

pseudo-quadrupole effect,¹² and the interaction of the nuclear magnetic moments with each other through the intermediary of the electronic magnetic moments.¹⁴ The former effect is not separable from the true nuclear quadrupole effect. The energy involved in the latter effect is less than 1 kc/sec in most known cases. In order to obtain more precise information a few cubic centimeters of liquid NH₃ were sealed in a thick walled glass tube and Hahn of the Watson Laboratories kindly examined the proton resonance in the NH₃ vapor in equilibrium with the liquid by means of the spin echo technique.¹⁵ The resonance was observed with a sample

¹⁴ N. F. Ramsey and E. M. Purcell, Phys. Rev. **85**, 143 (1952).

¹⁵ E. L. Hahn, Phys. Rev. **80**, 580 (1950); **88**, 1070 (1952).

vapor pressure of several atmospheres to a sample vapor pressure of the order of 40 atmospheres. The strong resonance signal was found to be without a trace of the modulations which would be caused by the above-mentioned effect. From this result Hahn was able to inform us that the magnitude of the interaction is certainly less than 300 cps and most probably less than 100 cps. Thus it would not be experimentally detectable by us.

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Hyperfine Structure in the Spectrum of N¹⁴H₃.† II. Theoretical Discussion

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The new features in the hyperfine spectrum of N¹⁴H₃ described in the preceding paper are shown to be due to the interactions of the magnetic moments of the three protons with the molecular magnetic field caused by rotation and with the magnetic moment of the N¹⁴ nucleus. Since the protons are off the molecular symmetry axis, these interactions are of a form different from that usually encountered. They possess matrix elements connecting states differing by two units in symmetric top quantum number K and are capable, therefore, of lifting the degeneracy between states for which $K = -1$ and $K = 1$. A systematic treatment of the problem of the hyperfine interactions in this molecule has been made in order to find any other effects detectable with present equipment.

I. INTRODUCTION

EARLY measurements of the hyperfine structure of the inversion spectrum of ammonia were interpretable¹ as due to an interaction between molecular electric fields and the quadrupole moment of N¹⁴. More accurate measurements² indicated that small interactions between the N¹⁴ magnetic moment and a magnetic field due to molecular rotation were also present.³ The new experimental data presented in the previous paper (which we shall refer to as I) shows that several other types of effects are also of importance. Hence, a systematic and comprehensive treatment of the problem has been undertaken in order to find all effects which

could conceivably be observed with a microwave spectrometer of sensitivity and resolving power comparable with what is now available. Doubling of the $K = 1$ lines is shown to be a new manifestation of magnetic hyperfine interactions.

II. FORMULATION OF THE PROBLEM

For the purposes of this calculation, the molecular Hamiltonian based on the Pauli approximation to the wave equation can be written as:^{4,5}

$$\mathcal{H} = A(J_x - L_x)^2 + A(J_y - L_y)^2 + C(J_z - L_z)^2 \quad (1.0)$$

$$+ (e\mu_0/c) \sum_{K_i} r_{iK}^{-3} (\mathbf{r}_i - \mathbf{r}_K)$$

$$\times \left(\mathbf{v}_i - \left(1 + \frac{Z_K M_p}{g_K M_K} \right) \mathbf{v}_K \right) \cdot g_K \mathbf{I}_K \quad (1.1)$$

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¹ W. E. Good and D. K. Coles, Phys. Rev. **70**, 979 (1946); J. H. Van Vleck, Phys. Rev. **71**, 468 (1947).

² J. W. Simmons and W. Gordy, Phys. Rev. **73**, 713 (1948).

³ R. S. Henderson, Phys. Rev. **74**, 107, 626 (1948); see, also, J. M. Jauch, Phys. Rev. **74**, 1262 (1948).

⁴ J. H. Van Vleck, Revs. Modern Phys. **23**, 213 (1951).

⁵ L. H. Thomas, private communication. The equation derived on the basis of footnote (35) of Van Vleck's paper (reference 4) is not entirely correct since factors of $1/r_{jK}^3$ and $1/r_{jK}^3$ were inadvertently left out of his Eq. (37) and the factor $(1 + Z_K M_p / g_K M_K)$ replaces the factors $\frac{1}{2}$ in a fashion evident by comparing the expressions (1.1) and (1.3) with his Eq. (37).

$$+ g_e \mu_0 \mu_e \sum_{i,K} r_{jK}^{-5} (g_K \mathbf{I}_K \cdot \mathbf{S}_j r_{jK}^2 - 3g_K \mathbf{I}_K \cdot (\mathbf{r}_K - \mathbf{r}_j) \mathbf{S}_j \cdot (\mathbf{r}_K - \mathbf{r}_j)) \quad (1.2)$$

$$- (e\mu_0/c) \sum_{K,L} \sum_{K \neq L} Z_L r_{KL}^{-3} (\mathbf{r}_K - \mathbf{r}_L) \times \left[\left(1 + \frac{Z_K M_P}{g_K M_K} \right) \mathbf{v}_K - \mathbf{v}_L \right] \cdot g_K \mathbf{I}_K \quad (1.3)$$

$$+ \mu_0^2 \sum_{K,L} \sum_{K > L} r_{KL}^{-5} [g_K \mathbf{I}_K \cdot g_L \mathbf{I}_L r_{KL}^2 - 3g_K \mathbf{I}_K \cdot (\mathbf{r}_K - \mathbf{r}_L) g_L \mathbf{I}_L \cdot (\mathbf{r}_K - \mathbf{r}_L)] \quad (1.4)$$

$$+ \mathcal{H}_{\text{nitrogen quadrupole interaction}} \quad (1.5)$$

$$+ \frac{1}{3} (16\pi\mu_0\mu_e) \sum_{K,j} g_K \delta(\mathbf{r}_K - \mathbf{r}_j) \mathbf{S}_j \cdot \mathbf{I}_K. \quad (1.6)$$

In (1), capital subscripts refer to nuclei and lower case to electrons. These particles have, respectively, position vectors \mathbf{r}_K , \mathbf{r}_j , and velocities \mathbf{v}_K , \mathbf{v}_j relative to the molecular center of mass which is assumed to coincide with the center of mass of the nuclei. They have charges $Z_K e$, $-e$; spins \mathbf{I}_K , \mathbf{S}_j , and g factors g_K , g_e , respectively. μ_e and μ_0 are the Bohr and nuclear magnetons, respectively, while M_P is the proton mass and M_K the mass of the K th nucleus.

The inversion vibration which gives rise to the microwave spectrum ($\approx 24\,000$ Mc/sec) is a "tunnelling" of the nitrogen, which is normally at the apex of the NH_3 pyramidal structure, through the plane of the three protons. This inversion energy⁶ has been omitted from (1) since it has a negligible effect on the hyperfine interactions.

The terms (1.0) represent the rotational energy of the nuclei.⁷ A and C are the transverse and axial rotational constants exclusive of the electrons; J_x , J_y , J_z are the components of the total molecular angular momentum exclusive of nuclear spin; and L_x , L_y , L_z are the total electronic orbital angular momentum operators. The cross terms of (1.0),

$$-2[A(J_x L_x + J_y L_y) + C J_z L_z], \quad (2)$$

represent the interactions of rotational and electronic angular momenta neglected in the Born-Oppenheimer approximation and cause the excitation of electronic states above the ground $^1\Sigma$ state. The presence of such excited states gives rise to a magnetic field at the nuclei and consequently contributes to hyperfine effects.⁸ The effect of terms (1.1) which express the interaction of the nuclear magnetic moments with electronic currents, does not vanish because of the rotational perturbation terms (2) and is partly responsible for the experimentally observed doubling. Terms (1.2) and (1.6)⁹ are

⁶ Sheng, Barker, and Dennison, *Phys. Rev.* **60**, 786 (1941).

⁷ H. B. G. Casimir, *The Rotation of a Rigid Body in Quantum Mechanics* (J. B. Wolters, Groningen, 1931).

⁸ The "physical" basis of these interactions has been given by G. C. Wick, *Phys. Rev.* **73**, 51 (1948).

⁹ For diatomic molecules this term is more carefully considered by R. A. Frosch and H. M. Foley, *Phys. Rev.* **88**, 1337 (1952).

interactions between electron and nuclear magnetic moments with the currents set up by the rotation of nuclear charges. We shall not discuss the nitrogen quadrupolar interaction (1.5) since it has been treated elsewhere.¹

III. THE MOLECULAR WAVE FUNCTIONS

Fortunately, the complexity of (1) can be greatly reduced by considering the relative magnitude of the energies involved, by eliminating effects which are too small to be observed experimentally by present techniques, and by taking into account the symmetry of the molecule and the statistics of the protons.

From its geometry it is clear that the molecule NH_3 is left unchanged in any physically observable way when transformed by any of the members of the rotation-reflection point group C_{3v} which is isomorphic to the permutation group P_3 of the protons. We are concerned here only with the ground electronic state and the ground vibrational states (excepting the inversion, which can be considered a type of vibration). Hence, the electronic and vibrational parts of the wave function are symmetric (symmetry A_1) relative to the group C_{3v} . In addition the nitrogen spin function has symmetry A_1 . We need only to examine in detail the product function of the other variables

$$\psi = \psi_R(\phi, \theta, \chi) \psi_V(z) \psi(\sigma_1) \psi(\sigma_2) \psi(\sigma_3), \quad (3)$$

where ϕ , θ , χ are the Eulerian angles of the nuclear framework, σ_1 , σ_2 , σ_3 represent the proton spin coordinates, and z is the inversion coordinate. The coordinate system used is that of Hund.¹⁰ It is described, the Eulerian angles defined, and the symmetric top rotation functions $\psi_R(\phi, \theta, \chi)$ given in Appendix I. Hund¹⁰ and Dennison^{11,12} have shown that for the lowest of the two inversion states between which the microwave transition occurs,

$$\psi_{V=0}(z) = \psi_{V=0}(-z), \quad (4)$$

and for the upper inversion state $\psi_{V=1}(z) = -\psi_{V=1}(-z)$.

From the results of the symmetry operations P_3 on the coordinate space of the functions of (3), the representative matrices of the group for each of these functions belonging to the same energy level can be found and reduced to its irreducible constituents.¹³ If the direct products of these irreducible representations are in turn reduced, the total irreducible representations of the molecule can be identified. There results a set of functions which have definite symmetry with respect to the

¹⁰ F. Hund, *Z. Physik* **43**, 823 (1927).

