factor which is essentially $1+3\epsilon_1/2A+\cdots$, through the effect mentioned after (20). This is a small effect, and amounts, in the case mentioned above, to a 0.2 percent range increase.

B. Range Distribution

The mean square straggling is given by the old expression of Bohr, and can be expressed asymptotically by

$$\beta_2 = \langle \Delta R^2 \rangle = r^2 [1 + 3/2A + 3/A^2 + 15/2A^3 + \cdots]$$

where $r^2 = \epsilon_1 E_0^4 / k^2 A^3$, and

$$A = A_1(E_0) \approx 2 \ln(\epsilon_1 E_0/I) - 3\epsilon_1/2 + \cdots.$$

If we define $y = (x - \langle x \rangle)/\beta_2^{\frac{1}{2}}$, and $\gamma_\nu = \beta_\nu/\nu!\beta_2^{\nu/2}$, with the β_ν given by $(23^{\frac{1}{2}})$, then the range distribution is $h(y) \exp[-y^2/2]$, with $h(y)$ given as an expansion in hermite polynomials by (24). This function has a pronounced tail toward shorter-than-average range.

C. Most Probable Range

The most probable range is somewhat longer than the mean range, to compensate for the short range tail. One can estimate from the above that the displacement is

$$R_{\text{prob}} - R_{\text{mean}} \sim -3\gamma_3\beta_2^{\frac{1}{2}} = -\beta_3/2\beta_2$$

which is about 0.1 unit in Fig. 1, and is indicated there.

Rotational Magnetic Moments of $^1\Sigma$ Molecules*†

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(Received September 11, 1951)

The theory of the rotational magnetic moment in $^1\Sigma$ molecules is presented. This theory is applied in particular to describe experiments on the Zeeman effect for a linear rotor, OCS, and a symmetric top, NH₃.

1. THEORY

THE recent development of experimental techniques for observing low energy quantum transitions in the microwave and radiofrequency parts of the spectrum permits the study of molecular interactions which were previously not observable. These include internal molecular interactions, as well as the interaction of molecules and their component particles with externally applied fields. This report is concerned in particular with the magnetic moment generated by a molecule due to its free rotation, and the interaction of this moment with an external magnetic field, the Zeeman effect.

The measurements reported in Part 2 were made on molecular absorption lines in the microwave region. Other methods are available for making somewhat similar Zeeman measurements, notably the very precise molecular-beam technique.[1,2] These other experiments will not be discussed here except to point out that the various methods complement each other, since each has its own experimental difficulties, with the result

that some types of molecules and interactions can be effectively studied by one method and not by another. In some instances the various methods may serve as a check on each other.

The molecules to which the following discussion applies are those with $^1\Sigma$ electronic ground states, that is, those with zero total orbital and zero total spin angular momenta. Such molecules include by far the majority of the known cases, since the pairing of electrons with oppositely directed spins and the filling of electronic shells are so important to the formation of a chemical bond. The oxygen and nitric oxide molecules are important exceptions, each possessing a magnetic moment about equal to a Bohr magnetron since the electronic angular momenta are not zero in the ground state. For the $^1\Sigma$ molecules the rotational magnetic moment is much smaller and can be pictured as the result of electric currents due to the circulation of the charged nuclei and electrons. The nuclei can be considered to rotate as a semirigid framework, but, as will be seen, it is too naive to assume that the electronic contribution will be that of the electronic charge cloud frozen and rotating with the nuclear framework. Rather, the molecular rotation perturbs the electronic motion, due to the noncentral nature of the potential within a molecule, and internal electric currents are set up even though the electronic charge density distribution remains essentially unchanged from that of the fictitious nonrotating molecule.

[1] Rabi, Millman, Kusch, and Zacharias, Phys. Rev. 55, 526 (1939).

[2] Kellogg, Rabi, Ramsey, and Zacharias, Phys. Rev. 56, 728 (1939).

The theory of the Zeeman effect on the energy levels of a system involving a given magnetic moment or interacting moments is well known, and examples are provided in the experiments described later. But to interpret properly these experimental results it is also necessary to investigate how the rotational molecular moment actually arises and, in particular, its dependence on the rotational state of the molecule, and the molecular structural constants. This theory is implicit in Van Vleck's classic work on susceptibilities[3,4] and has been carried out by others for some cases of specific symmetry. Condon,[5] using wave mechanics, calculated the Zeeman effect for a symmetric top due to a point charge rigidly fixed on the top. This calculation, of course, includes the linear rotor as a special case and represents quite well the nuclear contribution to these moments. Wick[6-8] was first to calculate the electronic contribution to the rotational moment in the case of a diatomic molecule with two equivalent nuclei. Ramsey[9] has extended his theory to the case of a diatomic molecule with isotopic nuclei. Wick's immediate purpose was to explain the results of experiments by Frisch and Stern[10] and Estermann and Stern[11] on the hydrogen molecule. These experiments represent the initial measurements of such moments aside from susceptibility determinations. The measured moment of hydrogen indicated that the electronic contribution was much smaller than that of a rigid charge cloud, but Wick showed that it was indeed of the order of magnitude that one would expect on a more realistic picture of the electronic motion. Wick's considerations in one of his earlier papers[6] on the diatomic molecule are quite simple and instructive and are repeated here to preface the derivation given later for the general rotating molecule.

As shown by Van Vleck,[3] two terms are of importance for the susceptibility theory of $^1\Sigma$ molecules. One is a diamagnetic term resulting from the Larmor precession of the electrons in a magnetic field and the other is an induced electronic paramagnetism due to the non-central potential for electronic motion which hinders the pure Larmor precession. These terms are given in Eq. (1).

$$\bar{\chi}_{\text{molecule}} = -\frac{e^2}{4mc^2} \sum_i \langle X_i{}^2 + Y_i{}^2 \rangle_{\text{Av}}$$
$$+ \frac{e^2}{2m^2c^2} \sum_n{}' \frac{\langle |(0|L_Z|n)|^2 \rangle_{\text{Av}}}{E_n - E_0} \quad (1)$$

where $\bar{\chi}_{\text{molecule}}$ is the average susceptibility per molecule and the magnetic field is assumed to be along the space-fixed Z-axis.

The first term is the diamagnetic term and represents the average of the squared distance of an electron from the Z-axis summed over the electrons of the molecule. The second term gives a positive contribution to the susceptibility and is a sum over the electronic states of terms involving the matrix elements of the Z-component of the total electronic orbital angular momentum. Van Vleck shows that the right side of Eq. (1) is invariant to changes in the position of the Z-axis with respect to the molecule. For convenience in the following discussion the Z-axis will here be taken to pass through the center of mass of the molecule. Van Vleck also points out that the second term is zero for atoms if the Z-axis is taken through the atomic nucleus, that is to say, the Larmor precession is unhindered since the potential function is spherically symmetric.

