 ± 0.5 | i |
| | H | 6.5 ± 3.0 | 1.0 ± 1.4 | 0.3 ± 1.3 | |
|  | ^{14}N | -6.71 ± 0.02 | -6.77 ± 0.02 | -6.77 ± 0.02 | i |
| | H | 18.9 ± 1.0 | 1.62 ± 1.0 | 16.1 ± 1.0 | |

^a R. E. Davis and J. S. Muentzer, *J. Chem. Phys.*, **57**, 2836 (1972). ^b J. McGurk, C. L. Norris, H. Tigelaar, and W. H. Flygare, *ibid.*, **58**, 3118 (1973). ^c F. H. DeLeeuw and A. Dymanus, *Chem. Phys. Lett.*, **7**, 288 (1970). ^d I. Ozier, L. M. Crapo, and S. L. Lee, *Phys. Rev.*, **172**, 63 (1968). ^e S. C. Wofsy, J. S. Muentzer, and W. Klemperer, *J. Chem. Phys.*, **55**, 2014 (1971). ^f W. H. Flygare and J. T. Lowe, *ibid.*, **43**, 3654 (1965). ^g W. H. Flygare and V. W. Weiss, *ibid.*, **45**, 2785 (1966). ^h J. H. S. Wang and S. G. Kukolich, *J. Amer. Chem. Soc.*, **95**, 4138 (1973). ⁱ S. G. Kukolich, J. H. S. Wang, and D. J. Ruben, *J. Chem. Phys.*, **59**, 5268 (1973). ^j S. G. Kukolich and S. C. Wofsy, *ibid.*, **52**, 5477 (1971).

$$\sigma_{av}(\text{linear}) = \sigma_{av}^d(\text{atom}) + \left(\frac{e}{3m\hbar c}\right)R_{\perp}I \quad (101)$$

Returning to Table VIII, we note that the net shielding at O in CO, N in N_2 , and F in F_2 is negative (paramagnetic). Thus, the actual fields in these nuclei are larger than the external fields. The other examples in Table VIII indicate a net shielding at the nuclei.

Returning to eq 94 or 95 and Figure 7 for the energy levels, we note that in the absence of any other nuclear coupling the sign of the spin-rotation constant cannot be determined. However, if the average shielding is known, eq 100 and 101 can be used to determine the signs of the spin-rotation constants.^{26,27} In the presence of another nuclear coupling, such as the nuclear quadrupole coupling, the signs of the spin-rotation constants can be uniquely determined.^{28,29}

In summary we note again that the average shielding, σ_{av} , for a nucleus in a specific molecule allows a standard of comparison for the shielding at this nucleus in other molecules. The average magnetic shielding cannot be measured directly by nuclear magnetic resonance. Only the chemical shift which is the *difference* in the magnetic shielding is obtained. Thus, in order to obtain the average shielding in any molecule, the shifts must be related to the actual shieldings as in Table VIII. The standard shielding is obtained by the link with the spin-rotation interaction and the calculated diamagnetic shielding. A summary of the interconnections between the spin-rotation and shielding tensor elements is shown in Figure 9. This figure is similar in design to Figure 2, showing the relations between molecular g values and magnetic susceptibilities.

We can now use the above principles to assign an absolute nuclear magnetic shielding scale for the nuclei involved.

The magnetic shielding for protons in a number of molecules is shown in Figure 10. The standard is the bare proton nucleus which shows that the proton shielding is positive in all molecules. Thus, the field at the protons is always reduced due to the molecule's electrons. The original reference for this scale is the hydrogen molecule. By combining M_H to give σ_{av}^p , and the calculated σ_{av}^d we have the absolute shielding which provides the reference for the other molecules listed in Figure 10.

In Figure 11 we show the shielding scales for the ^{19}F , ^{17}O , ^{14}N , and ^{13}C nuclei. The standards of reference are from the results in Table VIII. Both shielding and antishielding are evident for these nuclei in various molecules.

A great deal of interpretation has been applied to the observed chemical shifts in molecules. The major share of these theories assume that the chemical shifts arise primarily from the change in the paramagnetic terms. However, it is evident from Table VIII and eq 99 that the diamagnetic shielding can also vary considerably at the same nucleus in two different molecules.

VII. Molecular Zeeman Effect in the Presence of Nuclear-Rotational Coupling

We are now prepared to describe the molecular Zeeman effect in the presence of nuclear-rotational coupling. Combining eq 74 and 91 along with the nuclear quadrupole coupling at a single nucleus where we relate the molecular fixed quantities to the laboratory values with the direction cosines gives eq 102. The \mathbf{g} , χ , σ , \mathbf{M} , and \mathbf{q} tensors are all defined in the principal inertial axes systems. Q_{zz} is the scalar quadrupole moment of the nucleus (defined by the convention in eq

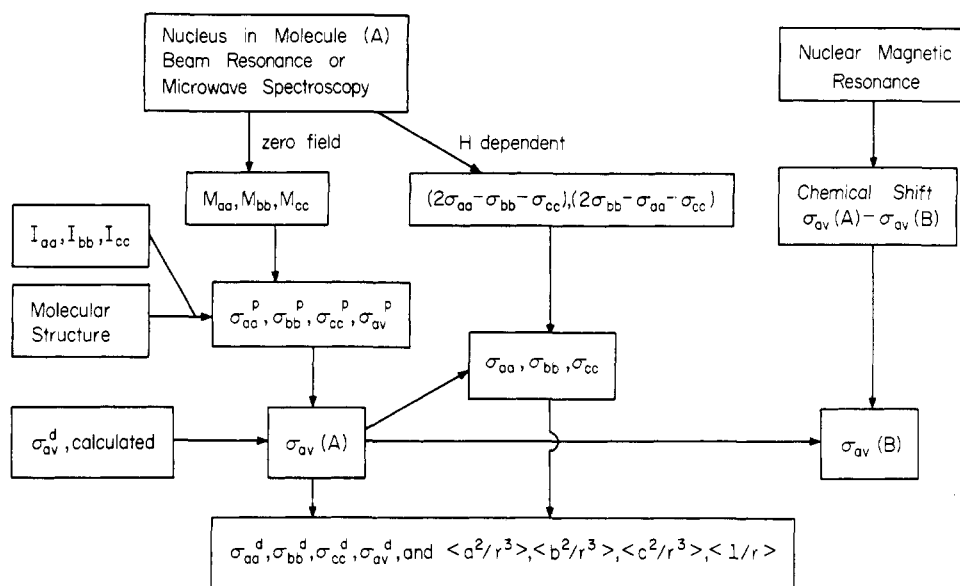


Figure 9. Diagram showing the relation between the diagonal elements in the spin-rotation and magnetic shielding tensor elements. $\sigma_{av}^d = \frac{1}{3}(\sigma_{aa}^d + \sigma_{bb}^d + \sigma_{cc}^d)$, $\sigma_{av}^p = \frac{1}{3}(\sigma_{aa}^p + \sigma_{bb}^p + \sigma_{cc}^p)$, and $\langle a^2/r^3 \rangle = \langle \sigma | \sum_i (a_i/r_i^3) | 0 \rangle$.

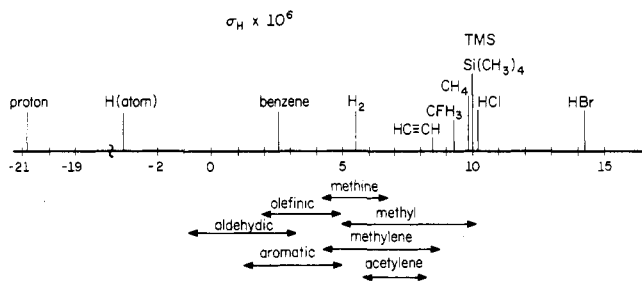


Figure 10. Diagram showing the proton chemical shifts of many compounds relative to an arbitrary origin. The origin or reference is the proton magnetic shielding in $\text{Si}(\text{CH}_3)_4$ which is arbitrarily (for convenience) set at $\sigma_{\text{H}}(\text{Si}(\text{CH}_3)_4) = 10.0 \times 10^{-6}$.

60) and \mathbf{q} is the field gradient tensor at the nucleus. All other terms have been defined previously.

$$\mathcal{H} = \mathcal{H}_{rr} - \frac{\mu_0}{\hbar} \mathbf{H} \cdot [\tilde{\Phi} \mathbf{g}] \cdot \mathbf{J} - \frac{1}{2} \mathbf{H} \cdot [\tilde{\Phi} \chi \Phi] \cdot \mathbf{H} - \gamma_I I \cdot (1 - \tilde{\Phi} \sigma \Phi) \cdot \mathbf{H} - \frac{1}{\hbar^2} \mathbf{J} \cdot [\mathbf{M} \Phi] \cdot \mathbf{I} + \frac{1}{2} Q_{zz} [\tilde{\Phi} \mathbf{q} \Phi]_{zz} \quad (102)$$

Hüttner and Flygare¹⁸ have discussed in detail the matrix representation of eq 102 in both the *coupled* and *uncoupled* bases. In the coupled basis, the matrix representations of the I^2 , J^2 , F^2 , and F_z operators are all diagonal. I is the angular momentum of the coupled nucleus, J the rotational angular momentum, F the vector sum of I and J , and F_z the z component of F . The quantum numbers labeling the coupled representation are $|JMF_F\rangle$. In the uncoupled representation the matrices of the z components of I and J , which are I_z and J_z , are each diagonal, as are I^2 and J^2 since the nuclear angular momentum is independent of the rotational angular momentum. The appropriate quantum numbers labeling the uncoupled representations are $|JM_I M_J\rangle$. One may use either representation to find diagonal and off-diagonal matrix elements of the interaction of the magnetic field with the molecule.

Hüttner and Flygare¹⁸ have decomposed the magnetic perturbation operators from eq 102, \mathcal{H}_m , into five parts: $\mathcal{H}_m = {}^I\mathcal{H}_m + {}^{II}\mathcal{H}_m + {}^{III}\mathcal{H}_m + {}^{IV}\mathcal{H}_m + {}^V\mathcal{H}_m$. The interaction of the external field H_z with the isotropic component of the shielded nuclear moment is given by

$${}^I\mathcal{H}_m = -\mu_0 g_I (1 - \sigma) H_z I_z \quad (103)$$

where $\sigma = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$. ${}^{II}\mathcal{H}_m$ gives the molecular linear field contribution.

$${}^{II}\mathcal{H}_m = -\frac{1}{2} \mu_0 H_z \sum_{g, g'} (g_{gg'} \phi_{gz} J_{g'} + g_{gg'}^* J_g \phi_{gz}) \quad (104)$$

where $g_{gg'}$ is the gg' element of the molecular g -value tensor, ϕ_{gz} the direction cosine between the g and z axes, and J_g the g -axis projection of the molecule's rotational angular momentum. ${}^{III}\mathcal{H}_m$ is the isotropic magnetic susceptibility term. It affects all levels the same amount in either representation and hence does not enter into the microwave Zeeman analysis. ${}^{IV}\mathcal{H}_m$ is the interaction of the anisotropy in the magnetic susceptibility with the field, a field-squared term

$${}^{IV}\mathcal{H}_m = -\frac{1}{2} H_z^2 \sum_g \chi_{gg} (\phi_{gz}^2 - \frac{1}{3}) \quad (105)$$

${}^V\mathcal{H}_m$ is the corresponding nuclear shielding anisotropy term

$${}^V\mathcal{H}_m = +\mu_0 g_I H_z I_z \sum_g \sigma_{gg} (\phi_{gz}^2 - \frac{1}{3}) \quad (106)$$

Let us now consider the quantum number dependence and magnitude of the various energy terms arising in a perturbation expansion of \mathcal{H}_m for a linear molecule. Terms with odd-power dependence on the field will split $\pm M_F$ pairs while even-power terms will shift the centers of the corresponding $\pm M_F$ pairs. The splittings and shifts of the microwave lines in coupled molecules are greatly different from those pertaining to uncoupled molecules. In terms of field-induced splittings of microwave lines, the principal difference between coupled and uncoupled molecules appears in the diagonal matrix elements of ${}^I\mathcal{H}_m$, the $g_I(1 - \sigma)$ terms. For an uncoupled linear molecule ${}^I\mathcal{H}_m$ leads to a dependence on the quantum number M_I giving

$${}^I E_m^{(1)} = \langle M_I J M_J | {}^I \mathcal{H}_m | M_I J M_J \rangle = -\mu_0 g_I (1 - \sigma) H_z M_I \quad (107)$$

In the coupled representation, ${}^I E_m^{(1)}$ is given by

$${}^I E_m^{(1)} = -\mu_0 g_I (1 - \sigma) H_z M_F \times \{ [I(I+1) + F(F+1) - J(J+1)] / 2F(F+1) \} \quad (108)$$

Since the selection rules for a microwave transition are $\Delta M_I = 0$, $\Delta M_J = 0, \pm 1$ for uncoupled molecules and since the

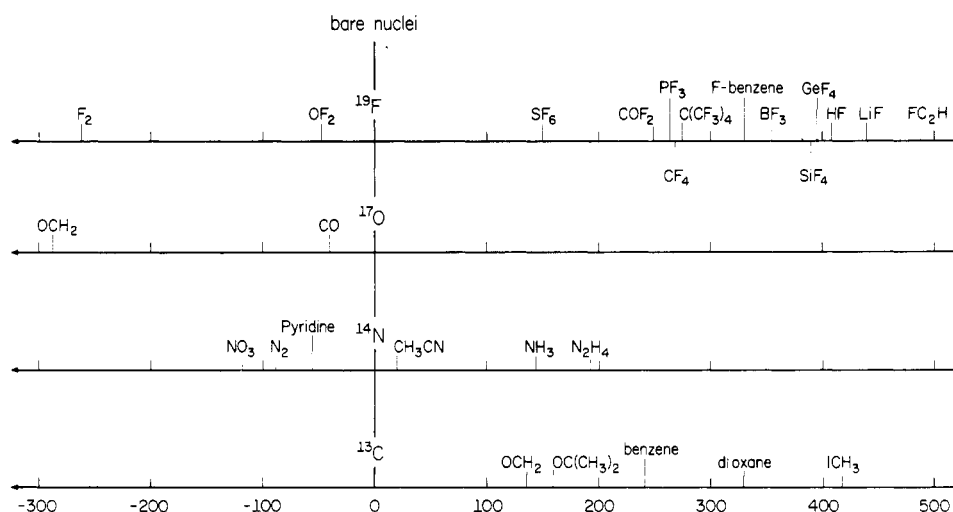


Figure 11. Summary of chemical shifts of ^{19}F , ^{17}O , ^{14}N , and ^{13}C nuclei in different chemical environments relative to the bare nuclei.