¹¹ G. Herzberg, *Infrared and Raman Spectrum* (D. Van Nostrand Company, Inc., New York, 1945) describes these modes and gives their symmetries relative to the point group C_{3v} of the molecule.

¹² Z. I. Slawsky and D. M. Dennison, *J. Chem. Phys.* **7**, 509 (1939); D. M. Dennison, *Revs. Modern Phys.* **3**, 281 (1931).

¹³ E. Wigner, *Gruppentheorie und ihre Anwendung* (F. Vieweg, Braunschweig, 1931). See also E. B. Wilson, *J. Chem. Phys.* **3**, 276 (1935) for applications to molecules. Note that he uses a different coordinate system from ours.

group P_3 and of these only those belonging to the irreducible representation A_2 , are to be kept in accord with the statistics of the protons.

The wave functions of (3) form irreducible representations of the three-dimensional rotation group and of the various angular momenta involved in the problem. Since the permutation and rotation groups commute, these wave functions must form simultaneous irreducible representations of these groups. The order in which the reductions of the direct products of these simultaneous irreducible representations are made will depend on the choice of coupling scheme. We shall choose it as follows: since magnetic interactions are much smaller than the nitrogen quadrupole coupling energy, the nitrogen spin, \mathbf{I}_N is first coupled to \mathbf{J} to give \mathbf{F}_1 . The protons can then be numbered according to their positions relative to the chosen molecular axes and coupled together to give a resultant \mathbf{I} , which is in turn coupled to \mathbf{F}_1 to give the total angular momentum of the molecule \mathbf{F} . We are thus led to the coupling scheme in Fig. 1 which is

$$\mathbf{J} + \mathbf{I}_N = \mathbf{F}_1, \quad \mathbf{I}_1 + \mathbf{I}_2 + \mathbf{I}_3 = \mathbf{I}, \quad \mathbf{I} + \mathbf{F}_1 = \mathbf{F}. \quad (5)$$

The symmetry properties of all the possible wave functions of the molecule were found in accordance with the above discussion and are listed in Table I. This table shows that when K is a multiple of 3 ($|K| = 3n$), $I = \frac{3}{2}$ and only $\frac{1}{4}$ of the possible functions are physically allowed while when $|K| = 3n \pm 1$, $I = \frac{1}{2}$ and only $\frac{1}{8}$ of the possible functions are allowed. It may be seen from this table that when $|K| = 3n$ the two rotational levels have different symmetry and hence can be split by rotation-vibration interactions as found by Dennison and Nielsen.¹⁴ When $|K| = 3n \pm 1$ the rotation-vibration part of the wave function is degenerate and the levels cannot be split by the same type of effect.¹⁴ The levels can be split, however, by the effects of nuclear spin since the total wave functions including spin have a variety of symmetries as shown in Table I.

Before making detailed calculations of the effect of the Hamiltonian (1), it may be helpful to give a simple

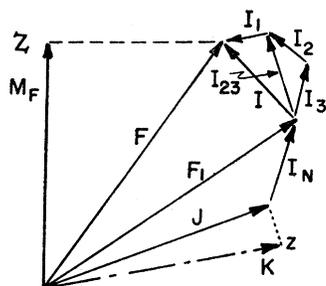


FIG. 1. N¹⁴H₃ molecular coupling scheme referred to laboratory axis. Z is the fixed direction in the laboratory, z is the axis coinciding with the molecular symmetry axis, and K is the projection of J on the molecular symmetry axis.

¹⁴ D. M. Dennison and H. H. Nielsen, Phys. Rev. 72, 86, 1101 (1947).

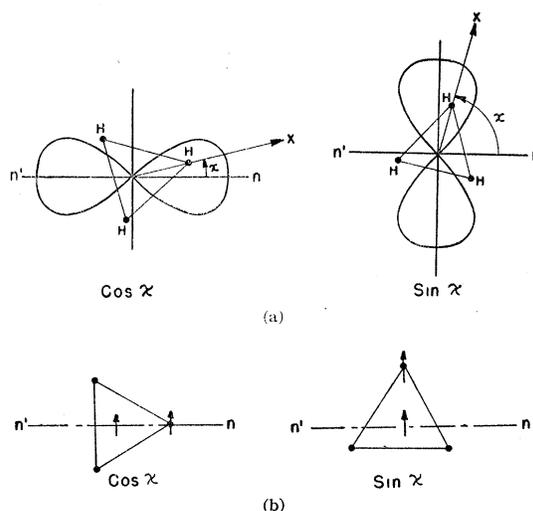


FIG. 2. (a) Azimuthal molecular wave functions ($M_J=0$, $K=1$). (b) Variation of magnetic energy with χ ($K=1$).

physical argument for the lifting of the K degeneracy by the magnetic interactions. For each value of $|K|$ the molecular wave function can contain a factor of either $\sin K\chi$ or $\cos K\chi$, where χ is the azimuthal angle about the molecular symmetry axis.

A plot of the probability of a given value of χ is given in Fig. 2(a) for $K=1$, with the nuclear position superimposed. If the molecule is in one or the other of the above two possible degenerate states, its most probable orientation relative to the fixed laboratory axis is different even though classically the probabilities of clockwise and counter clockwise rotation are equally represented. Picturing the molecule projected on the plane of the protons in Fig. 2(b), indicating a proton spin by an arrow at the vertex of the triangle, we can see why the interaction between the proton and nitrogen magnetic moments gives the two states different energies.¹⁵ The central arrow indicates the orientation of the magnetic moment of the nitrogen nucleus which can be assumed, neglecting the precession of \mathbf{I}_N about \mathbf{F} to remain fixed during the molecular rotation. For any constant assumed orientation of the proton spin relative to the fixed laboratory frame, clearly the two states have different energies, and thus the K degeneracy is removed.

The number of lobes of the χ dependence of the wave function increases with K and consequently the variation in dipolar interaction energy becomes essentially zero for $K > 1$.

IV. THE PERTURBATION CALCULATION

Introduction

The perturbation problem can be solved to second order⁴ in the ratio of hyperfine to electronic energies by

¹⁵ Interaction between the protons and the magnetic field due to molecular rotation gives the same type of effect if, as may be expected, the magnetic field at the proton varies with χ .

TABLE I. Symmetry properties of the $N^{14}H_3$ wave functions.

$ K $	$\psi(VKJIN F_1 M F_1)$ Wave function exclusive of proton spins ^a		$\psi(I_1 I_2 I_{22} I M I)$ Proton spin functions				$\Psi(VKJIN F_1 I F M F)$ Total molecular wave function					
	Number of functions	Irreducible representation	Value of I	Value of M_I	Number of functions	Irreducible representation	Value of F	Number of functions	Irreducible representation			
$3n$	$2F_1+1$	A_1	$3/2$	$\pm 3/2$	4	A_1	$F_1 \pm 3/2$	4($2F_1+1$)	A_1			
				$\pm 1/2$	2	E						
			$1/2$	$+1/2$	2	E						
	$2F_1+1$	A_2	$3/2$	$\pm 3/2$	4	A_1	$F_1 \pm 3/2$	4($2F_1+1$)	A_2			
				$\pm 1/2$	2	E						
			$1/2$	$+1/2$	2	E						
$3n+1^b$	$2(2F_1+1)$	E	$3/2$	$\pm 3/2$	4	A_1	$F_1 \pm 3/2$	8($2F_1+1$)	E			
				$\pm 1/2$	2	E						
			$1/2$	$+1/2$	2	E	$F_1 \pm 1/2$	2($2F_1+1$)	A_1			
				$-1/2$	2	E		2($2F_1+1$)	A_2			

^a For a change of v from even to odd or vice versa the functions identified by the symbols A_1, A_2 would be interchanged.

^b A similar tabulation holds for $|K| = 3n-1$.

diagonalizing an effective Hamiltonian G , obtained from the true Hamiltonian, H of (1) by the relations between matrix elements

$$\langle l_0 i | G | l_0 i' \rangle = \langle l_0 i | G_1 | l_0 i' \rangle + \langle l_0 i | G_2 | l_0 i' \rangle, \quad (6.1)$$

$$\langle l_0 i | G | l' i' \rangle = 0,$$

$$\langle l_0 i | G_1 | l_0 i' \rangle = \langle l_0 i | \mathcal{H} | l_0 i' \rangle, \quad (6.2)$$

$$\langle l_0 i | G_2 | l_0 i' \rangle = \sum_{l \neq l_0} (E_{l_0} - E_l)^{-1} \left(\sum_{i''} \langle l_0 i | \mathcal{H} | l i'' \rangle \right) \times \langle l i'' | \mathcal{H} | l_0 i' \rangle, \quad (6.3)$$

where E_{l_0} = energy of the ground electronic state and E_l = energy of an excited electronic state.

In our problem the l refer to excited electronic states, to the ground electronic state ($^1\Sigma$) and the quantum numbers i , to the rotation, vibration, and hyperfine quantum numbers $J, K; v; F_1, F$. Once the matrix G has been calculated, the energy of the ground state can be found by diagonalizing the matrix:

$$G = G_1 + G_2 = \{ \langle l_0 i | G | l_0 i' \rangle \}. \quad (7)$$

The matrix elements of the hyperfine interactions in G which are off-diagonal in J, K , or v can be neglected relative to those which are diagonal since their contribution in the perturbation calculation is smaller by a factor of at least 10^{-5} . Similarly, the matrix elements of the magnetic hyperfine interactions off-diagonal in the quadrupole interaction energy (off diagonal in F_1) make contributions smaller by a factor of at least $1/40$ than those of their diagonal elements and thus they too will be neglected.

The total Hamiltonian (1) can be broken up into two parts: \mathcal{H}_1 involving only these terms which are diagonal in the electronic quantum numbers and hence contribute to G_1 , and the terms \mathcal{H}_2 involving the remaining off diagonal terms which contribute to G_2 defined in (6.3).