Now consider, following Wick,[6] a diatomic molecule rotating about the Z-axis with an angular velocity ω_Z in a field-free space, the nuclear axis of the molecule rotating in the $X-Y$ plane. If the electrons rotated with the molecule as a frozen charge cloud, they would produce a magnetic moment along the Z-axis equal to

$$-(e/2c)\omega_Z \sum_i \langle X_i{}^2 + Y_i{}^2 \rangle_{\text{Av}}. \quad (2)$$

It may be seen, by inverting Larmor's theorem, that the motion of the electrons due to the molecular rotation will be the same to a first approximation as that which would have been produced by a magnetic field

$$H_Z = -2mc\omega_Z/e. \quad (3)$$

By multiplying this field by the molecular susceptibility, Eq. (1), the magnetic moment due to rotation-induced electronic currents is obtained. This result is added to Eq. (2), leaving only the paramagnetic term with a negative sign, since the diamagnetic circulation just cancels the moment due to the rotation of the electronic charge. Thus

$$m_{Z\,\text{elec}} = -\frac{e}{mc}\omega_Z \sum_n{}' \frac{|(0|L_Z|n)|^2}{E_n - E_0}. \quad (4)$$

With $\hbar\omega_Z = 2BJ_Z$, where B is the rotational constant, $\hbar^2/2I$, I is the moment of inertia, and J_Z is the rotational quantum number, Wick's result is

$$m_{Z\,\text{elec}} = -4B \sum_n{}' \frac{|(0|L_Z|n)|^2}{E_n - E_0} \quad (5)$$

Bohr magnetrons per rotational quantum number. This derivation shows the origin of the electronic contribution to the rotational moment. As Wick points out, this moment is of the same sign as that of a rigid electronic rotation but may be entirely different in magnitude. In another paper,[7] Wick derives this same result more rigorously.

[3] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Clarendon Press, Oxford, 1932).

[4] J. H. Van Vleck, Phys. Rev. **29**, 727 (1927); Phys. Rev. **30**, 31 (1927); Phys. Rev. **31**, 587 (1928).

[5] E. U. Condon, Phys. Rev. **30**, 781 (1927).

[6] G. C. Wick, Z. Physik **85**, 25 (1933).

[7] G. C. Wick, Nuovo cimento **10**, 118 (1933).

[8] G. C. Wick, Phys. Rev. **73**, 51 (1948).

[9] N. F. Ramsey, Jr., Phys. Rev. **58**, 226 (1940).

[10] R. Frisch and O. Stern, Z. Physik **85**, 4 (1933).

[11] I. Estermann and O. Stern, Z. Physik **85**, 17 (1933).

From Larmor's theorem for atoms it is seen that the inner shell electrons of atoms bound in a molecule will be permitted more nearly free diamagnetic circulation about their own nucleus than the outer or valence electrons, since the inner electrons are in an almost spherically symmetric potential with respect to their own nucleus. Their contribution to the rotational moment can therefore be described as effectively canceling some of the charge of their own nucleus, since they will precess about their nucleus at a velocity just equal to the rotational velocity. The magnetic moment along the axis of a linear molecule is handled in a fashion similar to that for atoms; since the potential is cylindrically symmetric, completely free diamagnetic circulation is possible and no magnetic moment exists.

Since the present work was undertaken, Jen[12] has derived an expression for the rotational magnetic moment of a symmetric top molecule whose electronic and nuclear charge principal axes are coincident with the principal axes of inertia. The resulting nuclear contribution is the same as in Condon's expression[5] and the electronic contribution involves terms of Wick's type as in Eq. (5). Jen unnecessarily separates the electrons into "firmly bound" (inner shell) and "free," and arrives at an expression containing some terms which are not obviously related to the total molecular wave functions. The concept of "firmly bound" and "free" electrons is useful for qualitative discussion or for the estimation of magnetic moments, but, since the demarcation is not at all sharp, the device has doubtful value in a quantitative expression. Jen's derivation for the symmetric top follows Condon's wave-mechanical analysis, but includes the electrons as mentioned. The wave mechanical analysis for the symmetric top, however, does not indicate a satisfactory approach to the calculation of the rotational moment of a more general molecule.

A more general formulation of the problem has been devised and is presented here. The approach differs from Condon's and Jen's in that the magnetic moment is calculated directly from the defining equation

$$\mathbf{m} = (1/2c) \sum_i e_i(\mathbf{r}_i \times \mathbf{v}_i). \qquad (6)$$

Such a starting point proves to yield general expressions more simply than the alternate method of calculating the Zeeman effect for the energy levels and inferring the moment from

$$m_Z(J, \tau) = -\partial W(J, \tau)/\partial H. \qquad (7)$$

$W(J, \tau)$ is the energy of the rotational state characterized by the rotational quantum numbers J and τ, and H is the magnetic field. As will be seen, by starting with Eq. (6) one naturally arrives at the complete matrix of $\mathbf{m}$, rather than the diagonal elements referred to a space-fixed axis, as is likely to be the case when

[12] C. K. Jen, Cruft Laboratory Technical Report No. 114, Harvard University, August 22, 1950, and Phys. Rev. 81, 197 (1951).

Eq. (7) is used. The complete matrix could be obtained from the wave-mechanical approach in certain cases, but with considerably more effort than by the method used here. The off-diagonal elements of the matrix are important for the general Zeeman effect, and add to the understanding of rotational moments. The present general formulation is actually simpler to carry out than the wave-mechanical calculation for the symmetric top since the rotational magnetic moment matrix is developed in terms of the molecular angular momenta and direction cosine matrices which are well known. Thus the rotational magnetic moment problem in the general molecule is solved to about the same degree that the free rotation problem has been solved, and any future simplification in the relevant matrices is immediately applicable to rotational moments through the relations given.

Theory of Rotational Magnetic Moments in $^1\Sigma$ Polyatomic Molecules

The magnetic moment of a system of particles is defined by the equation

$$\mathbf{m} = (1/2c) \sum_i e_i(\mathbf{r}_i \times \mathbf{v}_i) \qquad (8)$$

where e_i is the charge of the ith particle, $\mathbf{r}_i$ is the position vector of the ith particle from an arbitrary origin, $\mathbf{v}_i$ is the velocity vector of the ith particle, and the sum is over all particles. The magnetic moment due to the free rotation of a $^1\Sigma$ polyatomic molecule will be calculated using this definition, but before doing so it is necessary to derive what are essentially the velocities, $\mathbf{v}_i$, from the rotational problem.

In the conventional fashion, the nuclear system will be taken as a rigid framework. This introduces a tremendous simplification of the analytical problem, and in most cases the error incurred will be well beyond the accuracy of measurements. Vibrational and centrifugal effects on the rotational magnetic moments will be briefly discussed later. With this simplification, the hamiltonian for the molecular system, after the translational part has been separated, may be written

$$H = \tfrac{1}{2} \sum_g N_g^2/I_g + (1/2m) \sum_g \sum_j (p_g)_j^2 + V(a, b, c), \qquad (9)$$

where N_g is the instantaneous angular momentum of the nuclear system, referred to the principal axes of inertia, $g = a$, b, and c, fixed in the molecule; I_g is a principal moment of inertia of the nuclear system; p_g is an instantaneous linear momentum of the jth electron, referred to the principal inertial axis g; $V(a, b, c)$ is the potential function for electronic motion and involves only the relative coordinates of the particles. The total angular momentum of such a system of particles is a constant of the motion. Let this quantity be $\mathbf{P}$; then instantaneously

$$\mathbf{P} = \mathbf{N} + \mathbf{L} \qquad (10)$$

where $\mathbf{N}$ is the angular momentum of the nuclear

system and $\mathbf{L}$ is the total electronic angular momentum. Substituting for $\mathbf{N}$ in Eq. (9), one gets[13]

$$H = \frac{1}{2}\sum_g \frac{P_g^2}{I_g} - \sum_g \frac{P_g L_g}{I_g} + \frac{1}{2}\sum_g \frac{L_g^2}{I_g}$$
$$+ \frac{1}{2m}\sum_g \sum_i (p_g)_j^2 + V(a,b,c). \quad (11)$$