$g(1 - \sigma)$ term has no J dependence (in the uncoupled case), this nuclear term cannot be observed in microwave Zeeman spectroscopy. However, the anisotropy can be measured in the uncoupled case where the first-order expression for the energy contribution from the chemical shift anisotropy is obtained by the following expression derived from eq 39 of Hüttner and Flygare¹⁸ (see eq 106 above)

$${}^{\nu}E_m^{(1)} = 2\mu_0 g_I H M_I \left(\frac{M_J}{J} \right) [(2J + 3)(J + 1)]^{-1} \times \\ \sum_g (\sigma_{gg} - \sigma) \langle J\tau || J_{\alpha}^2 || J\tau \rangle = \\ \pm 2\mu_0 g_I H I [(2J + 3)(J + 1)]^{-1} \sum_g (\sigma_{gg} - \sigma) \langle J\tau || J_{\alpha}^2 || J\tau \rangle \quad (109)$$

where σ is the average shielding as before. Only two independent magnetic shielding anisotropies can be determined because

$$\sum_{\alpha} (\sigma_{\alpha\alpha} - \sigma) = 0$$

We take the two independent anisotropies to be

$$\sigma_{aa} - \sigma = \frac{1}{3}(2\sigma_{aa} - \sigma_{bb} - \sigma_{cc})$$

$$\sigma_{bb} - \sigma = \frac{1}{3}(2\sigma_{bb} - \sigma_{aa} - \sigma_{cc})$$

This discussion is nearly identical with the discussion involving magnetic susceptibilities following eq 75. We will return to a discussion of the measurement of shielding anisotropies in the uncoupled region later in this section. Now we return to the coupled case discussion where the nuclear Zeeman term in eq 108 enters very strongly for coupled molecules since ${}^{\nu}E_m^{(1)}$ depends on l , F , and J . This leads to microwave Zeeman splittings that can easily be 10 or 20 MHz in comparison to the purely molecular splittings of 1 to 3 MHz encountered in uncoupled molecules.

The diagonal elements of ${}^{\nu}\mathcal{H}_m$ give the leading, purely molecular term for uncoupled molecules. It depends on M_J ; ${}^{\nu}E_m^{(1)} = -\mu_0 g_{\perp} H_z M_J$ for a linear molecule. A coupled linear molecule has a different quantum number dependence for ${}^{\nu}E_m^{(1)}$

$${}^{\nu}E_m^{(1)} = -\mu_0 g_{\perp} H_z M_F \times \left(\frac{[J(J + 1) + F(F + 1) - l(l + 1)]}{2F(F + 1)} \right) \quad (110)$$

The size of the g_{\perp} term is about the same in both representations, typically about 1 to 3 MHz, but it is the second largest linear term for a coupled case.

A small, linearly field-dependent term due to the shielding

anisotropy, $g_l(\Delta\sigma)$, also enters in the coupled basis (the uncoupled basis is shown in eq 109). The quantum number expressions are developed by Hüttner and Flygare¹⁸ and are of course different in the two representations.

One distinct feature in the Zeeman splittings of coupled molecules is the need to include terms from higher orders of a perturbation expansion. Cubic-field dependent terms will split $\pm M_F$ states and enter into the analysis of splittings at larger fields where a certain degree of decoupling occurs. The degree of decoupling depends on the quadrupole splittings, of course, being least important for compounds with large quadrupole coupling and most important for the compounds with small quadrupole coupling. There are two important third-order terms. The first goes as $[g_l(1 - \sigma)]^3 H^3$, and the second depends on $[g_l(1 - \sigma)]^2 g_{\perp} H^3$. Both of these terms are larger than the $g_l \Delta\sigma H$ terms, and any careful spectral analysis aimed at obtaining $g_l(\Delta\sigma)$ and g_{\perp} will need to include these terms. Other cubic terms which contribute shifts are: $[g_l(1 - \sigma)](g_{\perp})^2 H^3$, $g_{\perp}^3 H^3$, $g_l(1 - \sigma)\Delta\chi H^3$, and $g_{\perp} \Delta\chi H^3$. Cubic-field-dependent splittings have not been observed in uncoupled molecules, and a discussion of the purely molecular H^3 term is given by Flygare and Benson.⁵

Perturbations which enter with even power field and M dependences will shift the center of a given pair of $\pm M_F$ states. In the case of the pure molecular Zeeman effect in uncoupled molecules, the leading quadratic field term is that due to the magnetic susceptibility anisotropy, $\Delta\chi H^2$, which enters in first-order perturbation theory and has an M^2 dependence as shown in section V. It is, of course, slightly different in the coupled representation, but the magnitude of this quadratic effect is similar in both representations.

For coupled molecules the most important even-power field-dependent terms are not those involving the susceptibility anisotropy but rather the terms *off-diagonal* in $g_l(1 - \sigma)$ and g_{\perp} which enter through second-order perturbation theory. The important second-order terms go as $[g_l(1 - \sigma)]^2 H^2$, $g_{\perp}^2 H^2$, and $g_l(1 - \sigma)g_{\perp} H^2$. More details on the perturbation and matrix diagonalization methods of extracting the Zeeman parameters in the presence of nuclear coupling is available in the original references^{18,30,31} where measurements of the field-dependent magnetic parameters in Figures 2 and 9 are discussed. In Figure 12 we show the field-off and field-on rotational spectrum of the $J = 0 \rightarrow 1$ transition in $\text{CH}_3\text{C}^{14}\text{N}$. It is evident that the nucleus is far from uncoupled from the rotational motion even at fields up to 25 kG. Thus, even in this case of relatively small nuclear coupling, considerable care must be exercised in extracting the magnetic parameters from the data.

TABLE X. ^{19}F Nuclear Magnetic Shielding Tensor Elements in CH_2F_2 in the Principal Inertial Axis System^a

| | $\sigma_{zz} \times 10^6$ total | $\sigma_{zz}^p \times 10^6$ para- magnetic | $\sigma_{zz}^d \times 10^6$ dia- magnetic | Atom dipole magnetic |
|---------------|------------------------------------|--|---|----------------------------|
| σ_{aa} | 398 | -104 | 502 | 511 |
| σ_{bb} | 388 | -186 | 574 | 576 |
| σ_{cc} | 225 | -378 | 603 | 595 |
| σ_{av} | 337 | -223 | 560 | 561 |

^a From ref 33. See Figure 9 for the interrelations between σ_{aa} , σ_{aa}^d , σ_{aa}^p , and the spin-rotation constants. The atom dipole evaluation of σ_{aa}^d is discussed in section VIII.

Some simplification in the above analysis can be found by analyzing the central doublets corresponding to $\Delta M_F = \pm 1$ transitions in the coupled basis: $F = I + J \rightarrow F' = I + J + 1$, $M_F = \pm F \rightarrow M_{F'} = \pm F'$.³² The deviation of these transition frequencies at high magnetic fields from their position at zero field (1) is independent of nuclear Zeeman effects, (2) depends on first-order expressions involving the magnetic susceptibility and the molecular Zeeman effects, and (3) is independent of the strength of quadrupolar coupling. In other words, these transitions appear at a frequency difference from the zero-field frequency which is the same as that expected in the absence of the quadrupolar interaction (the uncoupled case), and the second-order corrections are all of the form

$$|\langle 0 | H_{\text{pert}} | \rho \rangle|^2 / \Delta E$$

where H_{pert} involves either the molecular Zeeman or the susceptibility anisotropy terms and ΔE is of the order of rotation energy differences.

An interesting zero-field and high-field study in the uncoupled case is in CH_2F_2 . The principal inertial axis system in CH_2F_2 is shown in Table IX along with the values of the ^{19}F spin-rotation constants.³³ In addition to this work, Kukolich and Nelson³⁴ have reported the high-field Zeeman analysis in CH_2F_2 which yields through eq 109 the anisotropies in the ^{19}F nuclear magnetic shielding. The results are (see axis system in Table IX) $2\sigma_{cc} - \sigma_{aa} - \sigma_{bb} = (-335 \pm 35) \times 10^{-6}$ and $\sigma_{aa} - \sigma_{bb} = (9 \pm 13) \times 10^{-6}$. Combining these magnetic shielding anisotropies and experimental total magnetic shielding (using the scale in Figure 11) gives the diagonal total magnetic shieldings as listed in Table X. Using the spin-rotation constants for ^{19}F in CH_2F_2 from Table IX, the known molecular structure, and eq 96, gives the diagonal elements in the paramagnetic shielding tensor which are also listed in Table X. Thus, we obtain the experimental values for the individual elements in the diamagnetic shielding tensor as listed in Table X (see again the interrelationships in Figure 9). The experimental results for σ^d are compared in the last column of Table X with the atom dipole values (see next section).

VIII. Semiempirical Atom Dipole Approach to Predicting Molecular Properties

We will now discuss a localized model for the interpretation and prediction of several of the molecular properties obtained from the magnetic studies described in the previous sections. This localized model is called the *atom dipole model*.³⁵ The model replaces the ground electronic state average values of several molecular properties with sums over the corresponding free atom values plus corrections which depend on the atom dipoles. The *semiempirical* atom dipoles are obtained by fitting a set of molecular dipole and quadrupole moments to the expressions relating the experimental moments to the atom dipole dependent expressions. These atom dipole moments are useful in predicting molecular dipole and quadrupole moments in new molecules. In addition, we

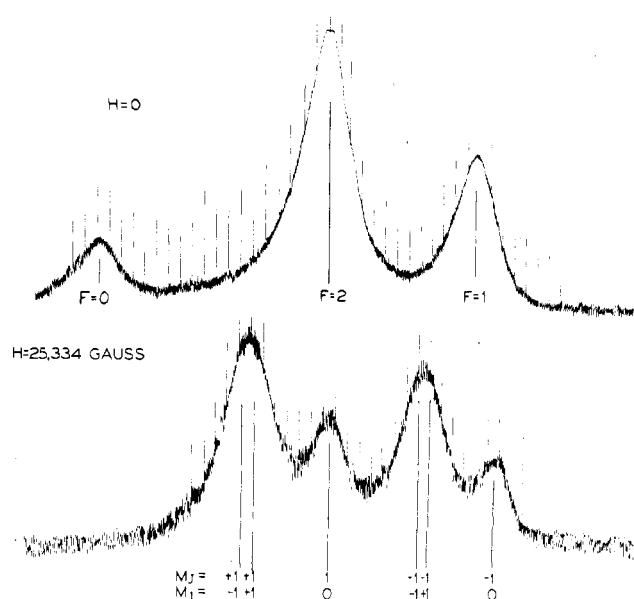


Figure 12. The $J = 0 \rightarrow 1$ rotational transition in $\text{CH}_3\text{C}^{14}\text{N}$. The upper trace shows the zero-field $F = 0$, $F = 1$, and $F = 2$ asymmetric triplet. The lower trace shows the nearly uncoupled spectra at 25 kG. The completely uncoupled spectra would give a symmetric quartet. Considerable deviation from the uncoupled limit was observed in $\text{H}_3\text{CC}^{14}\text{N}$ as shown here at 25 kG by J. M. Pochan, R. L. Shoemaker, R. G. Stone, and W. H. Flygare, *J. Chem. Phys.*, **52**, 2478 (1970).

outline the use of the atom dipole moments to evaluate the molecular diamagnetic susceptibilities and nuclear diamagnetic shielding in a molecule. Finally, we use the localized picture of electron distribution to obtain a semiempirical set of atom and bond magnetic susceptibility tensor elements.

A. Electric Multiple Moments, Second Moments of Charge, and Diamagnetic Susceptibilities

We start by examining the CM average value of r_i , the vector, from the CM to the i th electron in the molecule

$$\langle 0 | \sum_i r_i | 0 \rangle = \sum_n \langle 0 | \sum_{i_n=1}^{Z_n} r_i | 0 \rangle \quad (111)$$

where the sum over all molecular electrons i has been replaced by a double sum over the n nuclei in the molecule and an inner sum over the number of electrons in each of the n free atoms in the molecule. In each of the sums over i_n in eq 111, we now write

$$r_{i_n} = r_n + \rho_{i_n} \quad (112)$$

where r_n is the CM n th nucleus vector and ρ_{i_n} is the vector from the n th nucleus to the i th electron. Substituting eq 112 into eq 111 gives

$$\langle 0 | \sum_i r_i | 0 \rangle = \sum_n \langle 0 | \sum_{i_n=1}^{Z_n} (r_n + \rho_{i_n}) | 0 \rangle_n = \sum_n \langle 0 | \sum_{i_n=1}^{Z_n} r_n | 0 \rangle_n + \sum_n \langle 0 | \sum_{i_n=1}^{Z_n} \rho_{i_n} | 0 \rangle_n \quad (113)$$

The integral of a sum equals the sum of integrals which gives

$$\langle 0 | \sum_i r_i | 0 \rangle = \sum_n \langle 0 | r_n | 0 \rangle_n + \sum_n \sum_{i_n=1}^{Z_n} \langle 0 | \rho_{i_n} | 0 \rangle_n \quad (114)$$

Applying the Born-Oppenheimer approximation to the nuclear term in eq 114 and assuming the molecule is a rigid rotor gives

$$\sum_{i_n} \langle 0 | r_n | 0 \rangle_n = Z_n r_n \quad (115)$$

and defining

$$\sum_n^{z_n} \langle 0 | \rho_{in} | 0 \rangle_n = \langle \rho \rangle_n \quad (116)$$

gives

$$\langle 0 | \sum_i r_i | 0 \rangle = \sum_n Z_n r_n + \sum_n \langle \rho \rangle_n \quad (117)$$

The above discussion is quite general, as all electrons are included in the sum of $\langle 0 | \rho_{in} | 0 \rangle$ matrix elements. The ρ_{in} operator which originates at the n th nucleus can extend throughout the molecule. However, we will now assume that the ρ_{in} operator is localized to the n th atom. This assumption indicates that atoms in molecules maintain a major share of their free-atom electron densities. This viewpoint is substantiated by free atom-molecule difference density plots which indicate a relatively small electron reorganization when free atoms form molecules. If the electrons in a bonded atom are assumed to be localized, $\langle \rho \rangle_n$ represents the reduced dipole polarization of the electronic charge on nucleus n , or the reduced atom dipole. $e \langle \rho \rangle_n$ is the atom dipole moment.