Terms Involving Only the Ground Electronic States (G_1)

Terms which make up what we have called G_1 cannot include any operators involving either electronic velocities or angular momenta, for such operators are known to be off-diagonal in the electronic quantum numbers in a $^1\Sigma$ molecule.¹⁶ The matrix G_1 is thus made up of those terms which are left in (1) after the electronic velocities and angular momenta have been set equal to zero. The expression so obtained will contain the rotational energy (from 1.0), the quadrupole interaction energy (1.5), that part of the electron current terms diagonal in 1 (from 1.1), the nuclear current terms (1.4). The first two of these we have assumed are well known.¹ The next two can readily be calculated in the molecular representation using the substitution,⁴

$$\mathbf{v}_K = \boldsymbol{\omega} \times \mathbf{r}_K, \quad (8)$$

where $\omega_x = 2AJ_x \hbar^{-1}$, $\omega_y = 2AJ_y \hbar^{-1}$, $\omega_z = 2CJ_z \hbar^{-1}$. Appendix II shows details of this calculation. The dipolar terms (1.4) are conveniently separated into the dipolar interactions of the protons with each other and of the protons with the nitrogen.

Dipolar interactions of two magnetic moments transform under rotation as second degree spherical harmonics.¹⁷ Therefore, the only nonzero matrix elements of the proton proton dipolar interaction are those between the states $I = \frac{3}{2}$ and $I = \frac{3}{2}$ or between $I = \frac{1}{2}$ and $I = \frac{3}{2}$. The latter type exist only between states for which $|K| = 3n$ and $|K| = 3n \pm 1$, respectively. Since such states are off diagonal in the rotation energy, these matrix elements can be neglected. Allowed states for which $I = \frac{3}{2}$ must have $|K| = 3n$ and for such states the K degeneracy is lifted by a vibrational interaction.¹⁴

¹⁶ J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), p. 274.

¹⁷ J. H. Van Vleck, *Phys. Rev.* **74**, 1168 (1948).

Thus because of the small magnitude of the dipolar interaction ($\mu_{\text{H}}^2/h\nu_{\text{NH}_3} \approx 7$ kc/sec) matrix elements of the second type will not cause detectable splittings of these $|K| = 3n$ lines. For these reasons we shall drop the dipolar interactions of the protons with each other from further consideration. The nitrogen proton dipolar interaction produces a measurable effect on the spectrum and is discussed in Appendix II.

In order to be able to use matrix elements tabulated by Condon and Shortley¹⁸ we shall carry out the calculation of the coupling of the angular momenta referred to molecular axes.⁴ Angular momenta then have the same addition laws as in atomic cases if the internal angular momenta are reversed in sign.⁴ Let then the angular momenta \mathbf{J} , \mathbf{F}_1 , \mathbf{F} previously defined relative to laboratory axes (capital subscripts X, Y, Z) be referred to molecular axes. Let $\bar{\mathbf{O}}$ be the total reversed internal angular momentum defined by

$$\bar{\mathbf{O}}_\nu = \bar{L}_\nu + \bar{I}_{N\nu} + \bar{I}_\nu = -(L_\nu + I_{N\nu} + I_\nu),$$

$$J_\nu = F_\nu + \bar{\mathbf{O}}_\nu, \quad \nu = x, y, z; \quad (9.1)$$

then

$$[\bar{\mathbf{O}}_\nu, F_\rho] = 0, \quad [J_z, J_z] = 0, \quad T_x T_y - T_y T_x = -i\hbar T_z, \quad (9.2)$$

$$\nu = x, y, z; \quad \rho = x, y, z; \quad T = F, F_1, J, \bar{\mathbf{O}}.$$

These relations lead to the "molecular frame coupling scheme" given in Fig. 3 which should be compared with the "laboratory coupling scheme" of Fig. 1.

Based on the above considerations the calculation of the matrix elements of G_1 in the molecular representation gives

$$\{\langle l_0 i | G_1 | l_0 i' \rangle\} = A(J_x^2 + J_y^2) + C J_z^2 \quad (10.0)$$

$$- (a_1 + a_2)(J_x \bar{I}_{Nx} + J_y \bar{I}_{Ny}) - b_2 J_z \bar{I}_{Nz} \quad (10.1a)$$

$$- (\alpha_1 + \alpha_2)(J_x \bar{I}_{1x} + J_{x'} \bar{I}_{2x'} + J_{x''} \bar{I}_{3x''}) \quad (10.3a)$$

$$- (-\rho_1 + \rho_2)(J_y \bar{I}_{1y} + J_{y'} \bar{I}_{2y'} + J_{y''} \bar{I}_{3y''}) \quad (10.1b)$$

$$- (\gamma_1 + \gamma_2)(J_z \bar{I}_{1z} + J_{z'} \bar{I}_{2z'} + J_{z''} \bar{I}_{3z''}) \quad (10.3b)$$

$$+ \mu_0^2 g_{NH} [\langle v | r^{-3} | v \rangle \bar{\mathbf{I}}_N \cdot \bar{\mathbf{I}} - 3 \langle v | r^{-3} \sin^2 \beta | v \rangle$$

$$\times \{ \bar{I}_{Nx} \bar{I}_{1x} + \frac{1}{4} \bar{I}_{Nx} (\bar{I}_{2x} + \bar{I}_{3x}) - \frac{1}{4} \sqrt{3} \bar{I}_{Nx} (\bar{I}_{2y} - \bar{I}_{3y})$$

$$- \frac{1}{4} \sqrt{3} \bar{I}_{Ny} (\bar{I}_{2x} - \bar{I}_{3x}) + \frac{3}{4} \bar{I}_{Ny} (\bar{I}_{2y} + \bar{I}_{3y}) \}$$

$$+ 3 \langle v | r^{-3} \cos^2 \beta | v \rangle \bar{I}_{Nz} \bar{I}_{z}] \quad (10.4)$$

$$+ \mathfrak{C} \mathcal{C}_{QN}. \quad (10.5)$$

The terms listed in (10.0–10.5) have their origins in the correspondingly numbered terms of (1.0–1.5), $\langle v | r^{-3} | v \rangle$ indicates the inverse cube of the nitrogen-proton distance is to be averaged over the vibration. β is the angle between r and the symmetry axis. All other constants not previously identified are given in Appendix II and are dependent only on the electronic states. The meaning of the primes on the coordinate subscripts of the proton angular momenta will be discussed in con-

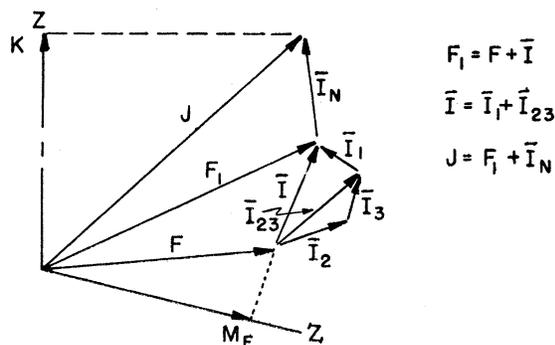


FIG. 3. N¹⁴H₃ molecular coupling scheme referred to laboratory axis.

nection with Eq. (12). We shall now turn to the calculation of G_2 , the part of G which comes from the second-order calculation.

Terms Off-Diagonal in Electronic States (G_2)

Terms of G_2 are of two types: (1) those off-diagonal in the electronic orbital quantum numbers and (2) those off-diagonal in the total electronic spin quantum numbers. (1.0) and (1.1) contain the terms of the first mentioned type while (1.2) and (1.6) contain the second-type terms. The perturbation of the electronic states by molecular rotation finds expression in Eq. (6.3) which will contain cross products of terms of type (2) and (1.1). The effect of the terms (1.1) will therefore be appreciable. On the other hand, since the total electronic spin is zero, electronic spin states are not perturbed by rotation. Hence, these latter terms are orders of magnitude smaller than the former and can be neglected. With this approximation, discussed in more detail in Appendix II, the off-diagonal terms left for consideration are

$$\mathfrak{C} \mathcal{C}_2 = A(L_x^2 + L_y^2) + C L_z^2 - 2A(L_x J_x + L_y J_y) - 2C L_z J_z$$

$$+ (l\mu_0/c) \sum_K i [r_{iK}^{-3} (\mathbf{r}_i - \mathbf{r}_K) \times \mathbf{v}_i] \cdot g_K \mathbf{I}_K. \quad (11)$$

The first two terms above do not affect the hyperfine structure and thus will be dropped. The interaction of the protons with the electrons expressed in the last term is the same at points separated by a 120° rotation about the molecular symmetry axis. Advantage can be taken of this fact by employing initially three molecular coordinate systems: x, y, z (described in Appendix I) in which proton (1) lies in the xz plane; x', y', z' in which proton (2) lies in the $x'z'$ plane; and x'', y'', z'' in which proton (3) lies in the $x''z''$ plane. These systems all have a common z axis (see Fig. 4). If advantage is taken of the above symmetry and the terms of (11) are substituted into (6), G_2 becomes

$$\{\langle l_0 i | G_2 | l_0 i' \rangle\} = -a_3 (\bar{I}_{Nx} J_x + \bar{I}_{Ny} J_y) - b_3 \bar{I}_{Nz} J_z \quad (12.1)$$

$$- \alpha_3 (\bar{I}_{1x} J_x + \bar{I}_{2x'} J_{x'} + \bar{I}_{3x''} J_{x''})$$

$$- \rho_3 (\bar{I}_{1y} J_y + \bar{I}_{2y'} J_{y'} + \bar{I}_{3y''} J_{y''}) \quad (12.2)$$

$$- \gamma_3 (\bar{I}_{1z} J_z + \bar{I}_{2z'} J_{z'} + \bar{I}_{3z''} J_{z''}),$$

¹⁸ E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1951).

where the coefficients of the angular momenta referred to the molecular frames depend only on the molecular electronic states. (12) contains only the parts of (6) significant for our purposes. A summary of its derivation together with the neglected terms is given in Appendix II.