For $^1\Sigma$ molecules $\mathbf{L}$ is zero if a nonrotating molecule is imagined and is quite small compared to $\mathbf{P}$ in the rotating molecule. This fact is substantiated by the magnetic moment measurements. The fact that the electron mass is small compared to nuclear masses means that for $^1\Sigma$ molecules the molecular rotation is essentially unchanged whether the presence of the electrons is acknowledged or not. But since the electronic charge is of the same size as nuclear charges, a very small fraction of a quantum of electronic angular momentum can produce a magnetic moment comparable to that of the nuclear system possessing a full quantum. For this reason, the third term of the right-hand side of Eq. (11) will be entirely negligible for the rotational problem, and the second term may be taken as a relevant perturbation term. This perturbation term may be considered to act on the electronic motion alone, since, as explained above, it yields the change in electronic motion which is far more important in giving rise to the existence of an electronic contribution to the molecular magnetic moment than as a small correction to the nuclear motion. This amounts to the separation of the wave function into that of the original rigid rotor wave function and of the new, perturbed, electronic wave function.

The nuclear motion can therefore be specified by P_a^2/I_a, P_b^2/I_b and P_c^2/I_c. The electronic motion can be found by first considering the unperturbed electronic problem, which is seen to be independent of the molecular rotation

$$H^0 = \frac{1}{2m}\sum_g \sum_i (p_g)_j^2 + V(a,b,c), \quad (12)$$

and then the rotation dependent perturbation

$$H^2 = -\sum_g P_g L_g/I_g. \quad (13)$$

Nuclear Contribution

By expanding Eq. (8) and referring all quantities instantaneously to the principal axes of inertia, one has

$(m_a)_{\text{nuc}} = (1/2c) \sum_k e_k[(b_k^2 + c_k^2)\omega_a$
$\qquad - (a_k b_k)\omega_b - (a_k c_k)\omega_c]$

$(m_b)_{\text{nuc}} = (1/2c) \sum_k e_k[-(b_k a_k)\omega_a$
$\qquad + (c_k^2 + a_k^2)\omega_b - (b_k c_k)\omega_c]$

$(m_c)_{\text{nuc}} = (1/2c) \sum_k e_k[-(c_k a_k)\omega_a$
$\qquad - (c_k b_k)\omega_b + (a_k^2 + b_k^2)\omega_c] \quad (14)$

[13] A similar derivation of this hamiltonian is given by H. B. G. Casimir, *Rotation of a Rigid Body in Quantum Mechanics* (J. B. Walter's Uitgevers-Maatschappj M. V., The Hague, 1931), p. 99.

where e_k is the charge of the kth nucleus, a_k, b_k, and c_k are the coordinates of the kth nucleus referred to the principal inertial axes, and ω_a, ω_b, and ω_c are the angular velocities resolved along the inertial axes. But

$$\omega_g = P_g/I_g \quad (15)$$

and thus

$$(m_g)_{\text{nuc}} = \sum_{g'=a,b,c} G_{gg'}' P_{g'} \quad (16)$$

where

$$G_{aa}' = (1/2cI_a) \sum_k e_k(b_k^2 + c_k^2)$$

is a typical diagonal element of the $G_{gg'}'$ tensor, and

$$G_{ab}' = -(1/2cI_b) \sum_k e_k(a_k b_k)$$

is a typical off-diagonal element.

Because of the initial assumptions, Eq. (16) does not involve the electronic coordinates, but this by no means indicates that the $\mathbf{m}_{\text{nuc}}$ matrix is independent of the electronic state; rather, this result is always to be applied only to $^1\Sigma$ states. The nuclear contribution to the rotational moment matrix will thus depend on the rotational state and is given in terms of constants of the molecule, the $G_{gg'}'$, and the matrices of the angular momenta P_g.

Electronic Contribution

Since all of the electrons have the same value for e/m, Eq. (8) reduces to

$$(m_g)_{\text{elec}} = -eL_g/2mc \quad (17)$$

where $\mathbf{L}$ will depend on $\mathbf{P}$ through the perturbation term Eq. (13). If $\mathbf{L}$ is calculated for the electronic ground state of a $^1\Sigma$ molecule using the wave functions of the unperturbed electronic problem Eq. (12), the result is of course zero. That is

$$(0|L_g|0) = 0 \quad (18)$$

where the 0's stand for the unperturbed electronic ground states, ψ_0^0. By ordinary perturbation theory, the first-order electronic state is given by

$$\psi_0^1 = \psi_0^0 + \sum_n{}' \sum_g \frac{P_g}{I_g} \frac{(n|L_g|0)}{E_n - E_0}\psi_n^0. \quad (19)$$

Thus, to the first order, the expectation value of L_g is

$$(0|L_g|0)^1 = (0|L_g|0) + \sum_n{}' \sum_{g'} \frac{P_{g'}}{I_{g'}}$$
$$\times \frac{(0|L_g|n)(n|L_{g'}|0) + (0|L_{g'}|n)(n|L_g|0)}{E_n - E_0}$$
$$+ \text{higher order terms} \quad (g' = a, b, c). \quad (20)$$

Combining Eqs. (20), (18), and (17), the result may be

written

$$(m_g)_{\text{elec}} = \frac{1}{2} \sum_{g'} (G_{gg'}'' + G_{gg'}''*) P_{g'} \qquad (21)$$

where

$$G_{gg'}'' = -\frac{e}{mcI_{g'}} \sum_n{}' \frac{(0|L_g|n)(n|L_{g'}|0)}{E_n - E_0}$$

and

$$G_{gg'}''* = -\frac{e}{mcI_{g'}} \sum_n{}' \frac{(0|L_{g'}|n)(n|L_g|0)}{E_n - E_0}.$$

As in the case of the nuclear contribution, the relation Eq. (21) gives the electronic contribution to the rotational magnetic moment matrix as a function of constants of the molecule, $G_{gg'}''$ and the matrices of the angular momenta P_g.

It can easily be shown that the $G_{gg'}'$ and the $G_{gg'}''$ transform in the same way under a rotation of the molecule fixed coordinate system from which they are calculated. Also, it is easily established that $I_{g'}G_{gg'}'$ and $I_{g'}G_{gg'}''$ will have a set of principal axes fixed in the molecule, which, in general will not be the same for each and neither need be the same as the principal axes of inertia. However, in the case of a true symmetric top these tensors possess only diagonal elements, the principal axes being the same as the principal inertial axes of the molecule. Even in the case of many asymmetric tops it is clear that some or all of the off-diagonal elements may be zero. Thus the situation is not quite so hopeless as one might expect on considering the general problem.