The square of electronic coordinates can be treated in the same way.

$$\begin{aligned} \langle 0 | \sum_i r_i^2 | 0 \rangle &= \sum_n \langle 0 | \sum_{i_n=1}^{z_n} r_{i_n}^2 | 0 \rangle_n = \\ &= \sum_n \langle 0 | \sum_{i_n} (r_n + \rho_{i_n})^2 | 0 \rangle_n = \sum_n Z_n r_n^2 + \\ &+ \sum_n 2r_n \cdot \sum_{i_n} \langle 0 | \rho_{i_n} | 0 \rangle_n + \sum_n \sum_{i_n} \langle 0 | \rho_{i_n}^2 | 0 \rangle_n \end{aligned} \quad (118)$$

We now define

$$\sum_n \langle 0 | \rho_{i_n}^2 | 0 \rangle_n = \langle \rho^2 \rangle_n \quad (119)$$

and using the definition of atom dipoles in eq 116, we rewrite eq 118 to give

$$\langle 0 | \sum_i r_i^2 | 0 \rangle = \sum_n Z_n r_n^2 + \sum_n 2r_n \cdot \langle \rho \rangle_n + \sum_n \langle \rho^2 \rangle_n \quad (120)$$

Again if the electrons in bonded atoms are localized, $\langle \rho^2 \rangle_n$ represents the average squared electronic distance from the n th nucleus and should be proportional to the average diamagnetic susceptibility of that atom.

It is evident that both eq 117 and 120 are also satisfied by the Cartesian components of each vector

$$\langle 0 | \sum_i x_i | 0 \rangle = \sum_n Z_n x_n + \sum_n \langle x \rangle_n \quad (121)$$

and

$$\langle 0 | \sum_i x_i^2 | 0 \rangle = \sum_n Z_n x_n^2 + \sum_n 2x_n \langle x \rangle_n + \sum_n \langle x^2 \rangle_n \quad (122)$$

where $\langle x \rangle_n$ and $\langle x^2 \rangle_n$ are the Cartesian components of $\langle \rho \rangle_n$ and $\langle \rho^2 \rangle_n$ along the x axis.

Substituting eq 117 and 120 into eq 38 defining the dipole moment and eq 52 defining the quadrupole moment gives

$$D_x = -e \sum_n \langle x \rangle_n \quad (123)$$

$$Q_{xx} = -\frac{e}{2} \left\{ \sum_n 2(3x_n \langle x \rangle_n - r_n \cdot \langle \rho \rangle_n) + \sum_n (3\langle x^2 \rangle_n - \langle \rho^2 \rangle_n) \right\} \quad (124)$$

$(e/2)(3\langle x^2 \rangle_n - \langle \rho^2 \rangle_n)$ is the atom quadrupole moment by analogy with the atom dipole moment defined in eq 116. However, there is good reason to believe that the atom quadrupole moment contribution to the total moment in eq 124 is negligible.³⁵ Therefore

$$Q_{xx} \cong -e \sum_n (3x_n \langle x \rangle_n - r_n \cdot \langle \rho \rangle_n) \quad (125)$$

The preceding analysis was based on a partition of the electrons among the nuclei of the molecule. Much the same treatment could be given for any other reasonable partition of electrons, provided only that the two conditions of independence from the rest of the molecule and constancy from molecule to molecule are met. Indeed, most past attempts to calculate molecular properties from local contributions, including dipole moments,³⁶ electric polarizabilities,³⁷ and magnetic susceptibility anisotropies,³⁸ have chosen bonds as the basic unit. A problem with this approach is ambiguity about the origin to be assigned to a bond. For properties such as the diamagnetic susceptibility, the quadrupole moment, and the magnetic shielding, all of which depend on the origin, the atom value approach would seem to be preferred. However, for a property such as the total or average susceptibility which depends only on the orientation of the groups, not their position, either approach should be equally effective.

We have written both the molecular dipole (eq 123) and the molecular quadrupole (eq 125) moments in terms of a set of atom dipole moments. The semiempirical atom dipole moments were obtained by fitting a large number of experimental moments to these equations. We use the following conventions in assigning the atom dipole moments. (1) Bonded atoms are always polarized collinear with the bond. (2) Atoms bonded to just one other atom will be chosen to be polarized into the bond if the atom dipole is positive. (3) Atoms bonded to more than one other atom will be chosen to be polarized into the bond of highest order; e.g., an sp^2 carbon will be polarized into the double bond. (4) sp^3 carbon atoms will be chosen to be polarized toward the most electronegative substituent. The exact direction is determined by symmetry. The first convention is quite reasonable, since by symmetry the average electronic coordinate perpendicular to a localized bond must be zero. The other conventions are also dictated by symmetry considerations and reduce the number of variables which must be considered. The resultant atom dipoles are listed in Table XI, and the resultant calculated dipole and quadrupole moments in several molecules are listed in Table XII.

We can also use the atom dipole concept to calculate by these semiempirical means the individual elements in the diamagnetic susceptibility tensor and the second moments of the electronic charge distribution. Substituting eq 118 or the components from eq 122 into eq 46 and multiplying by Avogadro's number, N , to obtain a molar value for χ_{xx}^d gives

$$\begin{aligned} \chi_{xx}^d &= -\frac{e^2 N}{4mc^2} \left\{ \sum_n Z_n (y_n^2 + z_n^2) + \right. \\ &\left. 2 \sum_n (y_n \langle y \rangle_n + z_n \langle z \rangle_n) + \sum_n (\langle y^2 \rangle_n + \langle z^2 \rangle_n) \right\} \end{aligned} \quad (126)$$

$$\langle 0 | \sum_i x_i^2 | 0 \rangle = \sum_n Z_n x_n^2 + \sum_n 2x_n \langle x \rangle_n + \sum_n \langle x^2 \rangle_n \quad (127)$$

The atom dipoles $\langle x \rangle_n$ appear in both of these equations. The values of $\langle x^2 \rangle_n$, $\langle y^2 \rangle_n$, and $\langle z^2 \rangle_n$ are also needed to evaluate χ_{xx}^d and $\langle 0 | \sum_i x_i^2 | 0 \rangle$ for a molecule by this method. We will use free atom values for $\langle x^2 \rangle_n = \langle r^2/3 \rangle_n$. This approximation is quite reasonable as shown from a close inspection of electron density maps in bonded atoms which reveals that changes in density with respect to the free atom distribution are relatively large only when the absolute elec-

Table XI. Reduced Atom Dipole Moments^a

| Hydrogen | | |
|--|--|-----------------------------|
| 1. H=C< | | +0.20 |
| 2. H-C=C | | +0.15 |
| 3. H-C≡C | | +0.06 |
| 4. H-C≡N | | +0.06 |
| 5. H-C=O | | +0.05 |
| 6. H-O | | +0.30 |
| 7. H-X (halogen) | | +0.31 |
| 8. H-N | | +0.25 |
| 9. H-C (aromatic) | | +0.16 |
| Fluorine | | |
| 1. F-C< | | -0.15 |
| 2. F-C=C | | -0.13 |
| 3. F-C≡C, F-C≡N | | -0.10 |
| 4. F-H | | -0.07 |
| 5. F-C (aromatic) | | -0.13 |
| 6. F-C=O | | (-0.20 to -0.29) |
| sp ³ Carbon | | |
| 1. C-H | | 0 |
| 2. C-F | | 0.0 to +0.03 |
| 3. C-C=C | | 0 |
| 4. C-C=O | | 0 |
| 5. C-O | | 0.06 to 0.08 |
| 6. C-C | | 0 |
| sp ² Carbon | | |
| 1. C=C | | +0.02 to +0.05 |
| 2. =C-H, =C-C, =C- | | 0 |
| 3. C=O | | +0.15 |
| 4. C (aromatic) | | -0.16 |
| 5. =C-F | | +0.02 |
| 6. =C-O | | ≈ 0 |
| sp Carbon | | |
| 1. C≡C | | +0.30 |
| 2. C≡N | | +0.39 |
| 3. O=C*=O | | 0.0 |
| 4. X=C*=O | | -0.02 to -0.07 |
| sp ² Oxygen | | |
| 1. O=C< | | -0.28 |
| 2. O=C=X | | -0.10 |
| 3. O=C=O | | -0.20 |
| sp ³ Oxygen | | |
| 1. O-H | | -0.02 |
| 2. O-C(sp ³) (C ₂ axis) | | -0.10 |
| 3. O-C(sp ³) (C ₂ axis) | | -0.12 |
| 4. O-C(sp) | | -0.15 |
| Nitrogen | | |
| 1. N≡C | | -0.17 |
| 2. NH ₃ | | +0.03 (C ₃ axis) |
| Chlorine | | |
| 1. Cl-C≡ | | -0.02 |

^a The plus sign means that the electrons in the *n*th atom are polarized away from the atom in the bond. These values along with eq 123, 125, 126, and 127 give the calculated values in Table XII. See ref 35 for more details.

tron density is relative small.³⁹ In other words, it appears that the charge distribution in atoms is not dramatically changed by covalent bonding. We obtain our values of $\langle r^2/3 \rangle_n$ from the free neutral atom values as listed in Table XIII. Using the values of $\langle r_2/3 \rangle_n$ in Table XIII, the atom dipoles in Table XI, and eq 126 and 127 gives the calculated results in Table XII under $\langle x^2 \rangle$ and χ_{xx}^d . These calculated values are also compared with the experimental results.

The calculated results in Table XII for χ_{xx}^d and $\langle x^2 \rangle$ are better than the results on molecular moments, since uncertainties in atom dipoles will introduce relatively small errors in the second moments of electronic charge. Deviations in second moments calculated with eq 127 are estimated to be 0.1–1.0 Å², which will produce deviations in the diamagnetic susceptibility of about $0-8 \times 10^{-6}$ erg/(G² mol). The values of the diagonal elements of the diamagnetic susceptibility tensor combined with the diagonal elements of the paramagnetic susceptibility (available from the molecular *g* values) allows a determination of the total susceptibility elements as well as the bulk susceptibilities.

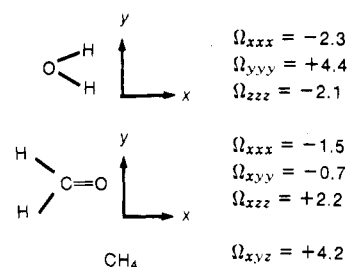
It is interesting to note that the methods developed here to evaluate molecular dipole and quadrupole moments by summing over atom dipole terms can also be applied to the estimation of higher order multipole moments. For instance, the molecular octapole moments are given in terms of the atom dipoles by³⁵ eq 128, where we have set the atom quadrupole

$$\Omega_{xxx} = -e \sum_n \{ \langle x \rangle_n (3x_n^2 - \frac{3}{2}y_n^2 - \frac{3}{2}z_n^2) - 3\langle y \rangle_n x_n y_n - 3\langle z \rangle_n x_n z_n \}$$

$$\Omega_{xyy} = -e \sum_n \{ \langle x \rangle_n (2y_n^2 - \frac{3}{2}x_n^2 - \frac{1}{2}z_n^2) + 4\langle y \rangle_n x_n y_n - \langle z \rangle_n x_n z_n \}$$

$$\Omega_{xyz} = -\frac{5}{2}e \sum_n \{ \langle z \rangle_n x_n y_n + \langle x \rangle_n y_n z_n + \langle y \rangle_n z_n x_n \} \quad (128)$$

and atom octapole moments to zero. We have used eq 128 and the atom dipole of Table XI to evaluate the octapole moments [in units of 10^{-34} (esu cm³)] for several molecules. We obtain the following results for water, formaldehyde, and methane.



These results can be compared with the *ab initio* calculated results for water:⁴⁰ $\Omega_{xxx} = -1.3$, $\Omega_{xyy} = +2.3$, $\Omega_{zzz} = -1.0$; for formaldehyde⁴⁰ $\Omega_{xxx} = -0.58$, $\Omega_{xyy} = -1.98$, $\Omega_{zzz} = +2.56$; and for methane $\Omega_{xyz} = +4.5$.⁴¹

In summary, it is evident from the above discussion and Table XII that **D**, **Q**, χ^d , $\langle x^2 \rangle$, $\langle y^2 \rangle$, $\langle z^2 \rangle$, and the higher order electrostatic moments for molecules are calculated quite accurately with the atom dipole method.