The Secular Equation

The matrix G , the important parts of which are given by the sum of (10) and (12), must be obtained in the molecular representation

$$|vM_F\bar{I}_1\bar{I}_{23}\bar{I}FF_1\bar{I}_N J_K\rangle.$$

According to the discussion in the introduction to this section, only matrix elements diagonal in J , K , and F_1 need be considered. Using the coupling scheme of Fig. 3, the appropriate matrix elements of G can be found by standard methods given in Condon and Shortley.¹⁸ The result of this calculation which is described in Appendix III is:

$$G = AJ(J+1) + (C-A)K^2 \quad (13.0)$$

$$+ eq_N Q_N \left[1 - \frac{3K^2}{J(J+1)} \right] \Omega_1(J, I_N) \quad (13.5)$$

$$+ \left[a + \frac{(b-a)K^2}{J(J+1)} \right] \mathbf{I}_N \cdot \mathbf{J} \quad (13.1a, 13.3a)$$

$$+ \frac{2g_H g_N \mu_0^2 \mathbf{F}_1 \cdot \mathbf{I}}{F_1(F_1+1)} \Omega_2(J, I_N) \quad (13.4)$$

$$\times \left[\langle v | r^{-3} (1 - \frac{3}{2} \sin^2 \beta) | v \rangle \left(1 - \frac{3K^2}{J(J+1)} \right) \right. \\ \left. - \frac{3}{8} \langle v | r^{-3} \sin^2 \beta | v \rangle \left(1 + \frac{3(I_1^2 - I_{23}^2)}{I(I+1)} \right) \frac{(J_x^2 - J_y^2)}{J(J+1)} \right]$$

$$+ \frac{3}{4} \sqrt{3} \langle v | r^{-3} \sin^2 \beta | v \rangle \frac{(I_2 - I_3) \cdot I (J_x J_y + J_y J_x)}{I(I+1) J(J+1)} \Big]$$

$$+ \frac{(\mathbf{I} \cdot \mathbf{F}_1)(\mathbf{F}_1 \cdot \mathbf{J})}{F_1(F_1+1)J(J+1)} \left[(\alpha + \rho)J(J+1) \right.$$

$$\left. + [\gamma - (\alpha + \rho)]K^2 + (\alpha - \rho) \left(1 - \frac{3I_{23} \cdot I}{I(I+1)} \right) \right]$$

$$\times (J_x^2 - J_y^2) - \frac{1}{2} \sqrt{3} (\alpha - \rho) \left(\frac{(I_2 - I_3) \cdot I}{I(I+1)} \right)$$

$$\times (J_x J_y + J_y J_x) \Big], \quad (13.1b, 13.3b)$$

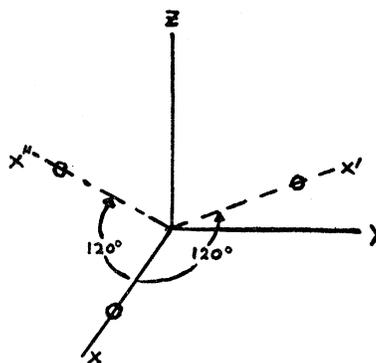


FIG. 4. The three initial proton coordinate systems.

where

$$\Omega_1(J, I_N) = \frac{3(\mathbf{I}_N \cdot \mathbf{J})^2 + \frac{3}{2}(\mathbf{I}_N \cdot \mathbf{J}) - I_N(I_N+1)J(J+1)}{(2J-1)(2J+3)2I_N(2I_N-1)},$$

$$\Omega_2(J, I_N) = \frac{3(\mathbf{I}_N \cdot \mathbf{J})^2 + 2J(J+1)\mathbf{I}_N \cdot \mathbf{J} - I_N(I_N+1)J(J+1)}{(2J-1)(2J+3)},$$

$$2\mathbf{I}_N \cdot \mathbf{J} = F_1(F_1+1) - J(J+1) - I_N(I_N+1),$$

$$2\mathbf{F}_1 \cdot \mathbf{J} = F_1(F_1+1) + J(J+1) - I_N(I_N+1),$$

$$2\mathbf{F}_1 \cdot \mathbf{I} = F(F+1) - F_1(F_1+1) - I(I+1).$$

$a = a_1 + a_2 + a_3$ is proportional to the transverse molecular magnetic field at the nitrogen nucleus and $b = b_2 + b_3$ is proportional to the axial field. The terms with subscripts 1, 3 are due to the electron currents, the terms with subscript 2 to the nuclear currents.

$$\alpha = \alpha_1 + \alpha_2 + \alpha_3,$$

$$\rho = \rho_1 + \rho_2 + \rho_3,$$

$$\gamma = \gamma_1 + \gamma_2 + \gamma_3,$$

where α is proportional to the total x molecular magnetic field at a given proton, and ρ is proportional to the y magnetic field and γ is the z magnetic field. The subscripts 1, 2, 3 have the same meaning as for a , b . Other quantities have been identified previously (see Appendix also). To find the energies of the perturbed levels in each inversion state, it is necessary to solve the secular equation:

$$\{ \langle \bar{I}_{23} \bar{I} J K | G | \bar{I}_{23}' \bar{I} J \pm K \rangle - E \delta(I_{23}, I_{23}') \delta(K, K') \} = 0, \quad (14)$$

with the aid of the matrix elements given in Appendix III. For $K \neq 1$ the Hamiltonian, to the approximations made above, is diagonal and the energy levels are given by

$$\begin{aligned}
W_{VJKF_1F} = & AJ(J+1) + (C-A)K^2 \\
& - eq_N Q_N \left(1 - \frac{3K^2}{J(J+1)}\right) \Omega_1(J, I_N) \\
& + \left(a + \frac{(b-a)K^2}{J(J+1)}\right) \mathbf{I}_N \cdot \mathbf{J} \\
& + \left(\alpha + \rho + \frac{(\gamma - (\alpha + \rho))K^2}{J(J+1)}\right) \frac{(\mathbf{I} \cdot \mathbf{F}_1)(\mathbf{F}_1 \cdot \mathbf{J})}{F_1(F_1+1)} \\
& + 2g_H g_N \mu_0^2 \langle v | r^{-3} (1 - \frac{3}{2} \sin^2 \beta) | v \rangle \\
& \times \left(1 - \frac{3K^2}{J(J+1)}\right) \frac{\mathbf{F}_1 \cdot \mathbf{I}}{F_1(F_1+1)} \Omega_2(J_N, J), \quad (15)
\end{aligned}$$

where $I = \frac{3}{2}$ for $|K| = 3n$, and $I = \frac{1}{2}$ for $|K| = 3n \pm 1$.

For $K \neq 3n$, a typical set of levels whose K and I_{23} degeneracy has not been lifted is shown in Fig. 5b. This figure shows the effect of terms of (15) for a given F_1 value in the upper and in the lower inversion states. Note that when $K \neq 1$ these are the final hyperfine levels and they are perfectly normal. They lead to a spectrum shown in full in Fig. 4 of I. For $K = 3n$ there are twice the number of levels since $I = \frac{3}{2}$. Experimentally

the presence of these multiple levels when $K \neq 1$ has not been detected (see I). A close examination of the fit of the spectral pattern deduced from (15) does show that it is necessary to allow for a small change in the gradient of the molecular electric field at the nitrogen nucleus with rotation to obtain the best fit. This variation is caused by centrifugal distortion of the molecule, which has not been considered in the above discussion.

For $K = 1$, the determinant (14) is not diagonal owing to the terms in $(J_x^2 - J_y^2)$ and $(J_x J_y + J_y J_x)$ which connect states differing in K by 2 units. Associated with these operators are ones dependent on I_{23} which connect states $I_{23} = 0$ with states $I_{23} = 1$. The magnetic perturbations thus simultaneously lift the degeneracy in the levels of $K = \pm 1$ and $I_{23} = 0, 1$. Employing the matrix elements calculated in Appendix III, one may easily solve the secular equation (14). Its roots are $E = W, \bar{W}, W + 2f, W - 2f$, where W is defined by Eq. (15) and

$$\begin{aligned}
f = \frac{1}{2} \left\{ \frac{3}{2} \langle v | r^{-3} \sin^2 \beta | v \rangle + \frac{2g_N g_H \mu_0^2 \mathbf{F}_1 \cdot \mathbf{I}}{F_1(F_1+1)} \Omega_2(J, I_N) \right. \\
\left. + (\rho - \alpha) \frac{(\mathbf{F}_1 \cdot \mathbf{I})(\mathbf{F}_1 \cdot \mathbf{J})}{F_1(F_1+1)J(J+1)} \right\} J(J+1). \quad (16)
\end{aligned}$$

With these roots the molecular wave functions can be determined and are given symbolically below in the laboratory frame:

$$\begin{aligned}
\Psi_{E=W} = & \frac{1}{\sqrt{2}} [|v, K=1, J, I_N, F_1, I_{23}=1, I=\frac{1}{2}, FM_F\rangle \\
& + i |v, K=1, J, I_N, F_1, I_{23}=0, I=\frac{1}{2}, FM_F\rangle], \\
\Psi_{E=W \pm 2f} = & \frac{1}{2} [|v, K=1, J, I_N, F_1, I_{23}=1, I=\frac{1}{2}, FM_F\rangle \\
& \pm |v, K=-1, J, I_N, F_1, I_{23}=1, I=\frac{1}{2}, FM_F\rangle \\
& + i |v, K=1, J, I_N, F_1, I_{23}=0, I=\frac{1}{2}, FM_F\rangle \\
& \mp |v, K=-1, J, I_N, F_1, I_{23}=0, I=\frac{1}{2}, FM_F\rangle] \equiv \Psi_2^1,
\end{aligned}$$

where the upper signs are to be associated together, etc. Inspection of Table I shows that the functions for $E=W$ clearly belong to the representation E and have the same type energy levels as are found for $K \neq 1$. The remaining two functions must then belong to the irreducible representations A_1 and A_2 . Which of these they belong to can readily be determined by applying the permutation operator P_{ij} or specifically P_{23} to the wave functions. Let us express the wave functions $\Psi_{1,2}$ in the representation

$$\begin{aligned}
\Psi_{1,2} = \frac{1}{2} [|v, K=1, J, F_1, M_{F_1}\rangle (|I_1 I_{23}=1, I=\frac{1}{2}, M_I\rangle \\
+ i |I_1 I_{23}=0, I=\frac{1}{2}, M_I\rangle) \pm |v, K=-1, J, F_1, M_{F_1}\rangle \\
\times (|I_1 I_{23}=1, I=\frac{1}{2}, M_I\rangle - i |I_1 I_{23}=0, I=\frac{1}{2}, M_I\rangle)]. \quad (17)
\end{aligned}$$