The $G_{gg'}'$ and $G_{gg'}''$ may of course be added to form a new tensor, $G_{gg'}$, in terms of which the total rotational moment is expressible as

$$m_g = \tfrac{1}{2} \sum_{g'} (G_{gg'} + G_{gg'}*) P_{g'} \qquad (g \text{ and } g' = a, b, c) \qquad (22)$$

where

$$\begin{aligned} G_{gg'} &= G_{gg'}' + G_{gg'}'' \\ G_{gg'}* &= G_{gg'}' + G_{gg'}''* \end{aligned} \qquad (23)$$

With a static magnetic field along a space-fixed axis $F(F = X, Y, Z)$ we are interested in the expectation of the magnetic moment along the axis. The transformation from molecule-fixed axes $g = a, b, c$ to the space-fixed axis F is given by the direction cosines as[14]

$$m_F = \sum_g \Phi_{Fg} m_g, \qquad (24)$$

where Φ_{Fg} is the direction cosine. Using Eq. (22) this relation may be written

$$m_F = \tfrac{1}{2} \sum_g \Phi_{Fg} \sum_{g'} (G_{gg'} + G_{gg'}*) P_{g'}. \qquad (25)$$

Let us consider first the nuclear contribution to the magnetic moment. Since in general $G_{gg'}' \neq G_{g'g}'$, the nuclear contribution to the magnetic moment in the molecule-fixed system does not commute with the

direction cosine transformation. Thus, in the usual quantum-mechanical fashion we use an average of the product to assure a hermitian matrix for m_F, which differs by only a scalar factor from an energy. Thus, the nuclear contribution is

$$(m_F)_{\text{nuc}} = \tfrac{1}{2} \sum \left[(m_g)_{\text{nuc}} \Phi_{Fg} + \Phi_{Fg} (m_g)_{\text{nuc}} \right]$$

or

$$(m_F)_{\text{nuc}} = \tfrac{1}{2} \sum_g \sum_{g'} G_{gg'}' (P_{g'} \Phi_{Fg} + \Phi_{Fg} P_{g'}). \qquad (26)$$

The electronic contribution to the magnetic moment must, of course, commute with the direction cosine transformation, since it differs only by a scalar factor from the electronic angular momentum. The commutation in this case results from the existence of matrix elements of Φ_{Fg} which are off-diagonal in n, the electronic quantum number. These off-diagonal elements in n are readily evaluated directly, using the wave function of Eq. (19), or, since we are interested in $\langle L_F \rangle$, the quantities $\langle \Phi_{Fg} L_g \rangle$ are more conveniently calculated. The resulting contribution by the electrons to the magnetic moment may be written in terms of the direction cosine matrix elements diagonal in n as

$$(m_F)_{\text{elec}} = \tfrac{1}{2} \sum_g \sum_{g'} (G_{gg'}'' P_{g'} \Phi_{Fg} + G_{gg'}''* \Phi_{Fg} P_{g'}). \qquad (27)$$

The total space-fixed rotational magnetic moment may thus be written conveniently in terms of our previous notation

$$m_F = \tfrac{1}{2} \sum_g \sum_{g'} (G_{gg'} P_{g'} \Phi_{Fg} + G_{gg'}* \Phi_{Fg} P_{g'}). \qquad (28)$$

In a representation in which P^2, P_z and $M(P_Z)$ are diagonal, the well-known matrix elements of the angular momenta are

$$(J, K, M | P_z | J, K, M) = \hbar K$$

$$\begin{aligned} (J, K, M & | P_y | J, K+1, M) \\ &= \pm i(J, K, M | P_x | J, K+1, M) \\ &= \tfrac{1}{2}\hbar [J(J+1) - K(K+1)]^{\frac{1}{2}}. \qquad (29) \end{aligned}$$

The association of a, b, and c with x, y, and z may be made in any of six different ways in the general polyatomic molecule. It should be apparent that for symmetric rotors, for example, the z-axis should be taken as the symmetry axis of the molecule for simplicity. For linear rotors, similarly, the z-axis would be taken as the internuclear axis. For asymmetric rotors the assignment should be made in the usual fashion, i.e., to minimize the free rotation problem.

The matrix elements for the direction cosines in factored form and in the above representation are given in Table I, which is copied from reference 14. Note that the total element is given as

$$\begin{aligned} (J, K, M | \Phi_{Fg} | J', K', M') &= (J | \Phi_{Fg} | J') \\ \cdot (J, K | \Phi_{Fg} | J', K') & \cdot (J, M | \Phi_{Fg} | J', M'). \qquad (30) \end{aligned}$$

Simple matrix multiplication of these elements thus gives the desired matrix for m_F for the general polyatomic molecule. A few generally pertinent matrix elements are given in the Appendix.

[14] See Cross, Hainer, and Wing, J. Chem. Phys. 11, 27 (1943); 12, 210 (1944), for an exhaustive general discussion of the transformations involved in the following section.

TABLE I. Direction cosine matrix elements.

Matrix element factor	Value of J'		
	$J+1$	J	$J-1$
$(J\|\Phi_{Fg}\|J')$	$\{4(J+1)[(2J+1)(2J+3)]^{\frac{1}{2}}\}^{-1}$	$[4J(J+1)]^{-1}$	$[4J(4J^2-1)^{\frac{1}{2}}]^{-1}$
$(J,K\|\Phi_{Fz}\|J',K)$	$2[(J+1)^2-K^2]^{\frac{1}{2}}$	$2K$	$-2(J^2-K^2)^{\frac{1}{2}}$
$(J,K\|\Phi_{Fy}\|J',K\pm1)$ $= \mp i(J,K\|\Phi_{Fx}\|J',K\pm1)$	$\mp[(J\pm K+1)(J\pm K+2)]^{\frac{1}{2}}$	$[J(J+1)-K(K\pm1)]^{\frac{1}{2}}$	$\mp[(J\mp K)(J\mp K-1)]^{\frac{1}{2}}$
$(J,M\|\Phi_{Zg}\|J',M)$	$2[(J+1)^2-M^2]^{\frac{1}{2}}$	$2M$	$-2(J^2-M^2)^{\frac{1}{2}}$
$(J,M\|\Phi_{Yg}\|J',M\pm1)$ $= \pm i(J,M\|\Phi_{Xg}\|J',M\pm1)$	$\mp[(J\pm M+1)(J\pm M+2)]^{\frac{1}{2}}$	$[J(J+1)-M(M\pm1)]^{\frac{1}{2}}$	$\mp[(J\mp M)(J\mp M-1)]^{\frac{1}{2}}$

Certain simplifications are possible in the case of linear and symmetric rotors. The matrix elements for these cases are given in the Appendix. No immediate reduction in the number of elements of m_F is possible for the general asymmetric molecule with no symmetry. It should be apparent, however, that in particular cases a charge symmetry axis may exist, e.g., H_2O, PH_2D, and in these cases the symmetry may be exploited to reduce the number of independent elements of m_F.

The magnetic moment matrix derived from the foregoing theory is applied in Part 2 for the case of linear rotors and symmetric top molecules. In these cases the diagonal elements of the magnetic moment m_F yield, by inspection, the "g-factor" associated with the F space-fixed axis. Work in progress in this Laboratory on asymmetric molecules will, when reported, discuss the practical application of the theory to asymmetric molecules. Stated simply, a certain transformation, XT, diagonalizes the free rotational energy matrix of an asymmetric top (since it is not diagonal in the representation of Eq. (27)). The evaluation of XT is given explicitly in reference 14. This same transformation must be applied to m_F, Eq. (25). The diagonal elements of $T'X'm_FXT$ are then used to determine, by inspection, the effective molecular "g-factor" in a particular rotational state, as in the case of linear and symmetric rotors. Off-diagonal elements may be handled in the case of near degeneracy by means of the usual perturbation theory applied to the actual interaction energy of m_F with the external F-axis magnetic field.