B. Nuclear Diamagnetic Shielding

Next we will apply the atom dipole method to the evaluation of the elements in the diamagnetic shielding tensor at a nucleus in a molecule.⁴² We start with the expression for the average diamagnetic shielding at nucleus A from eq 97

$$\sigma_{av}^d(A) = \frac{1}{3}(\sigma_{xx}^d(A) + \sigma_{yy}^d(A) + \sigma_{zz}^d(A)) =$$

$$\frac{e^2}{3mc^2} \langle 0 | \sum_i \frac{1}{r_i} | 0 \rangle = \frac{e^2}{3mc^2} [\langle 0 | \sum_k^{Z_A} r_k^{-1} | 0 \rangle + \sum_n \langle 0 | \sum_{l_n}^{Z_n} r_{l_n}^{-1} | 0 \rangle] \quad (129)$$

where we have merely partitioned the sum of all *j* electrons into the *Z_A* electrons "on" nucleus A and the *Z_n* electrons

TABLE XII. Calculated Molecular Dipole Moments (Eq. 123), Calculated Molecular Quadrupole Moments (Eq. 125), Second Moments of the Electronic Charge Distribution (Eq. 127), and Calculated Diamagnetic Susceptibilities (Eq. 126) Using the Atom Dipoles in Table XI and the Known Molecular Structure^a

| Molecule | $\left. \begin{matrix} D_a \\ D_b \\ D_c \end{matrix} \right\} \times 10^{18}$ | | $\left. \begin{matrix} Q_{aa} \\ Q_{bb} \\ Q_{cc} \end{matrix} \right\} \times 10^{+26}$ | | $\begin{matrix} \Sigma_n Z_n a_n^2 \\ \Sigma_n Z_n b_n^2 \\ \Sigma_n Z_n c_n^2 \end{matrix}$ | $\left. \begin{matrix} \langle a^2 \rangle \\ \langle b^2 \rangle \\ \langle c^2 \rangle \end{matrix} \right\} \times 10^{16}$ | | $\left. \begin{matrix} \chi_{aa}^{ad} \\ \chi_{bb}^{bd} \\ \chi_{cc}^{cd} \end{matrix} \right\} \times 10^6$ | |
|----------------------|--|-------|--|-------|--|--|-------|--|--------|
| | Exptl | Calcd | Exptl | Calcd | | Exptl | Calcd | Exptl | Calcd |
| | 0 | 0 | +1.2 ± 0.1 | +1.3 | 1.34 | 2.6 ± 0.4 | 2.5 | -19.3 ± 1.4 | -19.2 |
| | 0 | 0 | +1.2 ± 0.1 | +1.3 | 1.34 | 2.6 ± 0.4 | 2.5 | -19.3 ± 1.4 | -19.2 |
| | 1.47 | +1.44 | -2.4 ± 0.1 | -2.6 | 0.31 | 1.9 ± 0.4 | 2.0 | -22.0 ± 1.4 | -21.5 |
| <chem>CH3C#N+</chem> | -3.91 | -3.65 | -1.8 ± 1.2 | -1.0 | 30.77 | 34.7 ± 0.4 | 34.6 | -44.2 ± 0.5 | -44.5 |
| | 0 | 0 | +0.9 ± 1.2 | +0.5 | 1.64 | 5.2 ± 0.3 | 5.3 | -169.4 ± 1.1 | -169.3 |
| | 0 | 0 | +0.9 ± 1.2 | +0.5 | 1.64 | 5.2 ± 0.3 | 5.3 | -169.4 ± 1.1 | -169.3 |
| <chem>O=C=S</chem> | +0.71 | +0.72 | -0.8 ± 0.2 | -1.0 | 41.5 | 46.2 ± 0.6 | 46.7 | -38.6 ± 2.0 | -41.6 |
| | 0 | 0 | +0.4 ± 0.2 | +0.5 | 0 | 4.5 ± 0.6 | 5.0 | -215.5 ± 2.0 | -218.0 |
| | 0 | 0 | +0.4 ± 0.2 | +0.5 | 0 | 4.5 ± 0.6 | 5.0 | -215.5 ± 2.0 | -218.0 |
| <chem>O=C=O</chem> | 0 | 0 | -4.4 ± 0.2 | -4.4 | 21.64 | 25.5 ± 1.0 | 25.5 | -24.9 ± 3.0 | -27.6 |
| | 0 | 0 | +2.2 ± 0.2 | +2.2 | 0 | 2.9 ± 1.0 | 3.2 | -120.6 ± 2.0 | -122.0 |
| | 0 | 0 | +2.2 ± 0.2 | +2.2 | 0 | 2.9 ± 1.0 | 3.2 | -128.6 ± 2.0 | -122.0 |
| | 2.98 | -3.23 | -9.4 ± 1.2 | -8.8 | 55.3 | 63.2 ± 1.8 | 62.4 | -185.0 ± 3.9 | -182.4 |
| | 0 | 0 | +4.5 ± 1.1 | 3.6 | 26.9 | 32.8 ± 1.8 | 32.6 | -314.1 ± 5.2 | -309.1 |
| | 0 | 0 | +4.9 ± 1.7 | 5.2 | 4.9 | 10.8 ± 1.8 | 10.4 | -407.5 ± 5.6 | -403.4 |
| | 2.55 | -2.54 | -1.2 ± 1.5 | -2.9 | 28.9 | 32.3 ± 0.5 | 32.5 | -64.1 ± 1.4 | -62.5 |
| | 0.87 | +0.93 | +1.0 ± 0.9 | +1.9 | 5.5 | 9.6 ± 0.4 | 9.3 | -160.4 ± 1.8 | -160.1 |
| | 0 | 0 | +1.2 ± 1.8 | +1.0 | 1.5 | 5.6 ± 0.5 | 5.4 | -177.4 ± 1.8 | -177.0 |
| <chem>HC#CF</chem> | 0.75 | -0.77 | +4.0 ± 0.2 | +3.8 | 28.34 | 31.5 ± 0.6 | 31.0 | -31.0 | -31.0 |
| | 0 | 0 | -2.0 ± 0.2 | -1.9 | 0 | 3.5 ± 0.6 | 3.5 | -147.9 | -147.9 |
| | 0 | 0 | -2.0 ± 0.2 | -1.9 | 0 | 3.5 ± 0.6 | 3.5 | -147.9 | -147.9 |
| | 0 | 0 | +2.6 ± 0.1 | +2.5 | 1.14 | 1.9 ± 0.7 | 1.9 | -13.4 ± 1.0 | -13.4 |
| | -1.84 | -1.87 | -0.1 ± 0.1 | +0.0 | 0.57 | 1.7 ± 0.7 | 1.7 | -14.3 ± 1.0 | -14.6 |
| | 0 | 0 | -2.5 ± 0.1 | -2.5 | 0 | 1.4 ± 0.7 | 1.5 | -15.4 ± 1.0 | -15.3 |
| | +0.45 | +0.46 | -0.4 ± 0.4 | -0.3 | 13.91 | 17.8 ± 0.2 | 17.8 | -82.3 ± 0.4 | -82.2 |
| | 0 | 0 | +2.4 ± 0.3 | +2.4 | 10.03 | 13.5 ± 0.2 | 13.5 | -100.4 ± 0.4 | -100.5 |
| | 0 | 0 | -2.0 ± 0.6 | -2.1 | 1.67 | 5.8 ± 0.2 | 5.8 | -133.4 ± 0.4 | -133.0 |
| | 0 | 0 | +2.5 ± 0.4 | +2.3 | 12.89 | 16.3 ± 0.4 | 16.4 | -85.4 ± 0.9 | -85.5 |
| | 1.88 | -1.85 | -4.3 ± 0.5 | -5.5 | 9.07 | 13.3 ± 0.4 | 13.5 | -97.7 ± 1.1 | -98.2 |
| | 0 | 0 | +1.8 ± 0.8 | +2.2 | 3.38 | 6.8 ± 0.4 | 6.8 | -125.4 ± 2.0 | -126.0 |
| | 0.66 | -1.05 | +0.2 ± 0.4 | +1.2 | 30.2 | 36.2 ± 0.7 | 36.0 | -189.5 ± 1.8 | -188.0 |
| | 0 | 0 | +5.9 ± 0.3 | +5.6 | 32.6 | 37.8 ± 0.7 | 37.7 | -182.5 ± 1.8 | -182.0 |
| | 0 | 0 | -6.1 ± 0.4 | -6.8 | 0.0 | 6.8 ± 0.7 | 6.8 | -313.9 ± 1.8 | -314.0 |
| | 3.67 | -3.17 | -3.1 ± 0.3 | -4.8 | 50.77 | 57.2 ± 4.0 | 57.6 | -158.9 ± 6.0 | -158.6 |
| | 1.99 | +1.84 | -1.9 ± 0.4 | -0.3 | 22.51 | 28.8 ± 4.0 | 28.7 | -279.6 ± 6.0 | -280.9 |
| | 0 | 0 | +5.0 ± 0.6 | +5.1 | 3.24 | 8.6 ± 4.0 | 8.6 | -365.5 ± 6.0 | -366.3 |
| | 3.03 | -3.05 | -2.5 ± 0.3 | -5.7 | 100.0 | 107.6 ± 6.0 | 108.8 | -173.0 ± 9.0 | -172.9 |
| | 2.24 | +1.98 | +1.5 ± 0.4 | +3.9 | 25.0 | 32.1 ± 6.0 | 32.0 | -493.7 ± 18.7 | -497.0 |
| | 0 | 0 | +1.0 ± 0.6 | +1.8 | 1.6 | 8.7 ± 6.0 | 8.8 | -592.7 ± 19.0 | -595.0 |
| | 0 | 0 | +2.8 ± 1.4 | +3.3 | 53.6 | 60.1 ± 1.5 | 60.8 | -286.0 ± 10.0 | -295.0 |
| | 0 | 0 | +2.8 ± 1.4 | +3.3 | 53.6 | 60.1 ± 1.5 | 60.8 | -286.0 ± 10.0 | -295.0 |
| | 0 | 0 | -5.6 ± 2.8 | -6.6 | 0 | 7.7 ± 1.2 | 8.7 | -508.0 ± 20.0 | -516.0 |
| | 1.66 | -1.34 | -1.9 ± 0.8 | -2.1 | 103.6 | 111.8 ± 0.7 | 112.9 | -293.3 ± 1.7 | -302.3 |
| | 0 | 0 | +5.1 ± 1.0 | +6.1 | 53.6 | 60.8 ± 0.7 | 61.8 | -509.7 ± 3.6 | -519.0 |
| | 0 | 0 | -3.2 ± 1.0 | -4.0 | 0 | 8.4 ± 0.7 | 9.4 | -732.4 ± 5.0 | -741.0 |
| | 0 | 0 | -1.8 ± 1.0 | -2.5 | 10.54 | 13.0 ± 0.7 | 13.3 | -33.1 ± 1.6 | -34.1 |
| | 0 | 0 | -1.8 ± 1.0 | -2.5 | 1.66 | 3.9 ± 0.7 | 4.0 | -71.9 ± 1.8 | -73.0 |
| | -1.64 | -1.68 | +3.6 ± 2.0 | +5.0 | 1.66 | 3.9 ± 0.7 | 4.0 | -71.9 ± 2.3 | -73.5 |
| | 0 | 0 | -1.7 ± 0.4 | -0.6 | 62.40 | 68.2 ± 4.8 | 68.6 | -145.7 ± 10.6 | -149.0 |
| | 2.42 | -2.40 | +3.0 ± 0.3 | +2.3 | 24.00 | 25.2 ± 4.8 | 29.4 | -312.1 ± 10.7 | -315.0 |
| | 0 | 0 | -1.3 ± 0.5 | -1.7 | 0 | 5.3 ± 4.8 | 5.6 | -413.1 ± 10.8 | -417.0 |
| | 0.36 | -0.34 | +0.6 ± 0.3 | +2.1 | 33.52 | 37.5 ± 0.5 | 37.1 | -73.3 ± 1.3 | -73.3 |
| | 0.05 | -0.05 | +2.9 ± 0.5 | +2.2 | 7.58 | 11.2 ± 0.5 | 11.2 | -184.8 ± 1.6 | -183.5 |
| | 0 | 0 | -3.5 ± 0.7 | -4.3 | 1.54 | 6.1 ± 0.5 | 6.1 | -206.6 ± 1.7 | -205.3 |

^a The experimental results are also shown. The numbers are from ref. 35.