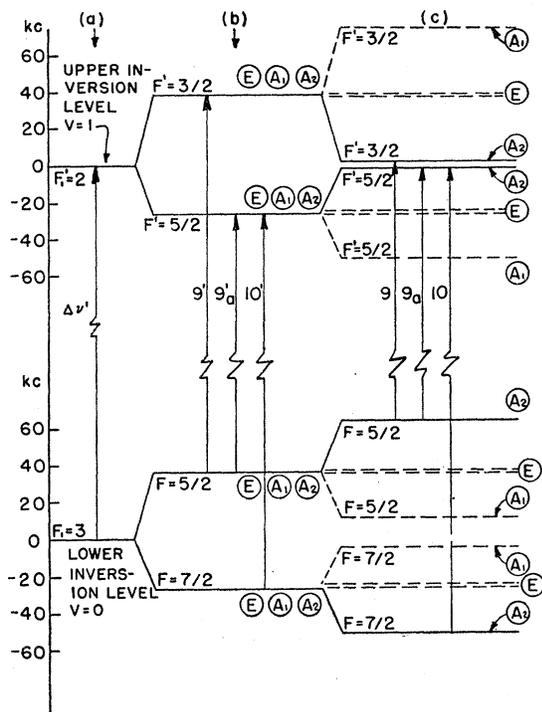


FIG. 5. Energy levels and transitions for the levels $J=3, K=1$ ($V=0, F_1=3; V=1, F_1=2$). (a) Energy levels omitting proton effects quadruply degenerate. (b) Energy levels including proton effects diagonal in K -neglecting lifting of K degeneracy. (c) Actual energy levels—full lines; forbidden levels—dashed lines; E levels are degenerate lines corresponding to allowed transitions shown in right-hand set of Fig. 3(b) of (I). A_1 refers to symmetric levels; A_2 refers to antisymmetric levels.

In this representation the operator P_{23} can be expressed as¹⁹

$$P_{23} = P_{23}^{(x)} P_{23}^{(\sigma)} = P_{23}^{(x)} \left(\frac{1}{2} + 2\mathbf{I}_2 \cdot \mathbf{I}_3 \right). \quad (18)$$

In the representation $|I_1, I_{23}, I, M_I\rangle$, $\mathbf{I}_2 \cdot \mathbf{I}_3$ can readily be calculated from the identity

$$\mathbf{I} \cdot \mathbf{I} = (\mathbf{I}_1 + \mathbf{I}_2 + \mathbf{I}_3) \cdot (\mathbf{I}_1 + \mathbf{I}_2 + \mathbf{I}_3) = I(I+1),$$

from which

$$\mathbf{I}_2 \cdot \mathbf{I}_3 = \frac{1}{2} [I(I+1) - 3 \cdot \frac{3}{4} - 2(\mathbf{I}_1 \cdot \mathbf{I}_{23})] = \frac{1}{2} (I_{23}(I_{23}+1) - \frac{3}{2}).$$

Thus,

$$\begin{aligned} P_{23}^{(\sigma)} |I_1 I_{23} = 1 I = \frac{1}{2} M_I\rangle &= |I_1 I_{23} = 1 I = \frac{1}{2} M_I\rangle, \\ P_{23}^{(\sigma)} |I_1 I_{23} = 0 I = \frac{1}{2} M_I\rangle &= - |I_1 I_{23} = 0 I = \frac{1}{2} M_I\rangle. \end{aligned} \quad (19)$$

Also, from Appendix I,

$$\begin{aligned} P_{23}^{(x)} |v K J F_1 M_{F_1}\rangle &= (-1)^{J+v} |v - K J F_1 M_{F_1}\rangle, \\ P_{23}^{(x)} |v - K J F_1 M_{F_1}\rangle &= (-1)^{J+v} |v K J F_1 M_{F_1}\rangle, \end{aligned} \quad (20)$$

where $v=0$ for the lower inversion state and $v=1$ for the upper inversion state. Therefore, applying P_{23} to Ψ_2 expressed in (17a), we find

$$P_{23}\Psi_2^1 = \pm (-1)^{J+v}\Psi_2^1. \quad (21)$$

Thus if $(-1)^{J+v} = -1$ the function Ψ^1 is physically allowed and the energy is $E=W+2f$ while when $(-1)^{J+(v+1)} = -1$ the function Ψ_2 is physically allowed and the energy is $E=W-2f$. These results can be summarized by writing

$$E = W - (-1)^{J+v} 2f, \quad \text{for } |K|=1. \quad (22)$$

Note that if the levels marked A_1 were allowed, the intensity pattern would be reversed similar to that of Fig. 2b of I.

Interpretation of the Magnetic Constants

Evaluation of the magnetic effects discussed above gives the three components of magnetic field at the hydrogen nuclei produced by rotation and the two independent components at the nitrogen nucleus. In addition, the magnetic moment of the molecule due to rotation about the symmetry axis or perpendicular to it are known from earlier work.²⁰ These seven pieces of information about the magnetic properties of NH_3 should in principle be interpretable in terms of its structure.

The electric currents which produce the magnetic fields associated with rotation of a $^1\Sigma$ molecule can be divided into those due to motions of the electrons and those due to the nuclei. The currents due to nuclear motion may be satisfactorily calculated from a knowledge of the equilibrium nuclear distances. Unfortunately a calculation of electronic currents is very difficult

because it requires a fairly detailed knowledge of the ground and excited electronic states. However, the following simple model probably corresponds roughly to the behavior of the electron distribution as the molecule rotates and gives approximately correct values for the various magnetic effects.

Assume that the nitrogen nucleus, which stays essentially stationary at the center of mass as the molecule rotates, is surrounded by a fixed spherical cloud of electrons which includes all of its own valence electrons plus one-half of the valence electrons of the hydrogen atoms. Assuming further that the amount of electron charge in this fixed cloud at radii larger than the nitrogen-proton distance corresponds to one electron. The protons rotating about the nitrogen, then each carries one-half an electron around with them, slipping through the fixed spherical charge distribution (see slip effect).^{8,20} The one-half electron carried around with each proton is assumed to spherically surround this proton, and hence will rotate about the nitrogen with the proton while staying fixed in orientation like the chair of a Ferris wheel (see slip effect again).^{8,20} A simple classical calculation shows that this model gives the two different components of the molecular magnetic moment and the three different components of the magnetic field at the protons due rotation to an accuracy of about 15 percent.

The magnetic field at the nitrogen nucleus due to rotation is considerably larger than that produced by the above simple model, and to understand its large value, one must consider an excited electronic state of the molecule and the molecular orbitals of electrons which rotate with the protons. These electrons have angular momentum of about 3×10^{-4} if the protons have angular momentum \hbar and may be considered as excited a fraction of the time near 3×10^{-4} into an electronic state of angular momentum \hbar . Near the nitrogen nucleus, the wave function of the excited electron should involve a $2p$ nitrogen wave function, and hence produce a hyperfine interaction near 1.5×10^{-4} of that expected for a $2p$ electron in the nitrogen atom. This is in fact very close to the observed magnetic hyperfine interaction for the N^{14} nucleus in NH_3 .

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APPENDIX I. THE MOLECULAR WAVE FUNCTIONS AND THEIR SYMMETRY PROPERTIES

Molecular Coordinates and Eulerean Angles (see Fig. 6)

With the origin at the center of mass of the nuclei, the z molecular axis is taken as positive in the direction of advance of a right-handed screw rotating in the

¹⁹ P. A. M. Dirac, *The Principles of Quantum Mechanics* (Clarendon Press, Oxford, 1947), third edition.

²⁰ C. K. Jen, *Phys. Rev.* **81**, 197 (1951); J. R. Esbach and M. W. P. Strandberg, *Phys. Rev.* **85**, 24 (1952).

order of the numbering of the protons 1, 2, 3. The x axis lies in the plane containing the axis and the proton numbered (1). The Eulerian angles are taken as follows relative to the fixed laboratory frame:

- ϕ —the fixed frame azimuthal angle, is measured from the fixed x axis to the line of nodes, on;
- θ —the polar angle, is measured from the fixed z axis to the molecular z axis;
- χ —the molecular frame azimuthal angle, is measured from the line of nodes to the molecular x axis.

The angles ϕ , χ are defined in the range $0 \leq \phi, \chi < 2\pi$ and are positive in the direction of rotation $x \rightarrow y$. θ is defined in the range $0 \leq \theta \leq \pi$ and is positive for the rotation $y \rightarrow z$.

The Symmetric Top Functions, $U_{KM}^J(\phi, \theta, \chi)$, and Their Properties

These functions are:²¹

$$U_{KM}^J(\phi, \theta, \chi) = (-1)^K e^{i(M+K)\pi/2} N_{JKM} \times e^{i(M\phi+K\chi)} P_{KM}^J(\theta) \quad \text{for } M \geq K$$

$$= (-1)^M e^{i(M+K)\pi/2} N_{JKM} \times e^{i(M\phi+K\chi)} P_{KM}^J(\theta) \quad \text{for } K \geq M,$$

where

$$N_{JKM} = \left[\frac{(2J+1)(J+\frac{1}{2}d+\frac{1}{2}s)!(J-\frac{1}{2}s+\frac{1}{2}d)^{\frac{1}{2}}}{8\pi^2(J-\frac{1}{2}s+\frac{1}{2}d)!d!(J+\frac{1}{2}s-\frac{1}{2}d)^{\frac{1}{2}}} \right]^{\frac{1}{2}},$$

$$P_{KM}^J(\theta) = t^{-\frac{1}{2}d}(1-t)^{-\frac{1}{2}s} \frac{d!}{(d+p)!} \frac{d^p}{dt^p} (t^{d+p} + (1-t)^{s+p}), \quad (\text{A1})$$

$$d = |M-K|, \quad s = |M+K|,$$

$$t = (1 - \cos\theta)/2, \quad 2p = 2J - (d+s).$$

The proper choice of phases has been discussed by Van Vleck²¹ and by Casimir⁷ and is determined for us by the requirement that the matrix elements of J_x, J_y, J_z obtained from the above representation have the same phase convention as is established by Condon and Shortley¹⁸ whose tabulated matrix elements of angular momenta we propose to use in further calculations. This choice is such that

$$\langle J M K | J_z \pm iJ_y | J M K \pm 1 \rangle = [J(J+1) - K(K \pm 1)]^{\frac{1}{2}}, \quad (\text{A2})$$

$$\langle J M K | J_z \mp iJ_y | J M \pm 1 K \rangle = [J(J+1) - M(M \pm 1)]^{\frac{1}{2}}.$$

By using the functions so defined, it can be shown that

$$U_{KM}^J(\phi, \pi - \theta, \chi) = (-1)^{J+M} U_{-KM}^J(\phi, \theta, \chi). \quad (\text{A3})$$

²¹ J. H. Van Vleck, Phys. Rev. **33**, 467 (1929), especially p. 476 and 480. Also L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935).