Vibrational and Centrifugal Effects

The gyromagnetic tensor elements, $G_{gg'}$, are seen from Eqs. (16) and (21) to be constants for a molecule under the assumption of a rigid nuclear structure. These factors will in general be a function of the vibrational state and will vary with centrifugal distortion in an actual molecule. However, it is to be expected that these effects will be small and the $G_{gg'}$ would only involve the vibrational and rotational quantum numbers if their calculation were carried to a high approximation.

The nuclear contribution, for example, is essentially the ratio of the second moment of charge

$$\sum_k e_k(b_k^2+c_k^2)$$

to the moment of inertia

$$I_a=\sum_k M_k(b_k^2+c_k^2).$$

Therefore, if the ratio e_k/M_k were the same for all nuclei, vibrational and centrifugal effects would indeed be negligible. But it is in fact true that for most nuclei, except that of hydrogen, the ratio of atomic number to mass number is about the same, namely about one-half. Thus, for molecules not involving hydrogen and for those with only hydrogen off the axis concerned, these effects on the nuclear contribution may be neglected.

Isotopic Effects

The application of the above theory to isotopic molecules is straightforward, since it is only necessary to transform the G-tensor, Eq. (22), by translation and rotation in order to correct it to the new center of mass and the new principal inertial axes. Rotation of the G-tensor is straightforward. Translation may be accounted for by relations such as the invariance of expressions of the form of Eq. (1).[15] In fact, when the first moments of the nuclear and electronic charge are identical at a point on the axis along which translation is being performed, i.e., no electric dipole moment exists on that axis, it is evident that the change in G' cancels the change in G''. When the nuclear and electronic charge centers do not coincide on the axis along which translation is being performed a slight correction must be made in terms of the electric dipole moment. Finally, the scale factors such as the I_g's must be revised.

The Zeeman Effect on Rotational Absorption Lines

The Zeeman effect is the splitting of a spectral line into several components accompanying the application of a magnetic field to the emitting or absorbing system. This splitting is of course the result of the removal of the spatial degeneracy of the energy levels concerned

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[15] See reference 3, Chapter X, Sec. 68.

and is intimately related to the magnetic moment of the system.

For the molecules under discussion, the perturbation energy due to the magnetic field may be written[16]

$$E_m^1 = -(J, \tau, M | m_Z | J, \tau, M)_H, \qquad (31)$$

where $(J, \tau, M | m_Z | J, \tau, M)$ is a diagonal matrix element of Eq. (25) (transformed if necessary for an asymmetric rotor). This matrix element is directly a function of the rotational quantum numbers, J, τ, and M, but may depend slightly on the vibrational state as explained previously. Examples for linear and symmetric top molecules are given in the Appendix. It may be shown in general[17] that Eq. (31) may be rewritten as

$$E_m^1 = -\mu_0 M g H \quad (M = J, J-1, \cdots, -J) \qquad (32)$$

where $\mu_0 = eh/2M_p c$, the nuclear magneton, and g is the splitting factor for the particular level. For symmetric tops g is found from the Appendix to be

$$g(J, K) = g_{xx} + (g_{zz} - g_{xx}) K^2 / J(J+1), \qquad (33)$$

where z refers to the symmetry axis and $g_{xx} = g_{yy}$.[18] Therefore, the total energy may be written

$$E = E^0 + E_m^1 = E^0(J, K) - \mu_0 M g H, \qquad (34)$$

where E^0 is the unperturbed energy of the particular vibrational-rotational level.

Dipole selection rules for M are $\Delta M = 0$, which applies when the electric vector of the incident radiation is parallel to the magnetic field (π-transitions), and $\Delta M = \pm 1$, which applies if it is perpendicular to the magnetic field (σ-transitions). Thus the transition frequencies are

$$\begin{aligned} \nu_\pi &= \nu^0 - (\mu_0/h)(g_2 - g_1) H M \\ \nu_\sigma &= \nu_\pi \mp (\mu_0/h) g_2 H \end{aligned} \qquad (35)$$

where $\nu^0 = (E_2 - E_1)/h$, the frequency of the unsplit absorption, and the subscripts 1 and 2 refer to the lower and upper levels respectively. From Eq. (35) it is seen that if $g_2 = g_1$, then $\nu_\pi = \nu^0$ and $\nu_\sigma = \nu^0 \mp (\mu_0/h) g_2 H$, which is a normal Zeeman effect; that is, there is no deviation for the π-components, and the σ-components form a symmetrically spaced doublet with respect to the unsplit line. This is the case for linear molecules in the ground bending vibrational states and symmetric top molecules if $K = 0$, since $\Delta K = 0$ for electric dipole transitions. In general, however, the Zeeman pattern is anomalous and may consist of several components for both π- and σ-transitions. In any case, the π-transition measurements give $g_2 - g_1$ directly, and the combination of π- and σ-measurements is necessary to evaluate both

g_1 and g_2. It is to be expected that due to centrifugal distortion many "normal" patterns would become anomalous to some degree of resolution.

In some molecules one or more of the nuclei may interact with the molecular rotation because of the nuclear moments in the presence of the internal fields of the molecule. If such an interaction is of sufficient strength, the rotational absorption lines will exhibit a resolvable hyperfine structure. Since molecular rotational magnetic moments are of the same order of magnitude as nuclear magnetic moments, the analysis of the Zeeman effect in terms of these moments becomes more complicated. The theory of the Zeeman effect under these conditions has been adapted to molecular rotational absorptions by Jen[19] and Coester[20] from a similar case in atomic spectra.[21] It should be stressed that the molecular g-factors entering this theory are not constants of the molecule, but depend on the rotational state and the $g_{gg'}$-tensor just developed.

Relation of Rotational Moments to Magnetic Susceptibilities

The magnetic susceptibility for $^1\Sigma$ molecules given by Van Vleck,[3] is

$$\chi_{\text{mole}} = -\frac{Le^2}{6mc^2} \sum_i \langle r_i^2 \rangle_{Av} + 2L \left(\frac{e}{2mc}\right)^2$$
$$\times \sum_n' \frac{|(n|L_Z|0)|^2}{E_n - E_0} \qquad (36)$$

where L is Avogadro's number and i refers to the ith electron of the molecule. Aside from dimensional factors, the only difference of the second term of Eq. (36) from the diagonal elements of the electronic contribution to the rotational moment tensor, Eq. (21), is that in Eq. (36) the matrix elements are referred to the space-fixed Z-axis, while the diagonal rotational moment tensor elements are referred to the molecule-fixed axes, a, b, and c. However, in averaging over a volume of gas the following replacement may be made

$$\text{Av} | (n|L_Z|0)|^2 = \tfrac{1}{3} \{ |(n|L_a|0)|^2 + |(n|L_b|0)|^2 + |(n|L_c|0)|^2 \}. \qquad (37)$$

Thus, once the diagonal elements g_{aa}'', g_{bb}'', and g_{cc}'' are known, the paramagnetic term in the susceptibility can be calculated.