"on" the other n nuclei. The prime on the summation indicates that the $n = k$ term is omitted. If the bonded atom re-

tains a major share of the free atom electron distribution, we have a free atom term for the first term in eq 129

$$\frac{e^2}{3mc^2} \langle 0 | \sum_k^{Z_A} r_k^{-1} | 0 \rangle = \sigma_{\text{atom}}^d(A) \quad (130)$$

We evaluate the second term in eq 129 by using the substitution in eq 112 giving

$$\sum_n' \langle 0 | \sum_{i_n}^{Z_n} (r_{i_n})^{-1} | 0 \rangle = \sum_n' \langle 0 | \sum_{i_n}^{Z_n} (|r_n + \rho_i|)^{-1} | 0 \rangle$$

This equation can be expanded in a Taylor series about the n th nucleus. Retaining the first three terms of the expansion gives eq 131, where we have used the Born-Oppenheimer

$$\begin{aligned} \sum_n' \langle 0 | (r_i)^{-1} | 0 \rangle &= \sum_n' \frac{Z_n}{r_n} - \sum_n' (r_n)^{-3} \times (r_n \cdot \langle \rho \rangle_n) + \\ &\sum_n' \left[-\frac{\langle \rho^2 \rangle_n}{2r_n^3} + \left(\frac{3}{2r_n^5} \right) (x_n^2 \langle x^2 \rangle_n + \right. \\ &y_n^2 \langle y^2 \rangle_n + z_n^2 \langle z^2 \rangle_n) + (3/r_n^5) (x_n y_n \langle xy \rangle_n + \\ &\left. x_n z_n \langle xz \rangle_n + y_n z_n \langle yz \rangle_n) \right] \quad (131) \end{aligned}$$

approximation and we have assumed the molecule is a rigid rotor. Referring to our earlier arguments following eq 127 we assume that the charge distribution on the n th atom will be nearly spherically symmetric; therefore

$$\langle x^2 \rangle_n \cong \langle y^2 \rangle_n \cong \langle z^2 \rangle_n \cong \langle \rho^2 \rangle_n / 3 \quad (132)$$

and

$$\langle xy \rangle_n \cong \langle xz \rangle_n \cong \langle yz \rangle_n \cong 0 \quad (133)$$

Substituting the results of eq 130, 131, 132, and 133 into eq 129, we obtain the average diamagnetic shielding in terms of the atom dipoles⁴²

$$\sigma_{\text{av}}^d(A) = \underbrace{\sigma_{\text{atom}}^d(A)}_I + \underbrace{\frac{e^2}{3mc^2} \sum_n' \frac{Z_n}{r_n}}_{II} - \underbrace{\frac{e^2}{3mc^2} \sum_n' \frac{r_n \cdot \langle \rho \rangle_n}{r_n^3}}_{III} \quad (134)$$

The corresponding result for the individual diagonal tensor elements is easily derived giving eq 135.⁴²

$$\begin{aligned} \sigma_{xx}^d(A) &= \underbrace{\sigma_{\text{atom}}^d(A)}_I + \underbrace{\frac{e^2}{2mc^2} \sum_n' \frac{Z_n}{r_n^3} (y_n^2 + z_n^2)}_{II} + \\ &\underbrace{\frac{e^2}{2mc^2} \sum_n' [(2r_n^{-3}) (y_n \langle y \rangle_n + z_n \langle z \rangle_n) - (3r_n^{-5}) (y_n^2 + z_n^2) (r_n \cdot \langle \rho \rangle_n)]}_{III} + \\ &\underbrace{\frac{e^2}{2mc^2} \sum_n' [2(r_n^{-3}) \langle \rho^2 \rangle_n - 3(r_n^{-5}) \times (y_n^2 + z_n^2) \langle \rho^2 \rangle_n]}_{IV} \quad (135) \end{aligned}$$

There are four types of contributions to eq 134 and 135. The first term is the free atom contribution which can be obtained from free atom Hartree-Fock calculations. A tabulation of $\sigma_{\text{atom}}^d(A)$ for several atoms A is given in Table XIV. The second terms (II) in eq 134 and 135 are atomic number weighted sums over all nuclei. These first two terms (I and II) were used in eq 99 to estimate the diamagnetic shielding in

TABLE XIII. Calculated Values of $\chi_{\text{av}}^d = (e^2 N / 6mc^2) \langle 0 | \sum_i r_i^2 | 0 \rangle$ and $\langle 0 | 1/3 \sum_i r_i^2 | 0 \rangle = \langle r^2/3 \rangle_n$ for Several Neutral Atoms of Interest

| Atom | $-\chi^d \times 10^6$ | $\langle r^2/3 \rangle_n \times 10^{16}$ | Atom | $-\chi^d \times 10^6$ | $\langle r^2/3 \rangle_n \times 10^{16}$ |
|------|-----------------------|--|------|-----------------------|--|
| H | 2.4 | 0.28 | Ca | 44.83 | |
| He | 1.88 | | Sc | 42.13 | |
| Li | 14.76 | 1.74 | Ti | 39.76 | |
| Be | 13.72 | 1.62 | V | 37.67 | |
| B | 12.56 | 1.48 | Cr | 30.11 | |
| C | 10.93 | 1.29 | Mn | 34.14 | |
| N | 9.57 | 1.12 | Fe | 32.59 | |
| O | 8.85 | 1.04 | Co | 31.22 | |
| F | 8.11 | 0.95 | Ni | 29.98 | |
| Ne | 7.43 | | Cu | 26.30 | |
| Na | 21.50 | | Zn | 27.69 | |
| Mg | 23.45 | | Ga | 32.42 | |
| Al | 26.52 | | Ge | 32.95 | |
| Si | 25.56 | | As | 32.53 | |
| P | 23.99 | 2.82 | Se | 32.59 | 3.83 |
| S | 23.11 | 2.72 | Br | 32.10 | 3.78 |
| Cl | 21.89 | 2.58 | Kr | 31.32 | |
| Ar | 20.63 | | Xe | 44.85 | |
| K | 40.57 | | | | |

^a From G. Malli and S. Fraga, *Theor. Chim. Acta*, **5**, 284 (1966). Only $\langle r^2/3 \rangle_n$ values for the most common atoms in molecules are listed. The conversion factor between $-\chi^d$ and $\langle r^2/3 \rangle_n$ is 8.4850×10^{10} .

several molecules.²⁶ The third term, III, arises if the point charges are not centered on the n th nucleus but are displaced by a distance $\langle \rho \rangle_n$. This term (the dipole term) is in general quite small (normally less than a few parts per million) relative to the preceding terms. We now see the validity of using eq 99 to estimate the average diamagnetic susceptibilities as shown in Table VIII. The fourth term, IV, only appears in $\sigma_{xx}^d(A)$ in eq 135 and arises because the electronic charge distribution on the n th nucleus is not a point charge but is spatially extended.

In Table XV we list the values of σ_{xx}^d , σ_{yy}^d , σ_{zz}^d , and σ_{av}^d calculated from eq 134 and 135 and the numbers in Tables XI and XIV. Of course, the molecular structure must be known also. The first column in Table XV lists the diamagnetic susceptibilities and the numbers in parentheses are from reliable *ab initio* calculations. It is evident that the values of σ_{av}^d are in excellent agreement. The individual diagonal elements in σ^d are also in quite good agreement in most cases. The second column lists the values of σ_{xx}^p , σ_{yy}^p , σ_{zz}^p , and σ_{av}^p which are calculated with eq 96 and 97 with the known moments of inertia, the molecular structure, and the spin rotation constants (see Table IX). The total values of the magnetic shielding, $\sigma = \sigma^d + \sigma^p$, are also listed along with any available experimental data. These data are used to fix the magnetic shielding scales in Figures 10 and 11.

C. Localized Magnetic Susceptibilities

We now turn to a final analysis which uses a localized approach to magnetic parameters: the concept of localized magnetic susceptibilities. We discussed in sections V and VI the measurement of the molecular magnetic susceptibility anisotropy by spectroscopy. We also noted that the bulk susceptibility, $\chi = 1/3(\chi_{aa} + \chi_{bb} + \chi_{cc})$, could not be measured by the molecular Zeeman effect. However, there are a variety of methods to measure χ and a great number of results are available, some of which are listed in Table XVI. All of the diamagnetic molecules listed in Table XVI have zero spin and orbital angular momenta in their ground electronic states. The individual elements in the magnetic susceptibilities can be obtained by combining the bulk values, χ , with the anisotropies (see Table I-VI) as discussed previously (see also Figure 2). We will now give a theoretical justification for using localized

atomic bulk as well as localized atomic (or bond) individual total susceptibility tensor elements to describe the corresponding molecular values.

We start with eq 46 which defines the diamagnetic, χ_{xx}^d , and paramagnetic, χ_{xx}^p , tensor elements in the molecular CM coordinate system. We use again the concepts introduced at the beginning of this section. We partition the sum over all molecular electrons into sums over each free atom number of electrons. Using this, substituting the transformation in eq 112 into eq 46, applying again the Born–Oppenheimer approximation, and making use of eq 52 lead to the values for the diamagnetic and paramagnetic susceptibilities shown in eq 136.

$$\chi_{zz}^d = -\frac{e^2}{4mc^2} \left\{ \sum_n Z_n (x_n^2 + y_n^2) + 2 \sum_n (x_n \langle x \rangle_n + y_n \langle y \rangle_n) + \sum_n (\langle x^2 \rangle_n + \langle y^2 \rangle_n) \right\}$$

$$\chi_{zz}^p = \frac{e^2}{4mc^2} \left\{ \sum_n Z_n (x_n^2 + y_n^2) + 2 \sum_n (x_n \langle x \rangle_n + y_n \langle y \rangle_n) \right\}$$

$$- \frac{e^2}{2m^2c^2} \sum_n \sum_{k>0} \left\{ \frac{\langle 0 | \sum_{i=1}^{Z_n} (\mathbf{L}_{i^n})_z | 0 \rangle \langle k | \sum_{i=1}^{Z_n} (\mathbf{L}_{i^n})_z | 0 \rangle + CC}{E_0 - E_k} \right\} \quad (136)$$

We have used

$$\sum_{i=1}^{Z_n} \langle 0 | r_n | 0 \rangle = Z_n r_n \quad (137a)$$

$$\sum_{i=1}^{Z_n} \langle 0 | \rho_{i^n} | 0 \rangle = \langle \rho \rangle_n \quad (137b)$$

and

$$\sum_{i=1}^{Z_n} \langle 0 | \rho_{i^n}^2 | 0 \rangle = \langle \rho^2 \rangle_n \quad (137c)$$

as defined previously. The vector $\mathbf{L}_i^n = -i\hbar (\rho_{i^n} \times \nabla_i)$ is the electronic angular momentum of the i th electron about the n th nucleus. χ_{xx} and χ_{yy} are given by cyclic permutation of the indices.

Considering $\chi_{xx} = \chi_{xx}^p + \chi_{xx}^d$ we note from eq 136 that the first two terms in χ^d and χ^p cancel, removing all explicit dependences on molecular coordinates. Hence, χ is "gauge invariant" while χ^d and χ^p are not. What remains is eq 138. The bulk value is given by eq 139.

$$\chi_{zz} = \sum_n \left\{ -\frac{e^2}{4mc^2} (\langle x^2 \rangle_n + \langle y^2 \rangle_n) - \left(\frac{e^2}{2m^2c^2} \right) \times \sum_{k>0} \frac{\langle 0 | \sum_{i=1}^{Z_n} (\mathbf{L}_{i^n})_z | k \rangle \langle k | \sum_{i=1}^{Z_n} (\mathbf{L}_{i^n})_z | 0 \rangle + CC}{E_0 - E_k} \right\}$$

$$\sum_n (\chi_n^d + \chi_n^p)_{zz} \quad (138)$$

$$\chi = \frac{1}{3} (\chi_{xx} + \chi_{yy} + \chi_{zz}) =$$

$$\sum_n (\chi_n^d + \chi_n^p) = \sum_n \chi_n \quad (139)$$

The total molecular susceptibility has now been expressed as a sum over operators localized on the various atomic nuclei. But they operate on wave functions which extend over the whole molecule. If the average values of these atomic operators are not greatly dependent on parts of the wave function far removed from the nucleus in question and if the relevant properties of the electron distribution around each nucleus are not much different for a given type of atom in different molecules, the terms within each sum over n in eq 138 and

TABLE XIV. Nuclear Diamagnetic Shielding in Atoms^a

| Atom | $\sigma_{av}^d \times 10^6$ ^b | Atom | $\sigma_{av}^d \times 10^6$ ^b |
|------|--|------|--|
| H | 17.7 | Sc | 1521.4 |
| He | 59.9 | Ti | 1622.7 |
| Li | 101.5 | V | 1726.6 |
| Be | 149.3 | Cr | 1833.0 |
| B | 202.0 | Mn | 1942.1 |
| C | 260.7 | Fe | 2052.9 |
| N | 325.5 | Co | 2166.4 |
| O | 395.1 | Ni | 2282.3 |
| F | 470.7 | Cu | 2400.7 |
| Ne | 552.7 | Zn | 2521.7 |
| Na | 628.9 | Ga | 2638.6 |
| Mg | 705.6 | Ge | 2757.1 |
| Al | 789.9 | As | 2877.2 |
| Si | 874.1 | Se | 2998.4 |
| P | 961.1 | Br | 3121.2 |
| S | 1050.5 | Kr | 3245.6 |
| Cl | 1142.6 | Rb | 3366.8 |
| Ar | 1237.6 | : | : |
| K | 1329.4 | I | 5501.6 |
| Ca | 1422.9 | Xe | 5642.3 |

^a The values of $\langle 0 | \sum_i (1/r_i) | 0 \rangle$ are calculated with the atomic Hartree–Fock functions and the resultant values are from G. Malli and C. Froese, *Int. J. Quant. Chem.*, **15**, 95 (1967). The value for hydrogen is easily computed. $\sigma_{av}^d = (e^2/3mc^2) \langle 0 | \sum_i (1/r_i) | 0 \rangle$.

139 will be independent and constant. They will, in short, be additive atomic susceptibilities which can be evaluated from measured molecules and used to predict the susceptibility of any desired molecule.

The applicability of the above two conditions to the diamagnetic first terms of eq 138 and 139 has been discussed earlier in this section (see Table XII, and the calculated values of χ^d). The average values of the squared coordinates around a nucleus are dominated by the electron distribution near that nucleus and are relatively constant from molecule to molecule. In fact, these atomic values in molecules are nearly identical with the free atom values and χ_n^d can be evaluated accurately from properties for almost any molecule as shown earlier.

It is hard to show theoretically that the average values of the atomic angular momentum operators in χ_n^p of eq 138 and 139 are localized. Physically this requirement can be understood to imply that there be no long-range circulation of electrons; in other words, each electron circulation is confined to localized orbitals. However, the usual model for aromatic compounds which involves a molecular ring current would indicate that this class of molecules cannot be treated by localized theories. There is also question as to whether small strained rings meet this localization criterion. In conclusion, there is reason to believe that an attempt to construct a system of local rules for the diagonal components of the susceptibility tensor might succeed for nonstrained, nonaromatic molecules.