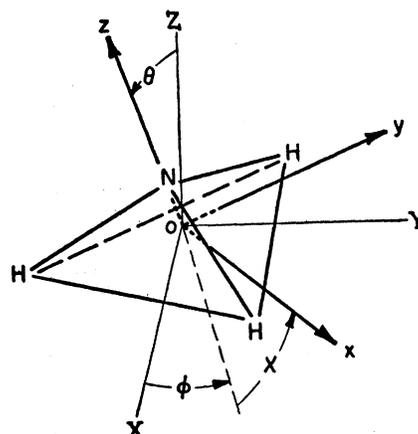


FIG. 6. Molecular coordinates and Eulerian angles.

We shall write

$$U_{KM}^J(\phi, \theta, \chi) = |vKJM\rangle \text{ in the laboratory frame} \\ = |vMJJK\rangle \text{ in the molecular frame.}$$

The operator P_{23} which exchanges protons 2, 3 and thus corresponds to the coordinate transformations

$$\phi \rightarrow \phi + \pi, \quad \chi \rightarrow \pi - \chi, \\ \theta \rightarrow \pi - \theta, \quad z \rightarrow -z, \quad (\text{A4})$$

when applied to the rotation vibration function $|vKJM\rangle$, gives

$$P_{23}|vKJM\rangle = (-1)^{J+v}|v-KJM\rangle, \\ P_{23}|v-KJM\rangle = (-1)^{J+v}|vKJM\rangle. \quad (\text{A5})$$

APPENDIX II. CALCULATION OF THE TERMS IN EQ. (10) FROM EQ. (1)

Terms Involving Only the Ground Electronic State (G_1)

The contribution of the term (1.3) and of the nuclear velocity dependent parts of the term (1.1) lead, respectively, to the terms (10.3a, b) and (10.1a, b) if the molecular coordinates are taken relative to the axis shown in Fig. 5 of Appendix I for the I_N dependent parts (10.3a, 10.1a) and relative to the axes of Fig. 3 for the proton dependent parts (10.3b, 10.1b). The coefficients of (10.1) all involve integrals over the electronic wave functions, for example,

$$\gamma_1 = -2e\mu_0 g_H C (1/c\hbar) \langle vl_0 | \sum_i r_{i1}^{-3} (\mathbf{r}_i - \mathbf{r}_1)_z (\mathbf{r}_1)_z | vl_0 \rangle, \quad (\text{A6})$$

where \mathbf{r}_1 is the position vector of proton 1 relative to the axes x, y, z of Fig. 3 or of proton 2 relative to the axis x', y', z' of Fig. 4, etc. Because of our lack of knowledge of the electronic functions, these integrals cannot be evaluated and thus will be treated as unknown parameters. From (1.3) the following coefficients can be identified and evaluated approximately since the geo-

TABLE II. Symbolic representation of the second-order electron orbital contributions to the perturbation calculation.

Matrix number	Term	Descriptive name usually applied—physical interpretation	Comments for NH ₃
(G ₂) ₁	(A'JL) ²	L uncoupling—exchange of angular momentum between electrons and rotation of nuclei	Contribute to apparent moments of inertia, no hyperfine effects
(G ₂) ₂	a''(I _N L) ²	Nitrogen pseudoquadrupole ^a interaction of electron orbital origin—perturbation of precession of perpendicular components of electron orbital momenta of N ¹⁴ spin	Appears as part of the experimentally measured <i>eqQ</i> . Estimated upper limit about 5 cps
(G ₂) ₃	α''(I ₁ ² L ² +I ₂ ² L ² +I ₃ ² L ²)	Proton pseudoquadrupolar interaction of electron orbital origin	Transforms like a 2nd degree spherical harmonic vanishes since I _ν = $\frac{1}{2}$
(G ₂) ₄	2A''L ² JI _N	Nitrogen magnetic moment interaction with molecular magnetic field	Discussed in detail below and in text
(G ₂) ₅	2A'''L ² J(I ₁ +I ₂ +I ₃)	Proton magnetic moment interaction with molecular magnetic field	Discussed in detail below and in text
(G ₂) ₆	α'''L ² I _N (I ₁ +I ₂ +I ₃)	A pseudomagnetic dipolar interaction in which the nuclear spins are coupled to each other by their magnetic polarization of the magnetic orbitals	Estimated in the order of a few cycles
(G ₂) ₇	ρ'L ² (I ₁ I ₂ +I ₁ I ₃ +I ₂ I ₃)	Similar to above (6)	Estimated negligible

^a So named by H. M. Foley, Phys. Rev. 72, 504 (1947), who treated this term of diatomic molecules.

metrical structure of the molecule is known:

$$a_2 = -6e\mu_0 g_N A (1/c\hbar) \langle v | \frac{1}{2} r^{-1} \{ (14/17) r^{-1} + (3/17) r^{-1} (1 + Z_N M_P / g_N M)_N \} \cos^2 \beta | v \rangle$$

$$= -3.6 \text{ kc/sec,}$$

$$b_2 = -6e\mu_0 g_N C (1/c\hbar) \langle v | r^{-1} \sin^2 \beta | v \rangle = 3.0 \text{ kc/sec,}$$

$$\alpha_2 = -2e\mu_0 g_H A (1/c\hbar) \langle v | r^{-1} \{ (2\sqrt{3} \sin \beta)^{-1} + (Z_N/17) [14(1 + g_H^{-1}) + 3] \cos^2 \beta \} | v \rangle$$

$$= - (8.0 + 4.0 Z_N) \text{ kc/sec,}$$

$$\rho_2 = -2e\mu_0 g_H A (1/c\hbar) \langle v | r^{-1} \{ [(3 + g_H^{-1})(2\sqrt{3} \sin \beta)^{-1}] + Z_N (1 + g_H^{-1} - (3/17) g_H) \cos^2 \beta \} | v \rangle$$

$$= - (27.0 + 29.4 Z_N) \text{ kc/sec,}$$

$$\gamma_2 = -2e\mu_0 g_H C (1/c\hbar) \langle v | r^{-1} \{ [(2 + g_H^{-1})(\sqrt{3} \sin \beta)^{-1}] + Z_N (1 + g_H^{-1}) \sin^2 \beta \} | v \rangle$$

$$= - (21.6 + 16.1 Z_N) \text{ kc/sec.}$$

Where the numerical values are obtained by substituting the geometrical constants of the molecule¹¹ and the nuclear constants²² given below (*I_A*, *I_C* transverse and axial moments of inertia, respectively)

$$I_A = 2.82 \times 10^{-40} \text{ g cm}^2, \quad B = 67^\circ 58', \quad A \equiv \hbar^2 / 2I_A,$$

$$I_C = 4.43 \times 10^{-40} \text{ g cm}^2, \quad g_H = 2 \times 2.7896, \quad C \equiv \hbar^2 / 2I_C,$$

$$r = 1.014 \times 10^{-8} \text{ cm}, \quad g_N = 0.403.$$

The effects of the "nuclear currents" which have thus been calculated can be subtracted from the experimentally measured effects to obtain those due to electronic currents only. This, of course, assumes that the effects of nuclear currents can be calculated from our model of NH₃ which disregards inversion. That this is a good approximation is demonstrated by the fact that the dipolar interaction calculated by this means gives good agreement with the data.

²² Segre's Chart (Addison Wesley Press, Cambridge, 1948).

Using the position of the nuclei relative to the molecular frame of Fig. 5, we have from (1.4) for the nitrogen proton dipolar interaction the terms

$$-3\mu_0^2 g_N g_H \langle v | r^{-3} \sin \beta \cos \beta | v \rangle$$

$$\times [\bar{I}_{N_x} \bar{I}_{1_z} - \bar{I}_{N_z} (\bar{I}_{2_z} + \bar{I}_{3_z}) + \frac{1}{2} \bar{I}_{N_y} (\bar{I}_{2_z} - \bar{I}_{3_z}) - \bar{I}_{N_z} (\bar{I}_{2_x} + \bar{I}_{3_x}) + \bar{I}_{N_z} \bar{I}_{1_x} + \frac{1}{2} \sqrt{3} \bar{I}_{N_z} (\bar{I}_{2_y} - \bar{I}_{3_y})],$$

in addition to the terms given in (10.4). According to the discussion in Appendix III, these terms are only off-diagonal in *K* by ± 1 and thus they may be dropped. The proton-proton dipolar interactions have been shown in the text to be negligible.

Second-Order Terms Involving Excited Electronic States (G₂)

In a light molecule like NH₃ the Russell-Saunders system of representation is a good approximation, so that the terms involving the *L_x*, *L_y*, *L_z* and the electron velocities will depend only on orbital quantum numbers *l*, while the operators *S_x*, *S_y*, *S_z* will involve the spin quantum numbers σ . Because of their larger magnitude we shall consider the former terms first and return to the latter at the end of this Appendix.

Calculation of the orbital perturbations is based on the last three terms of (11) which are to be substituted into (6.3). Rather than writing out in detail the seven different kinds of terms to which such a substitution leads, we shall use a symbolism to describe them according to their dependence on angular momenta and molecular parameters. We represent Eq. (6.3) as

$$G_2 = \{ \sum_{l \neq l_0} (E_{l_0} - E_l)^{-1} (\langle l | A J L + a' L \bar{I}_N + \alpha' (L \bar{I}_1 + L \bar{I}_2 + L \bar{I}_3) | l_0 \rangle \rangle^2 \}, \quad (A7)$$

which when expanded in an equally symbolic way gives the contributions to *G₂* listed in Table II.