Zeeman effect measurements on rotational absorptions do not yield the g_{gg}'' elements directly, but rather the elements g_{gg}, which are the sum of the electronic g_{gg}'' and the nuclear g_{gg}'. However, since the effective internuclear distances are usually known from analysis

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[16] Equation (31) is only true for the first-order Zeeman effect, but is sufficient for the present discussion. Detailed discussion of the Zeeman effect is given in the standard references.

[17] Since XT is diagonal in J and M, see second reference 14, p. 213.

[18] It is convenient to define the dimensionless gyromagnetic tensor elements as $g_{gg'} = (\hbar/\mu_0) G_{gg'}$.

[19] C. K. Jen, Phys. Rev. **74**, 1396 (1948); Phys. Rev. **76**, 1494 (1949).

[20] F. Coester, Phys. Rev. **77**, 454 (1950).

[21] E. Back and S. A. Goudsmit, Z. Physik **47**, 174 (1928).

of the rotational spectrum, the nuclear contribution to the g_{gg} can be easily calculated from Eq. (16), and thus the g_{gg}'' become known from Zeeman measurements.

The diamagnetic term in the susceptibility depends only on the electronic charge density distribution in the electronic ground state of the molecule. This can be estimated fairly well; or, if the susceptibility is also measured, then the diamagnetic term and thus the

$$\sum_i \langle r_i{}^2 \rangle_{\text{Av}}$$

for the electronic ground state becomes known.

The susceptibility expression in terms of the electronic part of the rotational gyromagnetic tensor elements becomes

$$\chi_{\text{mole}} = \frac{Le^2}{6mc^2}\left[-\sum_i \langle r_i{}^2 \rangle_{\text{Av}} + \frac{1}{2M_p}\sum_{g=a,b,c} g_{gg}''I_g \right]. \quad (38)$$

There would presumably be a temperature-dependent paramagnetic contribution to the susceptibility resulting from the rotational magnetic moments, since these are not field induced. However, such a term would be very small compared with those of Eq. (38).

2. MEASUREMENTS

Carbonyl Sulfide (OCS): A Linear Rotor

The Zeeman effect on the $J=1\rightarrow2$ rotational transition of $O^{16}C^{12}S^{32}$ in its ground vibrational state was observed. Experiments were performed for both π- and σ-transitions using linearly polarized radiation, and for the σ-transitions using circularly polarized radiation. The method and apparatus are described in a forthcoming report.

Carbonyl sulfide was known to be a linear molecule,[22,23] and therefore, on the basis of the theory of Part I, a normal Zeeman effect was to be expected and was in fact observed.

The π-transitions were observed at about 3000 gauss with a full line width at half-intensity of about 0.10 Mc/sec. No change in line shape or intensity was perceptible from that of the zero field line. The σ-observations resulted in a doublet, the components being of equal intensity. The measured splittings are given in Table II. The value of g for this line represents the g-factor along an axis normal to the nuclear axis, as may be seen from Part I and the Appendix.

The circular polarization experiment was set up for observing $\Delta M = +1$ transitions and again for $\Delta M = -1$ transitions. Both observations indicated that the g-factor was negative. A negative OCS g-factor was also required for consistency in experiments on the hyperfine pattern of the $J=1\rightarrow2$ transition of $O^{16}C^{12}S^{33}$ reported by Eshbach, Hillger, and Jen[24] and to be described in detail in a separate report.

TABLE II. σ Zeeman component measurements for the $J=1\rightarrow2$ rotational absorption of $O^{16}C^{12}S^{32}$ at 24,325.92 Mc/sec.

$\Delta\nu$ measured[a] (Mc/sec)	H (gauss)	$g = \Delta\nu/2\mu_0 H$ (nuclear units)
0.175	4929	0.0233
0.198	4664	0.0278
0.163	4496	0.0238
0.167	4280	0.0256
	average	=0.0251±0.002

[a] The measured $\Delta\nu$ represents the total splitting between the two σ-components.

Thus, the rotational moments of OCS in its ground vibrational state are describable by $g_{xx}=g_{yy}=-0.025\pm0.002$ nuclear unit.

Previous g-factor measurements on OCS have been made by Coles[25] and by Jen.[26] Neither of these observers determined the sign of the g-factor, and their results had rather large uncertainties. Since both the sign and magnitude were important for a check on the $O^{16}C^{12}S^{33}$ experiments, these measurements were repeated. Jen's measured value is $|g(\text{OCS})|=0.029\pm0.006$ nuclear unit.

Ammonia ($N^{15}H_3$) A Symmetric Top Molecule

The microwave spectrum of ammonia is unique in several respects. Besides being the first molecular absorption spectrum to have been observed and studied in the microwave region[27,28] and having unusually strong absorptions, this molecule has a large number of lines with quite different rotational quantum numbers in a compact region of the spectrum. The reason that this is possible lies in the unusual nature of the transition involved. Ammonia is a pyramidal, symmetric top molecule, whose microwave spectrum arises from transitions between vibrational inversion levels with the same rotational quantum numbers, J and K. The inversion which takes place is that of the nitrogen through the plane of the hydrogens along the axis of symmetry. There are two stable positions for the nitrogen nucleus, one on either side of this plane, with a rather low potential barrier separating them. The coupling or "tunnel" effect, between the two regions where classical vibrations could occur, splits the ground vibrational level into a closely-spaced doublet, of about 22,000 Mc/sec separation. The height of the barrier depends noticeably on centrifugal effects and therefore on the rotational quantum numbers, J and K. The resulting lines occur over a few thousand megacycles, centering at about 22,000 Mc/sec.[29]

The convenient position of these lines and their high

[22] Strandberg, Wentink, and Kyhl, Phys. Rev. **75**, 270 (1949).
[23] G. Herzberg, *Molecular Spectra and Molecular Structure: II. Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945).
[24] Eshbach, Hillger, and Jen, Phys. Rev. **80**, 1106 (1950).

[25] D. K. Coles, *Microwave Spectroscopy, Advances in Electronics* (Academic Press, Inc., New York, 1950), Vol. II.
[26] C. K. Jen, Cruft Laboratory Technical Report No. 116, Harvard, October 5, 1950; also as Phys. Rev. **81**, 197 (1951).
[27] C. E. Cleeton and N. H. Williams, Phys. Rev. **45**, 234 (1934).
[28] B. Bleany and R. P. Penrose, Nature **157**, 339 (1936).
[29] P. Kisliuk and C. H. Townes, J. Research Natl. Bur. Standards, RP 2107, **44**, 611 (1950).