The use of Pascal's rules for the semiempirical calculation of molecular magnetic susceptibilities reflects the above arguments. Pascal's rule for the empirical calculation of bulk magnetic susceptibilities is


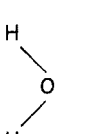
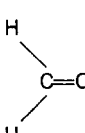



$$\chi = \sum_n \chi_n + \lambda \quad (140)$$

where χ_n are the empirical constants for each atom in a particular bonding situation and λ is a correction term due to the breakdown of the localized model in some molecules. Pascal's empirical constants for many atoms are shown in Table XVII. These empirical constants reflect the positive paramagnetic influence on the total susceptibility at each atom. For in-

TABLE XV. σ Tensor Elements in Several Molecules^a

| Molecule | Atom | σ_{xx}^d σ_{yy}^d σ_{zz}^d σ_{xy}^d | σ_{xx}^p σ_{yy}^p σ_{zz}^p σ_{xy}^p | σ_{xx} σ_{yy} σ_{zz} σ_{xy} | σ_{xx} (exptl) σ_{yy} σ_{zz} σ_{xy} |
|----------|------------------|--|--|--|--|
| H—H | ¹ H | 35.7 | 0.0 | 34.7 | |
| | | 30.4 | -8.4 | 22.0 | |
| | | 30.4 | -8.4 | 22.0 | |
| | | 32.9 (32.0) | -5.6 | 26.3 | 26.6 |
| H—F | ¹ H | 54 | 0 | 54 | |
| | | 137 | -119 | 18 | |
| | | 137 | -119 | 18 | |
| | | 109 (109) | -80 | 29 | 29.2 |
| | ¹⁹ F | 480 | 0 | 480 | |
| | | 487 | -94 | 393 | |
| | | 487 | -94 | 393 | |
| | | 484 (482) | -63 | 421 | 415 |
| H—Cl | ¹ H | 54 (45) | 0 | 54 | |
| | | 187 (190) | -166 | 21 | |
| | | 187 (190) | -166 | 21 | |
| | | 143 (142) | -111 | 32 | 31.5 |
| | ³⁵ Cl | 1146 (1148) | 0 | 1146 | |
| | | 1155 (1152) | -300 | 854 | |
| | | 1155 (1152) | -300 | 854 | |
| | | 1152 (1150) | -200 | 952 | |
| F—F | ¹⁹ F | 480 | 0 | 480 | |
| | | 555 | -1124 | -569 | |
| | | 555 | -1124 | -569 | |
| | | 530 (530) | -750 | -219 | -210 |
| H—C≡N | ¹⁴ N | 348 | 0 | 348 | |
| | | 398 | -627 | -229 | |
| | | 398 | -627 | -229 | |
| | | 381 | -418 | -37 | |
| | ¹ H | 48 | 0 | 49 | |
| | | 121 | -109 | 12 | |
| | | 121 | -109 | 12 | |
| | | 97 | -71 | 26 | 28 |
| N≡N | ¹⁵ N | 349 (338) | 0 | 349 | |
| | | 402 (407) | -729 | -327 | |
| | | 402 (407) | -729 | -327 | |
| | | 384 (385) | -486 | -102 | -101 |
| C≡O | ¹³ C | 280 (271) | 0 | 280 | |
| | | 349 (354) | -484 | -135 | |
| | | 349 (354) | -484 | -135 | |
| | | 326 (326) | -323 | 3 | |
| | ¹⁷ O | 419 (410) | 0 | 419 | |
| | | 456 (461) | -690 | -234 | |
| | | 456 (461) | -690 | -234 | |
| | | 444 (444) | -460 | -16 | |
| O=C=S | ¹³ C | 299 | 0 | 299 | |
| | | 483 | -579 | -96 | |
| | | 483 | -579 | -96 | |
| | | 421 | -386 | 35 | |
| | ¹⁷ O | 421 | 0 | 421 | |
| | | 538 | -978 | -440 | |
| | | 538 | -978 | -440 | |
| | | 499 | -652 | -153 | |
| | ³² S | 1060 | 0 | 1060 | |
| | | 1141 | -810 | 331 | |
| | | 1141 | -810 | 331 | |
| | | 1114 | -540 | 574 | |

TABLE XV (Continued)

| Molecule | Atom | σ_{xx}^d σ_{yy}^d σ_{zz}^d σ_{av}^d | σ_{xx}^p σ_{yy}^p σ_{zz}^p σ_{av}^p | σ_{xx} σ_{yy} σ_{zz} σ_{av} | σ_{zz} (exptl) σ_{yy} σ_{zz} σ_{av} | | |
|--|-----------------|--|--|--|--|----|------|
|  H—C≡C—H | ¹ H | 50 • | 0 | 50 | | | |
| | | 120 | −99 | 21 | | | |
| | | 120 | −99 | 21 | | | |
| | | 97 | −66 | 31 | | | |
|  H O H | ¹ H | 103 (103) | −71 | 31 | | | |
| | | 78 (75) | −37 | 41 | | | |
| | | 129 (130) | −108 | 21 | | | |
| | | 103 (103) | −72 | 31 | 30.2 | | |
|  H C=O H | ¹ H | 87 (93) | −69 | 18 | | | |
| | | 94 (95) | −70 | 24 | | | |
| | | 137 (147) | −120 | 17 | | | |
| | | 106 (111) | −86 | 20 | 21.3 | | |
|  H N H | ¹⁷ O | 418 (415) | −1600 | −1182 | | | |
| | | 468 (462) | −870 | −402 | | | |
| | | 470 (475) | −10 | 460 | | | |
| | | 452 (452) | −827 | −375 | | | |
| NH ₃ | ¹ H | 111 | −88 | 23 | | | |
| | | 60 | −16 | 44 | | | |
| | | 115 | −104 | 11 | | | |
| | | 95 | −67 | 28 | 30.8 | | |
|  H P H | ¹⁴ N | 364 | −117 | 247 | | | |
| | | 358 | −78 | 280 | | | |
| | | 358 | −78 | 280 | | | |
| | | 360 | −91 | 269 | 266 | | |
|  PH ₃ | ¹ H | 80 | } −88 } | } 35 } | | | |
| | | 165 | | | | | |
| | | 136 | | | −108 | 28 | |
| | | 127 | | | −98 | 29 | 28.3 |
| | ³¹ P | 983 | −370 | 612 | | | |
| | | 983 | −370 | 612 | | | |
| | | 985 | −421 | 564 | | | |
| | | 984 | −387 | 597 | | | |

^a The first column gives the diamagnetic shieldings from eq 134 and 135 with the *ab initio* results in parentheses. The second column gives σ^p evaluated from the molecular structure, moments of inertia, and spin-rotation constants (eq 96 and 97). The final columns give the total calculated and experimental values of σ . The results are from ref 42.

stance, the atomic oxygen value of χ for an aldehyde or ketone is positive which indicates a dominant paramagnetic contribution. This probably arises because of the low-energy electronic transitions in the aldehyde or ketone group. As $E_0 - E_k$ appears in the sum over excited states, the low-energy transitions to states which have angular momentum will contribute the major share of the paramagnetic susceptibility.

Equation 140 is identical with eq 139 if we assume localized atomic (or bond) χ_n which are transferrable from molecule to molecule plus a correction factor λ which indicates the breakdown of the localized model. The constants in Table XVII are quite accurate in predicting molar bulk susceptibilities. For instance, $\chi = -53.15 \times 10^{-6}$ erg/(G² mol) for CH₃CH₂Br from Table XVII compared to the experimental result in Table XVI of -54.7×10^{-6} erg/(G² mol).

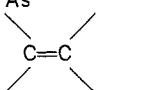
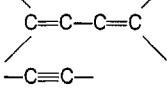
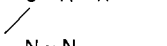
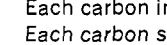
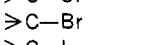
Being satisfied that the bulk or average magnetic susceptibilities are accurately described by localized atomic values we now return to eq 138 to determine a set of localized values for the individual elements, χ_{aa} , χ_{bb} , and χ_{cc} of the magnetic susceptibility tensor.⁴³ We list the experimental values for the individual components of the susceptibility tensor in a number of nonstrained molecules in Table XVIII.

TABLE XVI. Average Molar Magnetic Susceptibilities of a Number of Molecules^a

| Molecule | $-\chi \times 10^6$ | Molecule | $-\chi \times 10^6$ |
|-------------------|---------------------|------------------------------|---------------------|
| Acetaldehyde | 22.7 | 1,1-Dichlorodifluoroethylene | 60.0 |
| Acetic acid | 31.5 | Diethylamine | 56.8 |
| Acetone | 33.7 | Ethyl bromide | 54.7 |
| Acetonitrile | 28.0 | Ethylene oxide | 30.7 |
| Acetophenone | 72.05 | Methyl chloroacetate | 58.1 |
| Acetyl chloride | 81.5 | Nitrobenzene | 61.8 |
| Alanine | 50.5 | Propane | 40.5 |
| Anisole | 72.79 | Propene | 31.5 |
| Benzene | 54.8 | Propionic acid | 43.5 |
| Benzyl chloride | 81.98 | Thiazole | 50.55 |
| Butyl bromide | 77.14 | Toluene | 66.11 |
| Butane | 57.4 | 1,3,5-Trinitrobenzene | 74.55 |
| Bromobenzene | 79.98 | Triethylamine | 81.4 |
| Chloroacetic acid | 48.1 | <i>o</i> -Xylene | 77.78 |
| Chlorobenzene | 69.97 | <i>m</i> -Xylene | 76.56 |
| Cyclopropane | 39.9 | <i>p</i> -Xylene | 76.78 |

^a The units are cm³/mol. The source is "Handbook of Chemistry and Physics," The Chemical Rubber Co., Cleveland, Ohio, 1964.

TABLE XVII. Pascal's Constants for the Computation of Molecular Magnetic Susceptibility^a

| Atom or correction | $-x \times 10^{-6}$ |
|---|---------------------|
| H | -2.93 |
| C | -6.00 |
| N open chain | -5.57 |
| N ring | -4.61 |
| N monoamide | -1.54 |
| N diamide, imide | -2.11 |
| O alcohol, ether | -4.61 |
| O aldehyde, ketone | +1.73 |
| O carboxyl group | -3.36 |
| F | -11.5 |
| Cl | -20.1 |
| Br | -30.6 |
| I | -44.6 |
| S | -15.0 |
| Se | -23.0 |
| P | -26.0 |
| As | -43.0 |
|  | +5.5 |
|  | +10.6 |
|  | +0.8 |
|  | +8.2 |
|  | +1.8 |
| Each carbon in aromatic ring | -0.24 |
| Each carbon shared between rings | -3.10 |
| >C-Cl | +3.1 |
| >C-Br | +4.1 |
| >C-I | +4.1 |

^a The numbers are from P. W. Selwood, "Magnetochemistry," Interscience, New York, N. Y., 1943.

These molecules should all satisfy the criterion necessary to determine a set of localized atomic values.

For convenience in application we have obtained both atom and bond values. In the atom approach we have assumed that an atom in a particular bonding situation (particular hybridization) will always contribute the same amount to the molecular susceptibility. This contribution consists of the three principal components as shown in Table XIX under atom susceptibilities. To evaluate the molecular susceptibility the atom values are rotated into the principal inertial axis system (*a*, *b*, and *c*) of the molecule using the following equations

$$\chi_{aa} = \chi_{xx}\theta_{ax}^2 + \chi_{yy}\theta_{ay}^2 + \chi_{zz}\theta_{az}^2 \quad (141a)$$

$$\chi_{bb} = \chi_{xx}\theta_{bx}^2 + \chi_{yy}\theta_{by}^2 + \chi_{zz}\theta_{bz}^2 \quad (141b)$$

$$\chi_{cc} = \chi_{xx}\theta_{cx}^2 + \chi_{yy}\theta_{cy}^2 + \chi_{zz}\theta_{cz}^2 \quad (141c)$$

where θ_{ax} is the cosine of the angle between the principal inertial axis *a* and the atomic axis *x*. In order to use the transformation in eq 141 we require the atom or bond values of χ_{xx} , χ_{yy} , and χ_{zz} in Table XIX to be the principal values. These atomic contributions are then summed to give the molecular result. The same procedure can be followed in the bond approach with the bond values shown also in Table XIX. The atom and bond susceptibilities were determined by least-squares fitting of the experimental molecular susceptibility components of the 14 common nonstrained, nonaromatic molecules shown in Table XVIII.