To be specific, consider now the matrix $(G_2)_4$ as an example and define for convenience⁴

$$\eta_\nu = 2g_N e\mu_0(1/c) [\sum_j r_{jN}^{-3} (\mathbf{r}_j - \mathbf{r}_N) \times \mathbf{v}_j]_{\nu=x,y,z}. \quad (\text{A8})$$

In the molecular frame \mathbf{r}_N , the position vector of the nitrogen nucleus, is treated as a constant vector and its angular dependence relative to the laboratory axes is thrown over on the total angular momentum. Thus η_ν is, along with L_ν , independent of the rotational quantum numbers. The matrix $(G_2)_4$, for instance, has elements

$$\begin{aligned} & \langle l_0 i | (G_2)_4 | l_0 i' \rangle \\ &= \sum_{l \neq l_0} (E_{l_0} - E_l)^{-1} [\sum_{i''} \{ (\sum_\nu \langle l_0 | A_\nu L_\nu | l \rangle \langle i | J_\nu | i'' \rangle) \\ & \quad \times (\sum_{\nu'} \langle l | \eta_{\nu'} | l_0 \rangle \langle i'' | \bar{I}_{N\nu'} | i' \rangle) \\ & \quad + (\sum_\nu \langle l_0 | \eta_\nu | l \rangle \langle i | \bar{I}_{N\nu} | i'' \rangle) \\ & \quad \times (\sum_{\nu'} \langle l | A_{\nu'} L_{\nu'} | l_0 \rangle \langle i'' | J_{\nu'} | i' \rangle) \}]. \quad (\text{A9}) \end{aligned}$$

η_ν and $L_{\nu'}$ do not commute with each other if $\nu \neq \nu'$ but do commute with J_ν and \bar{I}_ν . Because only matrix elements diagonal in J and $|K|$ are needed, the lack of commutation of I_ν and $J_{\nu'}$ can be ignored. With the help of Eq. (A3), the matrix $(G_2)_4$ can be expanded as a sum of products of angular momentum operators $\bar{I}_\nu J_{\nu'}$ with coefficients dependent on the electronic states only.⁴ A typical coefficient would be:

$$M_{\nu\nu'} = \sum_{l \neq l_0} (E_{l_0} - E_l)^{-1} (\langle l_0 | \eta_\nu | l \rangle \langle l | A_{\nu'} L_{\nu'} | l_0 \rangle + \langle l_0 | A_\nu L_\nu | l \rangle \langle l | \eta_{\nu'} | l_0 \rangle). \quad (\text{A10})$$

And so

$$(G_2)_4 = \frac{1}{2} \sum_\nu \sum_{\nu'} M_{\nu\nu'} J \bar{I}_{N\nu'}, \quad (\text{A11})$$

where $M_{\nu\nu'}$ are the components of a symmetric tensor whose principal axes coincide with those of the molecule since the nitrogen nucleus is on the axis. From molecular symmetry, therefore,

$$M_{xx} = M_{yy} \neq M_{zz}, \quad M_{xy} = M_{xz} = M_{yz} = 0, \quad (\text{A12})$$

and so the result of Henderson, expression (12.1), is obtained with

$$M_{xx} = a_3 = M_{yy}, \quad M_{zz} = b_3. \quad (\text{A13})$$

Calculation of $(G_2)_5$ made in the manner above for each proton in turn in its "own" system of axes (Fig. 4) leads to the terms (12.2) if the reflection symmetry of the electronic functions in the xz plane is considered. The coefficients appearing in (12.2) are:

$$\begin{aligned} \alpha_3 = A \sum_{l \neq l_0} (E_{l_0} - E_l)^{-1} (\langle l_0 | \xi_x | l \rangle \langle l | L_x | l_0 \rangle \\ + \langle l_0 | L_x | l \rangle \langle l | \xi_x | l_0 \rangle) \quad (\text{A14}) \end{aligned}$$

$$\xi_x = (1/c) e g_H \mu_0 [\sum_j r_{1j}^{-3} (\mathbf{r}_j - \mathbf{r}_1) \times \mathbf{v}_j]_x,$$

with similar definitions for ρ_3 and γ_3 in terms of ξ_y , L_y , and ξ_z , L_z , respectively. α_3 , ρ_3 are not equal because of the off-axis position of the protons. An order of magnitude calculation of the term $(G_2)_2$ —the pseudoquad-

rupolar term, can be made²³ by assuming a case of "pure precession." The order of magnitude of $(G_2)_2$ is given by

$$(G_2)_2 \simeq \mu_0^2 \mu_e^2 g_N^2 \langle r_N^{-3} \rangle^2 \frac{I^2 l(l+1)}{4\Delta E_{\Sigma \rightarrow \pi}} \text{ ergs.} \quad (\text{A15})$$

$\langle r_e^{-3} \rangle$ can be estimated from the fine structure separation of atomic spectra,²⁴ which gives

$$\mu_e^2 \langle r_e^{-3} \rangle = \frac{\Delta \nu \hbar c}{2(l + \frac{1}{2}) Z_i},$$

$Z_i \simeq 3.5$ for nitrogen and assuming a p orbital of the bonding electron at the nitrogen $l=1$. $\Delta \nu$ is not directly available from experiment but can be estimated to be $\simeq 120 \text{ cm}^{-1}$ for a p state,²⁵ while $\Delta E_{\Sigma \rightarrow \pi}$ is of the order of $40\,000 \text{ cm}^{-1}$. One obtains with these values $(G_2)_2 \simeq 5$ cps which is negligible. A similar reasoning indicates that $(G_2)_6$, $(G_2)_7$ are negligible, while $(G_2)_3$ vanishes and $(G_2)_1$ does not affect the hyperfine spectrum.

A calculation of the perturbation of the electronic spin states can be carried out in a manner entirely analogous to the above orbital calculation, using in Eq. (6.3) the terms of (1.2) and of (1.6) instead of the terms of (11). Employing the same rough-type symbolism as in (A1), we may write

$$G_{2S} = \{ \sum_{\sigma \neq \sigma_0} (E_{\sigma_0} - E_\sigma)^{-1} (\langle \sigma | bS(I_N + I_1 + I_2 + I_3) | \sigma_0 \rangle) \}^2, \quad (\text{A16})$$

which leads to terms of the type listed in Table III.²⁴ The last two terms of Table III contain a part dependent on molecular orientation and a part independent of orientation both of about the same magnitude.²⁶ The orientation independent part has been determined experimentally for several molecules to be of the order of 1 to 100 cps. For NH_3 experimentally it is less than 300 cps (see I) and therefore we shall neglect these terms.

APPENDIX III. REDUCTION OF EQS. (10) AND (12) TO THE FORM OF EQ. (13)

Equations (10), (12) are in the form of sums of products of angular momentum operators with coefficients independent of these operators. The matrices are to be diagonalized in a representation

$$| \bar{I}_2 \bar{I}_3 \bar{I}_{23} \bar{I}_1 \bar{I} F F_1 \bar{I}_N J K \rangle,$$

for which the vector coupling scheme of Fig. 3 is understood. We shall first calculate the important matrix elements contributed to $G(7)$ by a typical

²³ H. A. Bethe and R. F. Bacher, *Revs. Modern Phys.* **8**, 209 (1937).

²⁴ N. F. Ramsey and E. M. Purcell, *Phys. Rev.* **85**, 143 (1952).

²⁵ This estimate is discussed by C. H. Townes and B. P. Dailey, *J. Chem. Phys.* **17**, 782 (1949).

²⁶ N. F. Ramsey, *Phys. Rev.* **91**, 303 (1953).

TABLE III. Symbolic representation of the second-order electron spin contribution to the perturbation calculation.

Matrix number	Term	Description	Comments for NH ₃
(G _{2S}) ₁	b' ² (I _N S) ²	Nitrogen pseudoquadrupolar interaction arising from the perturbation of electronic spin states by the nitrogen magnetic moment.	May not be negligible but not distinguishable from pure quadrupolar interaction.
(G _{2S}) ₂	b''S ² (I ₁ ² +I ₂ ² +I ₃ ²)	Proton pseudoquadrupolar interaction	Transforms like a 2nd degree spherical harmonic and therefore vanishes as I _ν =½
(G _{2S}) ₃	2b'''S ² I _N (I ₁ +I ₂ +I ₃)	A pseudo-dipolar interaction and an I _N ·I interaction ^a due to magnetic interactions of the nuclei with electron spins which are exchange-coupled together ^b	Experimentally determined to be negligible.
(G _{2S}) ₄	2ρS ² (I ₁ I ₂ +I ₂ I ₃ +I ₁ I ₃)	Similar to above	

^a E. L. Hahn, Phys. Rev. **80**, 580 (1950).

^b See reference 26.

product of two such operators. Then applying this result to the operators of Eqs. (10), (12) we shall deduce expression (13). Consider the matrix element from (10.4):

$$\mathfrak{M} = \langle \bar{I}_2 \bar{I}_3 \bar{I}_{23} \bar{I}_1 \bar{I} | \bar{I} F F_1 \bar{I}_N J K | \bar{I}_{Nz} \bar{I}_{2y} | \bar{I}_2 \bar{I}_3 \bar{I}_{23}' \times \bar{I}_1 \bar{I}' F' F_1' \bar{I}_N J' K' \rangle. \quad (\text{A17})$$

By noting the commutation properties and approximations previously discussed and by using the matrix elements tabulated in Condon and Shortley, we can reduce the above typical matrix element to the form

$$\mathfrak{M} = \frac{I_2 \cdot I_1}{I(I+1)} \frac{\mathbf{F}_1 \cdot \mathbf{I}}{F_1(F_1+1)} \times \langle \gamma F_1 \bar{I}_N J K | \bar{I}_{Nz} F_{1z} | \gamma F_1 \bar{I}_N J K' \rangle, \quad (\text{A18})$$

where we write for the coefficient

$$(\bar{I}_2 \bar{I}_3 \bar{I}_{23} \bar{I}_1 \bar{I} | \bar{I}_2 | \bar{I}_2 \bar{I}_3 \bar{I}_{23}' \bar{I}_1 \bar{I})$$

its value $I_2 \cdot I / I(I+1)$. The reduction of the terms (10.1a), (10.3a), and (12.1) to the corresponding terms (13.1a), (13.3a) can readily be accomplished with the help of the vector model of Fig. 3. Term (10.5) has been shown elsewhere¹ to be expressible as (13.5). The operators of (10.1b), (10.3b), and (12.2) can be transformed to a common system of axes (see Fig. 4) by expressing them in terms of the linear combinations:

$$T_1^{(1)} = J_x + iJ_y, \quad T_0^{(1)} = J_z, \quad T_{-1}^{(1)} = J_x - iJ_y,$$

and by noting that for a rotation $R(0,0,\chi)$ about the common z axis,

$$T_1'^{(1)} = e^{i\chi} T_1^{(1)}, \quad T_0'^{(1)} = T_0^{(1)}, \quad T_{-1}'^{(1)} = e^{-i\chi} T_{-1}^{(1)}.$$