TABLE III. σ component Zeeman measurements for ammonia inversion lines.

| | | $H = 5635$ gauss | | | |
Molecule	Line J, K	Frequency (29) (Mc/sec)	$\Delta\nu^{\mathrm{a}}$ (Mc/sec)	$K^2/J(J+1)$	$g(J, K)$
$N^{15}H_3$	3, 1	21,202.30	4.72	0.083	0.550
	2, 1	22,044.28	4.75	0.167	0.553
	3, 2	21,783.98	4.60	0.333	0.535
	1, 1	22,624.96	4.48	0.500	0.521
	6, 5	21,667.93	4.43	0.595	0.516
	3, 3	22,789.41	4.29	0.750	0.500
	6, 6	23,922.32	4.24	0.859	0.494
$N^{14}H_3$	3, 2	22,834.10	4.60	0.333	0.535

 a The measured $\Delta\nu$ represents the total splitting between the two components.

absorption coefficients allow one almost free choice of the values of J and K for the purpose of studying the rotational magnetic moment of this symmetric top. The g-factor for a symmetric top was given in Eq. (33). The value of $K^2/J(J+1)$ is just the square of the direction cosine between the total angular momentum vector, **J**, and the symmetry axis z, along which there is a component of the total angular momentum in an amount $K\hbar$. Thus it is seen that for $J = K$ the magnetic moment will be essentially due to g_{zz}, while for $K = 0$ it depends only on $g_{xx} = g_{yy}$. Therefore the measurements were made on lines chosen so as to give a wide range of values of $K^2/J(J+1)$.

For these inversion transitions, the selection rules, $\Delta J = 0$ and $\Delta K = 0$, result in the same g-factor for both the upper and the lower energy levels, since the change in $g(J, K)$ between the two inversion states is probably negligible. It should be noted that this is not the case for symmetric top rotational transitions, where the selection rules, $\Delta J = \pm 1$ and $\Delta K = 0$, give rise to an anomalous Zeeman effect.

The measurements were made on the isotopic molecule $N^{15}H_3$, since for the more abundant $N^{14}H_3$ a resolvable interaction between the N^{14} nuclear quadrupole moment and the gradient of the molecular electric field complicates the spectrum. This does not occur for $N^{15}H_3$ and the observed Zeeman effect was normal as expected. The splitting of the σ-component doublets was measured for seven lines with values of $K^2/J(J+0)$ ranging from 0.083 to 0.859 and all measurements were made in a field of 5635 gauss. The measured splittings and resulting $g(J, K)$'s are listed in Table III. Each entry in this table represents an average of from three to six measurements.

Figure 1 shows a plot of these results, with the estimated experimental error ($\sim \pm 1$ percent) indicated by the vertical bars through the plotted points. An additional consistent error of about ± 1 percent in the measurement of the magnetic field is possible. The intercepts at $K^2/J(J+1) = 1$ and 0 are g_{zz} and g_{xx}, respectively. Thus, $g_{xx} = g_{yy} = +0.560 \pm 0.007$ and $g_{zz} = +0.484 \pm 0.007$. The signs of the g-factors were again determined by the circular polarization method.

A measurement on the $N^{14}H_3$ line for $J = 3$, $K = 2$ was

made, since for this particular line there is no hyperfine pattern. Experimentally the $g(3, 2)$ for $N^{14}H_3$ coincides with that for $N^{15}H_3$; however, one would expect that a small difference actually exists. According to the theory of Part I, the g_{zz} should be the same for both molecules and a calculation shows that the $g_{xx}(N^{14}H_3)$ should be about 0.1 percent higher than the $g_{xx}(N^{15}H_3)$. Thus, to the accuracy of the present experiments no measurable difference between $g(3, 2)$ for $N^{14}H_3$ and $N^{15}H_3$ should exist.

Jen[19] has made similar measurements on $N^{15}H_3$ in connection with the Zeeman effect on the $N^{14}H_3$ hyperfine pattern. However, his measurements were only on components of lines for which $J = K$, and for these he of course detected no variation of g with J and K. He reports $g(N^{15}H_3) = 0.477 \pm 0.03$ and since he used only $J = K$ lines, this is essentially to be compared with g_{zz} above.

Correlation with Susceptibilities

The results of the measurements of the rotational g-factors of OCS and NH_3 may be used in conjunction with the published susceptibilities[30] to yield a value of

$$\sum_i \langle r_i^2 \rangle_{\mathrm{Av}}$$

for the ground electronic state of these molecules through Eq. (38). Solving Eq. (38) for
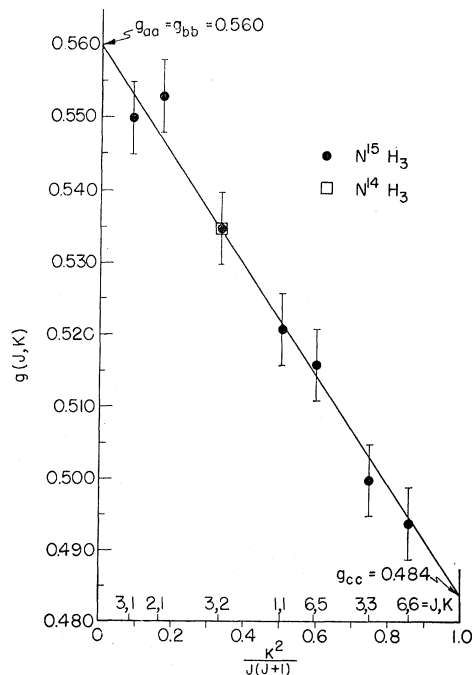
$$\sum_i \langle r_i^2 \rangle_{\mathrm{Av}}$$

FIG. 1. Ammonia molecular g-factor.

[30] Handbook of Chemistry and Physics (Chemical Rubber Publishing Company, Cleveland, Ohio, 1947), thirtieth edition, p. 1991.

and dividing by the total number of electrons yields an expression for $\langle r^2 \rangle_{\text{Av}}$ which is the sum of a term depending on the susceptibility and a term depending on the g_{gg}''''s. Both of these terms are positive for a diamagnetic gas.

The value of $\langle r_i^2 \rangle_{\text{Av}}$ has been calculated in this way for OCS, NH$_3$, and H$_2$ (using Ramsey's data).[9] The magnetic susceptibility of OCS is not listed but that of both CO$_2$ and CS$_2$ has been measured.[30] These specific susceptibility values are $\chi(\text{CO}_2) = -0.423 \times 10^{-6}$ and $\chi(\text{CS}_2) = -0.54 \times 10^{-6}$, and since the structures of the three molecules OCS, CO$_2$ and CS$_2$ are very similar, it is not unreasonable to take $\chi(\text{OCS})$ to be the average of that for the other two. In the following it is therefore taken as $\chi(\text{OCS}) = -0.48 \times 10^{-6}$. Calculations in the case of H$_2$ are given here for comparison purposes. The g-factor of H$_2$ is more accurately known than for any other molecule, the most precise measurement having been made by Ramsey[9] using the molecular beam technique.

The calculated values of the $\langle r^2 \rangle_{\text{Av}}$ for these molecules are given in Table IV, along with the values of the contributions of the susceptibility and g''-factor terms to the $\langle r^2 \rangle_{\text{Av}}$.

The distance, r, is here taken from the center of gravity of the molecule. In each case, rough calculations show that these results are reasonable numbers, and more precise evaluation would require use of specific wave functions.

The relative magnitudes of the contributing terms, $\langle r^2 \rangle_{\text{Av}}(\chi)$ and $\langle r^2 \rangle_{\text{Av}}(g'')$, should be noted. In the case of OCS the larger contribution comes from g'', which is to be expected, since the majority of the electrons are in the almost spherical potential of their own nucleus, that is to say, the inner shell electrons are fairly free to precess about their own nucleus, but $\langle r^2 \rangle_{\text{Av}}$ is measured from the molecular center of gravity. Thus, in the case of a molecule with nuclei far from the center of gravity, the main contribution will come from $\langle r^2 \rangle_{\text{Av}}(g'')$, while $\langle r^2 \rangle_{\text{Av}}(\chi)$ is a measure of the precession about the individual nuclei. The opposite case is demonstrated by the values for H$_2$, where an almost free precession can take place about the molecular center of gravity itself.