Even though the two approaches to the evaluation of the susceptibility are equivalent, no detailed relationship exists

TABLE XVIII. Experimental and Semiempirically Calculated Values of χ_{aa} , χ_{bb} , and χ_{cc} ^a






| Molecule | Exptl | χ_{aa} , χ_{bb} , χ_{cc} | |
|----------------------|-----------------|---|-------|
| | | Atom | Bond |
| Methyl formate | -28.3 ± 0.5 | -28.6 | -28.1 |
| | -30.9 ± 0.6 | -29.8 | -30.2 |
| | -36.7 ± 0.8 | -36.7 | -36.4 |
| Acetaldehyde | -20.0 ± 0.9 | -21.3 | -20.6 |
| | -19.5 ± 0.9 | -19.1 | -18.0 |
| | -28.6 ± 1.5 | -29.2 | -28.9 |
| Propene | -30.9 ± 1.0 | -28.5 | -28.0 |
| | -26.2 ± 1.0 | -26.6 | -25.9 |
| | -34.9 ± 1.1 | -34.9 | -35.9 |
| Acrolein | -16.0 ± 3.0 | -18.1 | -20.3 |
| | -18.3 ± 3.0 | -18.5 | -18.5 |
| | -37.7 ± 4.0 | -37.7 | -39.4 |
| Maleic anhydride | -25.7 ± 1.5 | -25.1 | -27.0 |
| | -28.2 ± 1.5 | -27.5 | -29.4 |
| | -53.5 ± 1.7 | -54.3 | -54.0 |
| Cyclopent-2-en-1-one | -33.1 ± 4.0 | -37.0 | -36.2 |
| | -39.6 ± 4.0 | -38.0 | -37.6 |
| | -55.4 ± 6.0 | -55.7 | -52.8 |
| Cyclopent-3-en-1-one | -34.3 ± 4.5 | -39.1 | -38.1 |
| | -40.0 ± 4.0 | -35.9 | -35.7 |
| | -53.9 ± 6.0 | -55.7 | -52.8 |
| Vinylene carbonate | -35.3 ± 4.0 | -32.0 | -34.1 |
| | -30.5 ± 4.0 | -32.0 | -34.3 |
| | -47.4 ± 5.0 | -48.1 | -48.2 |
| 2-Pyrone | -36.1 ± 4.0 | -32.9 | -35.2 |
| | -34.4 ± 4.0 | -34.5 | -36.3 |
| | -60.0 ± 6.0 | -60.0 | -61.0 |
| 4-Pyrone | -31.2 ± 4.0 | -32.6 | -37.4 |
| | -31.9 ± 4.0 | -34.8 | -34.8 |
| | -54.5 ± 6.0 | -60.0 | -61.0 |
| Isoprene | -35.4 ± 4.0 | -36.9 | -36.1 |
| | -34.5 ± 4.0 | -39.7 | -38.8 |
| | -52.8 ± 5.0 | -54.3 | -56.1 |
| Formic acid | -18.8 ± 1.5 | -16.9 | -17.9 |
| | -16.8 ± 1.5 | -16.3 | -15.7 |
| | -24.2 ± 2.0 | -25.8 | -25.4 |
| Glycolaldehyde | -27.6 ± 4.0 | -28.9 | -29.4 |
| | -23.7 ± 4.0 | -27.8 | -26.5 |
| | -38.6 ± 4.5 | -37.1 | -35.1 |
| Water | -12.2 ± 2.0 | -13.0 | -11.3 |
| | -13.4 ± 2.0 | -13.6 | -12.7 |
| | -13.4 ± 2.5 | -12.1 | -11.0 |

^a The calculated values are from the atom and bond values in Table XIX.

between the bond and atom parameters. The value of an atomic susceptibility depends on how the bonds to that atom are distributed between it and its neighbors. Similarly, the value of a bond susceptibility depends on how the electron density near a nucleus is divided among the bonds to that nucleus. Therefore, the only valid comparison of the methods is a comparison of the results they predict for entire molecules. In addition, agreement of the methods is a good check on the accuracy of the calculation.

It is evident from the results in Table XVIII that the molecular susceptibilities obtained from the local values in Table XIX

TABLE XIX. Local Atom and Bond Susceptibilities (from ref 43)

| y Atom Susceptibilities | | | | y Bond Susceptibilities | | | |
|---|-------|-------|-------|-------------------------|-------|-------|-------|
| z (out-of-plane) | x | y | z | z (out-of-plane) | x | y | z |
| H ^a | -2.0 | -2.3 | -2.3 | C-H ^a | -5.6 | -3.1 | -3.1 |
|  | -9.5 | -6.7 | -6.7 | C-C ^a | -7.9 | -0.2 | -0.2 |
| | | | | C=C ^a | -0.8 | +4.0 | -13.8 |
|  | -6.5 | -8.0 | -7.1 | C-O ^a | -7.2 | -6.7 | -3.8 |
| | | | | C=O ^a | -1.3 | +2.2 | -13.0 |
| O ^a - | -9.2 | -8.8 | -7.5 | O-H ^a | -4.5 | -7.5 | -5.5 |
|  | -2.9 | -3.5 | -7.4 | C-S ^d | -12.6 | -11.3 | -8.9 |
| O ^a = | -0.1 | -0.1 | -6.3 | C=S ^b | +5.8 | -11.0 | -28.8 |
| | | | | C≡C ^b | -13.7 | -14.2 | -14.2 |
| -C ^b ≡ | -9.9 | -7.4 | -7.4 | C≡N ^b | -16.5 | -11.6 | -11.6 |
| N ^b ≡ | -9.5 | -4.5 | -4.5 | C≡P ^b | -30.4 | -24.5 | -24.5 |
|  | -11.3 | -14.8 | -2.5 | | | | |
| S | -18.7 | -15.7 | -16.8 | | | | |
|  | | | | | | | |
| S ^b = | +4.7 | -13.1 | -23.0 | | | | |
| P ^b ≡ | -24.1 | -17.9 | -17.9 | | | | |

^a Determined from least-squares fit of molecules in Table XVIII. ^b Determined from a limited number of molecules assuming the least-squares values for the other parameters.

are in good agreement with experimental results. These local values can now be used to predict the molecular susceptibility of nonstrained, nonaromatic compounds on which measurements are not available. In conclusion we have extended the well-known Pascal's rules for bulk susceptibility to the individual diagonal elements in the molecular magnetic susceptibility tensor. Of course, the diagonal sums of the values given in Table XIX also allow a prediction of the bulk susceptibilities.

Since these local group susceptibility values are derived under the explicit assumption that all electron motions are localized, the difference between the observed magnetic susceptibility and that calculated from local group values should provide a quantitative measure of electron delocalization and hence aromaticity. Table XX provides a comparison between experimental and calculated molecular susceptibilities in a number of ring compounds. It is apparent that the calculated and experimental in-plane susceptibilities are in good agreement. It is also evident that electron delocalization influences only the out-of-plane component of the susceptibility. This is consistent with the ring current model of aromaticity which postulates a free circulation of electrons around closed conjugated rings in the presence of a magnetic field. This induced current should manifest itself as a large negative contribution to the out-of-plane component of the magnetic susceptibility which is what is observed.

The χ_{nonlocal} values in Table XX provide a quantitative method of comparing aromaticities relative to some standard such as benzene. It would appear that thiophene and pyrrole are virtually as aromatic as benzene while furan is less so. Cyclopentadiene is nearly as aromatic as furan (as hyperconjugation would suggest), while fulvene shows surprisingly small aromaticity. Benzene rings connected by σ bonds are virtually additive in their aromaticity while those linked by π bonds (where increased conjugation is possible) show increased aromaticity. Fused benzene rings also show enhanced aromaticity as predicted from the ring current model. It is also interesting to note that carbonyl insertion tends to

decrease aromaticity, e.g., quinone or naphthazarin and, of course, the pyrones and tropone.

Local susceptibility values are also useful in elucidating molecular structure. By comparing measured and calculated susceptibility elements, it is possible to obtain the broad features of molecular conformation. For example, hexa-2,4-dienoic acid has been considered planar. From crystal measurements it has been determined that $\chi_{cc} = -44.0 \times 10^{-6}$ erg/(G² mol);⁴⁴ however, a calculation of χ_{cc} from local values gives $\chi_{cc} = -75.5 \times 10^{-6}$ erg/(G² mol). Hence, it is evident that the planar structure is not correct and at least one of the functional groups must be twisted with respect to the plane of the molecule. In molecules containing groups with very high anisotropy such as aromatic rings even more detailed structural information can be obtained by calculating molecular anisotropy as a function of twist angle. While this procedure is not useful in obtaining small variations in bond angles or bond lengths, it should be a useful tool in conformational analysis.

Calculated magnetic susceptibility anisotropies may also find application in liquid crystal work. The ratio of the elastic constant to the volume susceptibility anisotropy of a liquid crystal can be measured with bulk techniques.⁴⁵ But without $\Delta\chi$ the elastic constant itself can be extracted only from microscopic measurements. While experimental determination of this anisotropy in liquid crystals is a formidable task, its calculation from local values is quite straightforward if the structure of the molecule is known.

Because the susceptibility anisotropy was nearly impossible to measure directly before the advent of Zeeman microwave spectroscopy, most past work has centered around deriving approximate susceptibilities from approximate values for other molecular quantities. With the availability of accurate susceptibility anisotropies, it has become profitable to reverse this procedure and use these susceptibilities to derive more accurate values for related molecular parameters.

Cotton-Mouton measurements provide a relationship

TABLE XX. Comparison between Experimental and Calculated Magnetic Susceptibilities in Ring Compounds (from Ref 43)






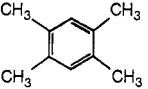
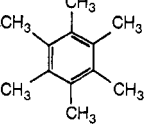
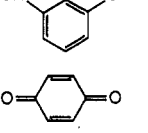
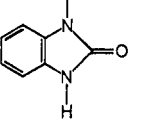
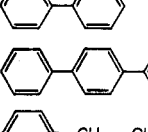
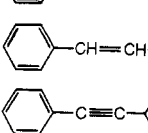
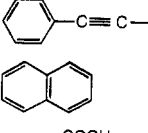
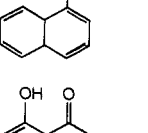
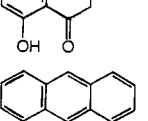

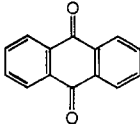
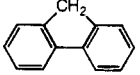
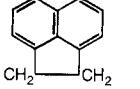
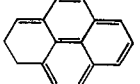
| Molecule | χ^a (av in-plane) | | χ_{cc}^c (nonlocal) |
|---|--|----------------------|----------------------------|
| | Exptl ^d | Calcd ^e | |
|  | -34.9 ± 2.0 -94.6 ± 2.5 | -33.4 -59.4 | -35.2^f |
|  | $-30.6 \pm 2.0^*$ $-67.6 \pm 2.5^*$ | -33.4 -59.4 | -8.2 |
|  | $-33.3 \pm 1.0^*$ $-67.5 \pm 1.5^*$ | -33.8 -50.5 | -17.0 |
|  | $-31.9 \pm 1.5^*$ $-70.6 \pm 2.0^*$ | -31.3 -47.0 | -23.6 |
|  | $-40.7 \pm 2.0^*$ $-90.8 \pm 2.5^*$ | -40.3 -56.8 | -34.0 |
|  | $-34.4 \pm 2.0^*$ $-76.8 \pm 2.5^*$ | -34.5 -42.4 | -34.4 |
|  | -79.8 -143.9 | -80.4 -100.8 | $-43.1 = (-35.2) - 7.9$ |
|  | -101.9 -163.4 | -107.0 -121.5 | $-41.9 = (-35.2) - 6.7$ |
|  | -49.2 -103.2 | -50.5 -71.1 | $-32.1 = (-35.2) + 3.1$ |
|  | -25.0 -65.2 | -28.8 -66.5 | $+1.3$ |
|  | -60.0 -124.2 | -59.8 -78.4 | $-45.8 = (-35.2) - 10.6$ |
|  | -64.7 -183.8 | -62.3 -113.0 | $-70.8 = 2(-35.2) - 0.4$ |
|  | -92.5 -271.3 | -91.2 -167.6 | $-103.7 = 3(-35.2) + 1.9$ |
|  | -90.8 -202.3 | -85.0 -135.0 | $-67.3 = 2(-35.2) + 3.3$ |
|  | -70.0 -209.6 | -73.2 -135.3 | $-74.3 = 2(-35.2) - 3.9$ |
| | -74.7 -198.3 | -77.4 -124.5 | $-73.8 = 2(-35.2) - 3.2$ |
| | -92.4 -206.7 | -87.2 -131.0 | $-75.7 = 2(-35.2) - 5.3$ |
| | -53.7 -173.5 | -51.3 -93.7 | $-79.8 = 2(-35.2) - 9.4$ |
| | -64.7 -192.5 | -63.5 -115.0 | $-77.5 = 2(-35.2) - 7.1$ |
| | -57.3 -140.1 | -62.5 -116.5 | $-23.6 = (-35.2) + 11.6$ |
| | -69.2 -251.6 | -69.2 -133.1 | $-118.5 = 3(-35.2) - 12.9$ |

TABLE XX (Continued)

| Molecule | χ^a (av in-plane) | | χ_{cc}^c (nonlocal) |
|---|------------------------|--------------------|--------------------------|
| | Exptl ^d | Calcd ^e | |
|  | -70.3 -217.6 | -64.6 -135.1 | -82.5 = 2(-35.2) - 12.1 |
|  | -68.0 -189.0 | -69.1 -119.0 | -70.0 = 2(-35.2) + 0.4 |
|  | -71.3 -185.5 | -69.4 -116.8 | -68.7 = 2(-35.2) + 1.7 |
|  | -80.6 -303.0 | -74.2 -142.6 | -160.4 = 4(-35.2) - 19.6 |

^a χ (av in-plane) = $1/2(\chi_{aa} + \chi_{bb})$, ^b χ_{cc} = out-of-plane component. ^c χ_{cc} (nonlocal) = χ_{cc} (exptl) - χ_{cc} (calcd). ^d Those values marked with an asterisk were measured by Zeeman-microwave techniques in this laboratory (see ref 5). The rest were obtained by single-crystal measurements. ^e These values are the average of those calculated using the atom and the bond contributions from Table XVIII. ^f -35.2 is the χ_{cc} (nonlocal) for benzene.

among the magnetic susceptibility anisotropy ($\Delta\chi$), the electric polarizability anisotropy ($\Delta\alpha$), and the electronic distortion anisotropy ($\Delta\eta$). According to the following equation⁴⁶

$$mC = \frac{2}{135} \pi N [\Delta\eta + \left(\frac{2}{3kT}\right) \Delta\alpha \Delta\chi] \quad (142)$$

where mC is the molar Cotton-Mouton constant, N is Avogadro's number, k is Boltzmann's constant, and T is the absolute temperature. η is related to the variation of electric polarizability with magnetic field. Several attempts have been made to evaluate susceptibility anisotropies by measuring the Cotton-Mouton constant and the polarizability anisotropy, and using eq 142 by assuming a value of zero for $\Delta\eta$ (spherical distortion).^{46,47} Using local values to obtain the susceptibility anisotropy we can now critically evaluate this assumption of spherical distortion, even in molecules where no experimental susceptibility anisotropy is available.⁴⁸ Table XXI shows the results of such calculations on several molecules. The contribution to mC from $\Delta\eta$ is certainly significant. Ignoring $\Delta\eta$ in eq 143 may introduce errors of as much as 20% into $\Delta\chi$.