The result of such a transformation is

$$\begin{aligned} & [(12.2) + (10.1b) + (10.3b)] \\ & \equiv -G_\rho = 2\sigma(J_x \bar{I}_x + J_y \bar{I}_y) + \gamma J_z \bar{I}_z + 2\epsilon(J_x \bar{I}_{1x} \\ & \quad - J_y \bar{I}_{1y} - \frac{1}{2} J_x (\bar{I}_{2x} + \bar{I}_{3x}) - \frac{1}{2} J_y (\bar{I}_{2y} + \bar{I}_{3y}) \\ & \quad - \sqrt{3}\epsilon [J_x (\bar{I}_{2y} - \bar{I}_{3y}) + J_y (\bar{I}_{2x} - \bar{I}_{3x})]. \quad (\text{A19}) \end{aligned}$$

By (A18),

$$(\bar{I}_\rho)_\nu = -\frac{(\bar{I}_\rho \cdot \bar{I})}{I(I+1)} \cdot \left(\frac{\mathbf{I} \cdot \mathbf{F}_1}{F_1(F_1+1)} \right) \times \left(\frac{\mathbf{F}_1 \cdot \mathbf{J}}{J(J+1)} \right)_{J_\nu} \quad \begin{matrix} \nu = x, y, z \\ \rho = 1, 2, 3, \end{matrix} \quad (\text{A20})$$

and thus substitution of (A20) into (A19) yields (13.1b) and (13.3b).

When substitutions of the type (A18) are made in 10.4 one obtains after some rearranging [(10.4) = G_d].

$$\begin{aligned} \frac{G_d}{\mu_0^2 g_H g_M} &= \frac{(\mathbf{F}_1 \cdot \mathbf{I})(\mathbf{F}_1 \cdot \mathbf{I}_N)}{F_1(F_1+1)} \langle v | r^{-3} (1 - \frac{3}{2} \sin^2 \beta) | v \rangle \\ &+ \frac{3\mathbf{F}_1 \cdot \mathbf{I}}{F_1(F_1+1)} \left[\langle v | r^{-3} (1 - \frac{3}{2} \sin^2 \beta) | v \rangle \bar{I}_{Nz} F_{1z} \right. \\ &+ \langle v | (8r^3)^{-1} \sin^2 \beta | v \rangle \left(1 + \frac{3(I_1^2 - I_{23}^2)}{I(I+1)} \right) \\ &\times (\bar{I}_{Nz} F_{1x} - \bar{I}_{Ny} F_{1y}) - \langle v | (\sqrt{3}/4r^3) \sin^2 \beta | v \rangle \\ &\left. \times \frac{(I_2 - I_3) \cdot \mathbf{I}}{I(I+1)} (\bar{I}_{Nz} F_{1y} + \bar{I}_{Ny} F_{1x}) \right]. \quad (\text{A21}) \end{aligned}$$

Recalling that $\mathbf{J} + \mathbf{I}_N = \mathbf{F}_1$ and making use of the vector model, one obtains

$$\begin{aligned} \bar{I}_{Nz} F_{1z} &= -\{\mathbf{I}_N \cdot \mathbf{J} / [J(J+1)]\} J_z^2 \\ &\quad - \frac{1}{3} (3\bar{I}_{Nz}^2 - \bar{I}_N^2) - \frac{1}{3} \bar{I}_N^2, \\ (\bar{I}_{Nz} F_{1x} - \bar{I}_{Ny} F_{1y}) &= -\{\mathbf{I}_N \cdot \mathbf{J} / [J(J+1)]\} \\ &\quad \times (J_x^2 - J_y^2) - (\bar{I}_{Nx}^2 - \bar{I}_{Ny}^2), \\ (\bar{I}_{Nz} F_{1y} + \bar{I}_{Ny} F_{1x}) &= -\{\mathbf{I}_N \cdot \mathbf{J} / [J(J+1)]\} \\ &\quad \times (J_x J_y + J_y J_x) - (\bar{I}_{Nx} \bar{I}_{Ny} + \bar{I}_{Ny} \bar{I}_{Nx}). \end{aligned} \quad (\text{A22})$$

The matrix elements of $(3I_{Nz}^2 - I_N^2)$, $(\bar{I}_{Nx}^2 - \bar{I}_{Ny}^2)$, and $(\bar{I}_{Nx}\bar{I}_{Ny} + \bar{I}_{Ny}\bar{I}_{Nx})$ transform under rotation as certain linear combinations of second-degree spherical harmonics and may therefore be written as:²⁷

$$\begin{aligned} \text{(a)} \quad & \langle \bar{I}_N F_1 JK | \bar{I}_{Nx}^2 - \bar{I}_{Ny}^2 | \bar{I}_N F_1 JK' \rangle \\ & = (\Omega_2(J, I_N) / J(J+1)) \langle JK | J_x^2 - J_y^2 | JK' \rangle, \\ \text{(b)} \quad & \langle \bar{I}_N F_1 JK | (\bar{I}_{Nx}\bar{I}_{Ny} + \bar{I}_{Ny}\bar{I}_{Nx}) | \bar{I}_N F_1 JK' \rangle \\ & = (\Omega_2(J, I_N) / J(J+1)) \langle JK | J_x J_y + J_y J_x | JK' \rangle, \\ \text{(c)} \quad & \langle \bar{I}_N F_1 JK | 3\bar{I}_{Nx}^2 - \bar{I}_{Ny}^2 | \bar{I}_N F_1 JK' \rangle \\ & = (\Omega_2(J, I_N) / J(J+1)) \langle JK | 3J_z^2 - J^2 | JK' \rangle, \quad (\text{A23}) \end{aligned}$$

where the factor of proportionality $(\Omega_2(J, I_N) / J(J+1))$ is the same for all matrix elements of this type. $\Omega_2(J, I_N)$ can most readily be evaluated from (A23c) with the help of matrix elements tabulated in Condon and Shortley.¹⁸ One finds after considerable algebra the result given in Eq. (13). Substituting relations (A22) and (A23) into (10.4) one obtains Eq. (13.4) of the text. (Note that the signs of I , I_N have been restored to their normal values and compensating changes in sign made in their coefficients.)

Finally the proportionality factors of the type (A18)

can be evaluated from Condon and Shortley.¹⁸ Thus

$$\begin{aligned} \left(1 + \frac{3(I_1^2 - I_{23}^2)}{I(I+1)} \right) &= \begin{pmatrix} -4 & 0 \\ 0 & 4 \end{pmatrix}, \\ \left(1 - \frac{3I_{23} \cdot I}{I(I+1)} \right) &= \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, \\ \frac{(I_2 - I_3) \cdot I}{I(I+1)} &= \begin{pmatrix} 0 & 2/\sqrt{3} \\ 2/\sqrt{3} & 0 \end{pmatrix}, \end{aligned}$$

where the rows and columns are to be labeled by values of $I_{23} = 1, 0$ in that order.

Elements of the type $\langle \bar{I}_N F_1 JK | J_x^2 | \bar{I}_N F_1 JK' \rangle$ are evaluated in a similar fashion substituting K for M in the Condon and Shortley matrix elements and changing the sign of i , thus:²⁷

$$\begin{aligned} \langle JK | J_x^2 - J_y^2 | JK \rangle &= 0, \quad \langle JK | J_x J_y + J_y J_x | JK \rangle = 0, \\ \langle J-1 | J_x^2 - J_y^2 | J+1 \rangle &= \frac{1}{2} J(J+1), \\ \langle J+1 | J_x J_y + J_y J_x | J-1 \rangle &= \frac{1}{2} i J(J+1), \\ \langle J+1 | J_x^2 - J_y^2 | J-1 \rangle &= \frac{1}{2} J(J+1), \\ \langle J-1 | J_x J_y + J_y J_x | J+1 \rangle &= -\frac{1}{2} i J(J+1). \end{aligned}$$

²⁷ See reference 13, Chap. XXI, Sec. 5.

Sulfur Bonds and the Quadrupole Moments of O, S, and Se Isotopes*

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Quadrupole couplings of S³³ in HDS, SO₂ and CH₃SH have been measured. These and previously measured quadrupole couplings of S³³ in OCS, HNCS, CS, and S₈ are examined to determine the nature of sulfur bonds and the best value for the S³³ quadrupole moment. $s-p$ hybridization is found to be common, but not universal, in sulfur bonds. The S³³ quadrupole moment is $-0.064 \pm 0.01 \times 10^{-24}$ cm². If O and Se bonds are assumed to be similar to those of S, the quadrupole moments of O¹⁷ and Se⁷⁹ are -0.004×10^{-24} cm² and 0.9×10^{-24} cm², respectively.

INTRODUCTION

COUPLING of the nuclear quadrupole moments of the halogens in molecules has been extensively studied and interpreted in terms of bond structure, but attention given to quadrupole hyperfine structure of O, S, or Se has been rather small by comparison. We have attempted to study the quadrupole coupling of S³³ in a variety of bond structures in order to obtain information about the nature of sulfur bonds, and in

addition to obtain improved values for the nuclear quadrupole moments of S³³, S³⁵, and isotopes of the chemically similar elements, O and Se.

The most abundant sulfur nuclei, S³² and S³⁴, have zero spin and hence no quadrupole moment, but the less common S³³ (0.75 percent abundance) has a spin of 3/2 and a quadrupole moment. ϵ quadrupole hyperfine structure due to this isotope was first observed by Townes and Geschwind¹ in OCS, and its quadrupole coupling constant in this molecule has been determined with increasing accuracy by several workers, White's value² $eqQ = -29.130 \pm 0.008$ Mc/sec being the most

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¹ C. H. Townes and S. Geschwind, Phys. Rev. **74**, 626 (1948).

² R. L. White, Columbia Radiation Laboratory Quarterly Report, March 31, 1953, p. 21 (unpublished).