TABLE IV. Calculated values of $\langle r^2 \rangle_{\text{Av}}$ for electronic ground states.

Molecule	Specific susceptibility (26) (cgs electromagnetic)	$\langle r^2 \rangle_{\text{Av}}(\chi)$ 10^{-16} cm^2	$\langle r^2 \rangle_{\text{Av}}(g'')$ 10^{-16} cm^2	$\langle r^2 \rangle_{\text{Av}}$ 10^{-16} cm^2	$[\langle r^2 \rangle_{\text{Av}}]^{\frac{1}{2}}$ 10^{-8} cm
OCS	$-0.48 \times 10^{-6\text{a}}$	0.34	1.44	1.78	1.34
NH$_3$	-1.1×10^{-6}	0.66	0.13	0.79	0.88
H$_2$	-1.97×10^{-6}	0.697	0.016	0.713	0.845

[a] Estimated, see text.

TABLE V. Estimated and measured g-factors.

Molecule	Estimated positive limit		Measured values	
	$g_{aa}(=g_{bb})$	g_{cc}	$g_{aa}(=g_{bb})$	g_{cc}
H$_2$[a]	$+1.0$	—	$+0.878$	—
NH$_3$	$+0.60$	$+0.50$	$+0.560$	$+0.484$
OCS	$+0.045$	—	-0.025	—

[a] See reference 9.

Estimation of the Positive Limit of Rotational g-Factors

Following the ideas in these susceptibility considerations, and the discussion of rotational moments given by Wick,[8] it is possible to formulate a means of estimating the rotational g-factors.

As has been pointed out, the nuclear part of the g-factors can be satisfactorily calculated from a knowledge of the effective internuclear distances in a given vibration-rotation state; but the electronic part is in general of comparable magnitude and more difficult to estimate. Thus, in general, the net g-factors become differences of two large numbers. However, following the previous discussion, the main effect of the inner electronic shells in the rotating molecule is a precession which cancels off a comparable amount of charge of their own nucleus as far as the magnetic moments are concerned. Further, from the case of hydrogen, it is seen that the valence electrons can very roughly be said to precess about an average position between the atoms they are binding and at about the rotational velocity. Thus, considering a charge at the position of the nuclei of a magnitude equal to the atomic number minus the number of inner shell electrons, and the valence electrons to be located at their average positions, the elements of the g-factor tensor can be estimated by calculating the second moments of such a charge distribution

$$\sum_i e_i(b_i^2 + c_i^2)$$

for example, and dividing by the corresponding moment of inertia.

One of the main errors in this procedure arises from the neglect of polarization effects on inner shells, and for nuclei of large atomic number this could cause a large relative error. However, for molecules containing such nuclei, the g-factors will generally be small and the absolute error will not be serious. It appears that this procedure will at least give the positive limit to the g-factors.

Table V is a comparison of the g-factors estimated in this way with the measured values.

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APPENDIX

Rotational magnetic moment matrix elements on the space-fixed $Z(M)$ axis.

1. General Molecule

$$(J, K, M | m_Z | J, K, M) = \mu_0 M \left\{ \frac{g_{xx} + g_{yy}}{2} + \frac{K^2}{J(J+1)} \left[g_{zz} - \frac{g_{xx} + g_{yy}}{2} \right] + i \frac{K}{J(J+1)} \left[\frac{g_{yx} - g_{yx}^*}{2} - \frac{g_{xy} - g_{xy}^*}{2} \right] \right\},$$

$$(J, K, M | m_Z | J, K+1, M) = \mu_0 M \frac{[J(J+1) - K(K+1)]^{\frac{1}{2}}}{4J(J+1)}$$

$$\times \{ i[K(g_{zx} + g_{xz}^*) + (K+1)(g_{xz} + g_{zx}^*)] + K(g_{zy} + g_{yz}^*) + (K+1)(g_{yz} + g_{zy}^*) \},$$

$$(J, K, M | m_Z | J, K+2, M) = \mu_0 M \frac{\{[J(J+1) - K(K+1)][J(J+1) - (K+1)(K+2)]\}^{\frac{1}{2}}}{8J(J+1)}$$

$$\times \{ 2(g_{yy} - g_{xx}) + i[g_{xy} + g_{xy}^* + g_{yx} + g_{yx}^*] \},$$

$$(J, K, M | m_Z | J+1, K, M) = \frac{1}{2(J+1)} \left\{ \frac{[(J+1)^2 - K^2][(J+1)^2 - M^2]}{(2J+1)(2J+3)} \right\}^{\frac{1}{2}}$$

$$\times \{ K(2g_{zz} - g_{xx} - g_{yy}) - i[J(g_{xy} - g_{yx}) + (J+2)(g_{xy}^* - g_{yx}^*)] \},$$

$$(J, K, M | m_Z | J+1, K\pm1, M) = \frac{1}{2(J+1)} \left\{ \frac{(J\pm K+1)(J\pm K+2)[(J+1)^2 - M^2]}{(2J+1)(2J+3)} \right\}^{\frac{1}{2}}$$

$$\times \{ -K(ig_{xz} \pm g_{yz}) - (K\pm1)(ig_{xz}^* \pm g_{yz}^*)$$

$$+ (J\pm K)(g_{zy} \pm g_{zx}) + (J\pm K+1)(g_{zy}^* \pm ig_{zx}^*) \},$$

$$(J, K, M | m_Z | J+1, K\pm2, M) = \frac{1}{4(J+1)} \left\{ \frac{(J\pm K)(J\pm K+1)(J\pm K+2)(J\pm K+3)[(J+1)^2 - M^2]}{(2J+1)(2J+3)} \right\}^{\frac{1}{2}}$$

$$\times \{ \pm(g_{xx} - g_{yy}) - \tfrac{1}{2}i(g_{xy} + g_{xy}^* + g_{yx} + g_{yx}^*) \}.$$

2. Special Cases

A. Linear Rotor (ground bending vibrational state): z refers to nuclear axis, thus $g_{xx} = g_{yy}$, $g_{zz} = 0$, $(J, M | m_Z | J, M) = \mu_0 M g_{xx}$.

B. Symmetric Rotor: z refers to symmetry axis, thus $g_{xx} = g_{yy}$.

$$(J, K, M | m_Z | J, K, M) = \mu_0 M \{ g_{xx} + (g_{zz} - g_{xx}) K^2 / J(J+1) \}$$

$$(J, K, M | m_Z | J+1, K, M) = \frac{\mu_0 (g_{zz} - g_{xx})}{(J+1)} \left\{ \frac{[(J+1)^2 - K^2][(J+1)^2 - M^2]}{(2J+1)(2J+3)} \right\}^{\frac{1}{2}}.$$

Note: The total matrix may be constructed from its hermitian property. The $g_{gg'}$'s are dimensionless and defined by

$$g_{gg'} = \hbar G_{gg'} / \mu_0,$$

where μ_0 is the nuclear magneton, $\mu_0 = e\hbar / 2M_p c$.