Finally we turn to the most common source of derived magnetic susceptibility anisotropies: chemical shift measurements. McConnell⁴⁹ has derived an expression relating a part of the magnetic shielding to the susceptibility anisotropy of neighboring atoms or bonds. If the many other contributions to the shielding can be calculated, estimated or cancelled out, chemical shifts can be used to derive magnetic susceptibility anisotropies. Numerous such attempts appear in the literature, but few of the values for group anisotropies derived from chemical shift measurements are in agreement with the values given here. They are generally much smaller in magnitude and sometimes not even of the right sign. In addition, the proper origin to be assigned to a bond susceptibility when relating it to magnetic shielding is not clear. This uncertainty in a quantity believed to be small has led to the practice of ignoring susceptibility contributions in treatments of the chemical shift.⁵⁰

The fact that magnetic susceptibility anisotropies derived from chemical shifts agree so poorly with direct measurements would seem to indicate that some other contribution to the chemical shift has not been properly evaluated. It would therefore be worthwhile to reexamine the interpretation of

magnetic shielding data in the light of a more accurate calculation of the neighbor group magnetic susceptibility contribution. The use of atom as well as bond susceptibilities makes possible an unambiguous choice of origin for such a calculation since the origin of an atom susceptibility is clearly the nucleus.

Magnetic susceptibilities evaluated by the numbers in Table XIX can be combined with g values obtained by other methods to extract quadrupole moments. Alternatively, calculated susceptibility anisotropies can be combined with calculated quadrupole moments to yield the g values. For instance, Hartford, *et al.*,⁵¹ recently used a series of substituted acetylenes and substituted cyanides to obtain the magnetic susceptibility of $\text{HC}\equiv\text{CH}$. Their result was $\chi_{\perp} - \chi_{\parallel} = (4.5 \pm 0.5) \times 10^{-6}$ erg/(G²mol), which is in excellent agreement with the values of $\chi_{\perp} - \chi_{\parallel}$ for acetylene obtained from Table XIX which are 4.4 from the atom values and 4.5 from the bond values. Using $\chi_{\perp} - \chi_{\parallel} = 4.5$ and a reliable calculated quadrupole moment in $\text{HC}\equiv\text{CH}$, Hartford, *et al.*,⁵¹ were able to show that the g value in this molecule must be positive rather than negative as reported in the literature.⁵²

It is also gratifying to note that the values of $\chi_{zz} - 1/2(\chi_{xx} + \chi_{yy})$ calculated with the atom contributions in Table XIX agree quite well with past attempts to evaluate this quantity for groups on a local basis.^{21,53,54}

Even though we have not given local values for fluorine atoms in Table XIX, a good deal of information is available on the effects of fluorine substitution and some systematic trends do emerge.⁵⁵ One general result which has been noted

TABLE XXI. Electronic Distortion Anisotropies

| Molecule | mC (expt) $\times 10^{18}$, ^a emu mol ⁻¹ | $\Delta\chi_{\text{calcd}}^b$ ($\Delta\eta = 0$) | $\Delta\chi_{\text{exptl}}$ erg G ⁻² mol ⁻¹ | $\Delta\eta_{\text{calcd}}$ $\times 10^{42}$, ^b emu |
|---------------------------------|---|---|---|---|
| H ₂ | 0.15 | 0.62 | 0.55 ^c | 0.6 |
| CO | -4.0 | -10.2 | -8.2 ^c | -24 |
| H ₃ CCH ₃ | -1.4 | -2.4 | -4.3 | 41 |
| H ₂ CCH ₂ | 4.4 | 3.2 | 5.1 ^d | -96 |
| C ₆ H ₆ | 231 | -53.9 | -49.7 ^e | -906 |

^a Reference 46. ^b Electric polarizability anisotropies are from N. J. Bridge and A. D. Buckingham, *Proc. Roy. Soc. A*, **295**, 334 (1966). ^c $\Delta\chi$ from ref 5. ^d $\Delta\chi$ calculated from Table XIX. ^e $\Delta\chi$ from ref 46.

in the case of C-H and C-F bonds is that successive replacement of hydrogens by fluorines in the molecular plane give positive contributions of decreasing magnitude to the out-of-plane (c axis) minus the average in-plane magnetic susceptibility anisotropy, $\chi_{cc} - \frac{1}{2}(\chi_{aa} + \chi_{bb})$ or $\Delta\chi$.⁵⁵⁻⁵⁷ A similar trend is evident for the H₂O, HOF, and F₂O series where (see Table III) the following $\Delta\chi$'s ($\times 10^{-6}$ erg/(G² mol)) were found: (H₂O) -0.13 ± 0.03 , (HOF) 3.4 ± 0.7 , (F₂O) 6.6 ± 0.8 . We see that the first fluorine being added gives a slightly larger positive contribution ($+3.5 \pm 0.7$) than the second fluorine ($+3.2 \pm 1.1$). These results are similar to the results for fluorine-substituted ethylenes and formaldehyde: the first fluorine gives a contribution of $(+4.8 \pm 0.7) \times 10^{-6}$ erg/(G² mol), the second fluorine $+2.2 \pm 0.8$, and the third $+0.6 \pm 0.8$.⁵⁷

Other recent results show similar trends. Using the local atom contributions for $\Delta\chi$ in Table XIX gives $\Delta\chi = -8.8 \pm 0.8$ for ethylene, and combining this with the vinyl fluoride result of $\Delta\chi = -4.4 \pm 0.2$ gives a $+4.4 \pm 1.0$ contribution for the first fluorine substitution onto ethylene. Combining the results on pyridine and 2-fluoropyridine (see Table VI) which have $\Delta\chi = -57.4 \pm 0.7$ and -52.2 ± 1.0 , respectively, yields $+5.2 \pm 1.7$ for the first fluorine addition to pyridine. The combination of all these results yields the following values for each successive in-plane fluorine substitution onto planar molecules in place of hydrogen atoms, $\Delta(\Delta\chi)$ ($\times 10^{-6}$ erg/(G² mol)): (first fluorine) $+4.5 \pm 1.2$, (second fluorine) $+2.5 \pm 1.1$, (third fluorine) $+0.6 \pm 0.8$. Note that here the first fluorine substitution is onto atoms that were originally $sp^2 \rightarrow sp^3$ hybridized.

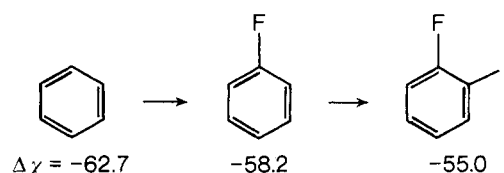
These trends are interesting in light of the results for linear molecules (see Table I) where the first fluorine substitution on an sp carbon gave essentially no change in $\Delta\chi$ [$\Delta\chi(\text{HCN}) = 3.6 \pm 0.2$ and $\Delta\chi(\text{FCN}) = 3.6 \pm 0.4$; $\Delta\chi(\text{HCCH}) = 2.2 \pm 0.3$ ⁵¹ and $\Delta\chi(\text{HCCF}) = 2.6 \pm 0.1$], where $\Delta\chi = \frac{1}{2}(\chi_{\perp} - \chi_{\parallel})$ by definition. It appears that fluorine cannot appreciably affect the sp orbital of carbon. The following is an analysis of why fluorine substitution gives varying positive contributions to $\Delta\chi$ for molecules other than those with sp carbons.

By correlating variations in bond lengths with changes in the electronegativity of one of the bonding atoms, Bent proposed that, when a substituent on a carbon atom is replaced by one of higher electronegativity, rehybridization occurs at the carbon atom, and the bond to the substituent has higher p character.⁵⁸ Bennett has extended this work to correlate the hybridization or amount of p character in the carbon-substituent bond with experimental bond angles.⁵⁹ In these approaches the bonding is described as involving orthonormal hybrid atomic orbitals (HAO's) at carbon formed by linear combinations of the atomic $2s$, $2p_x$, $2p_y$, $2p_z$ orbitals of carbon. On the basis of Bent's conclusion, if a hydrogen is replaced by fluorine, the carbon HAO used in the C-F bond will have higher p character than that of the original C-H bond, and the HAO used in the C-C bond in the fluorocarbon will have less p character due to the substitution of fluorine. For example, a carbon of ethylene is described as having three sp^2 HAO's, two for the hydrogens and one for the other carbon. On the other hand, in tetrafluoroethylene the HAO of carbon used in the bond to fluorine is now sp^3 while the HAO bonded to the other carbon is sp . This interpretation of the carbon HAO's fits nicely with our experimental $\Delta\chi$ results. Our work has shown that the first fluorine substitution on sp^2 carbons changes $\Delta\chi$ by about $+4.5$ while first fluorine substitution on an sp carbon produces essentially no change. In the ethylenes, for example, what appears to be happening is that the first fluorine changes the C-F HAO to higher p character than sp^2 while the C-C HAO is now less than sp^2 . Our results indicate that, when the carbon HAO is sp , fluorines will not affect $\Delta\chi$ and a carbon HAO between sp^2 and sp should be affected less by fluorine substitution than an sp^2 carbon HAO.

Our results support this concept since the second fluorine substitution changes $\Delta\chi$ by only $+2.5$. After the second fluorine is added, the new C-F HAO will now be about sp^3 , and the carbon HAO used in the C-C bond will be even closer to sp ; therefore the third fluorine should have an even smaller effect. We have found this to be true experimentally, as the third fluorine only contributes $+0.6$. Evidently, changing one carbon HAO used in the C-C bond affects the other carbon HAO and also makes it less than sp^2 , since second fluorine substitution onto vinyl fluoride produces nearly equal changes in $\Delta\chi$ for both *cis*-CHFCHF and CH₂CF₂. This interpretation also holds for the substituted formaldehydes and the water series, where the first fluorine is added to an approximately sp^3 oxygen. It should be noted that the interpretation has been restricted to planar molecules.

By combining the above additive value for first fluorine substitution of $+4.5 \pm 1.2$, which includes one ring substitution result (that of pyridine \rightarrow fluoropyridine, $\Delta(\Delta\chi) = +5.2$), and the susceptibility anisotropy for fluorobenzene ($\Delta\chi = -58.2 \pm 0.9$), we would predict $\Delta\chi$ for benzene to be -62.7 ± 2.1 , which is in fair agreement but more negative than $\Delta\chi = -59.7$ obtained from oriented crystal results.⁶⁰ Sutter has also used similar arguments based on the formyl fluoride, fluoropyridine, and fluorobenzene results to predict a $\Delta\chi$ for benzene of -63.2 .⁶¹ However, both the gas-phase prediction and the crystal work values of $\Delta\chi$ for benzene are significantly different from $\Delta\chi = -54 \pm 2$ obtained by Bogaard, *et al.*⁶² Indeed, in view of the pyridine-fluoropyridine series and the additive values for fluorine, it appears that the value of $\Delta\chi$ for benzene must be more negative than the value of $\Delta\chi = -58.3 \times 10^{-6}$ erg/(G² mol) for fluorobenzene. Available structural data on fluorobenzene and benzene can be used in conjunction with Bennett's correlation of bond angles and hybridization to indicate hybridization changes at the C-F carbon due to fluorine substitution. If the carbon atom where substitution will occur is designated as 1, the C(6)-C(1)-C(2) angle in benzene is 120° indicating an sp^2 carbon, while the analogous angle in fluorobenzene is 123.4° .⁶³ Based on Bennett's interpretation,⁵⁹ the C-F carbon HAO of fluorobenzene should therefore have greater p character than sp^2 and the C-C HAO's should be less than sp^2 . This is consistent with the prediction of $\Delta\chi$ (C₆H₅F) as more positive than $\Delta\chi$ (C₆H₆), since the results show that a positive contribution to $\Delta\chi$ results as the p character of the C-C HAO is lowered because of fluorine substitution.

We have indicated that the lower p character of one C-C HAO in vinyl fluoride is distributed so that both carbon HAO's used in the C-C bond have lower p character. Therefore, it might be expected that the lower p character of the carbon HAO in fluorobenzene would be distributed about the ring, and second fluorine substitution on the ring would give a smaller change to $\Delta\chi$ than the first. But because the lower p character is possibly distributed over six carbons and since it would be more difficult to distort the ring structure by a second fluorine than by the first fluorine, it would be expected that a second fluorine on the benzene ring would change $\Delta\chi$ by a somewhat larger amount than our additive values predict for a second fluorine. The available results support this idea as $\Delta\chi$ (C₆H₆F) = -58.2 ± 1.6 and $\Delta\chi$ (*o*-C₆H₄F₂) = -55.0 ⁶⁴ for a change of $+3.2$ as compared to our additive value of $+2.5$. From consideration of the series



we would expect $\Delta\chi \approx -(48-55) \times 10^{-6}$ erg/(G² mol) for any of the trifluorobenzenes which reflects some changes in $\Delta\chi$ depending on where the third fluorine is substituted. The result on 1,3,5-trifluorobenzene of $\Delta\chi = -39 \pm 2$ by Bogaard, *et al.*⁶² is considerably lower than our above estimate. However, the difference in $\Delta\chi$ between benzene and 1,3,5-trifluorobenzene given by Bogaard, *et al.*,⁶² overlaps with our estimated differences for the same two molecules. However, their absolute values of $\Delta\chi = -54 \pm 2$ for benzene and $\Delta\chi = -39 \pm 2$ for 1,3,5-trifluorobenzene are inconsistent with the above conclusions as extrapolated from the microwave experimental results on fluorobenzene and 1,2-difluorobenzene.

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