Rotational Magnetic Moments in Polyatomic Molecules*

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There is generally present in a molecule a small magnetic moment associated with its rotational degree of freedom. The rotational *g*-factor can be measured by an experimental method based upon the Zeeman effect. Previously, the most successful measurements have been made with the molecular beam resonance technique. More recently, the microwave Zeeman splitting of molecular rotation lines has offered another method for the determination of rotational *g*-factors. With this method, the *g*-factors of several molecules such as NH_3, H_2O, OCS, etc. have been measured. The quantum mechanical theory of the rotational magnetic moment of the symmetric top molecule has been developed, and the experimental results are discussed qualitatively in the light of this theory.

I. INTRODUCTION

SINCE a molecule is composed of charged particles, a molecular rotation can result in the existence of a magnetic moment. However, the magnetic effects of the positively charged nuclei and the negatively charged electrons would tend to cancel each other, thus leaving a residual moment due to the difference in the distribution and motion of the two kinds of charge. Because of this cancellation effect and the influence of large nuclear masses, the resulting rotational moment in a molecule is generally a very small quantity (of the order of one nuclear magneton or less).

One of the earliest theoretical investigations of the magnetic effect of charged particles in a rotating molecule was made by Condon.[1] He assumed a charged particle rigidly attached to a symmetric rotor and gave a wave-mechanical expression for the perturbed energy in a magnetic field. Several years later, Estermann and Stern[2] measured the rotational moment of the hydrogen molecule by the molecular beam deflection method and obtained a *g*-factor between 0.8 and 0.9 in the units of nuclear magnetons per rotational quantum number. They found the rigid rotor theory could not account for this result since it would give a *g*-factor of about 3. This difficulty was resolved by Wick,[3] who showed that the wave-mechanical perturbation theory did account for the experimental value if an appropriate wave function was employed. This explanation was made even more convincing when Ramsey[4] repeated the measurement of the H_2 rotational moment by the more powerful method of molecular beam resonance. Ramsey not only supplied a more accurate measurement for the H_2 rotational moment, the *g*-factor of which was given as 0.8787, but definitely established the sign of the moment as positive. This result gave, at least for the special case of H_2 molecule, a strong support for Wick's theory and a direct contradiction to the rigid rotor theory for the effect of the electrons. The rigid rotor theory predicted a net rotational moment which was incorrect in magnitude and also incorrect in sign.

The development of microwave spectroscopy in recent years has led to another method of measuring rotational magnetic moments.[5] This method depends on the existence of rotational quantum transitions in the microwave frequency range. The energy level of each rotational state is in general perturbed by a magnetic field and is split into a number of sublevels. From the Zeeman spectrum for a rotational line, information can be obtained on the over-all magnetic moment of the molecule. This over-all magnetic moment is the rotational moment if the molecular rotation has no coupling with any electron or nucleus in the molecule. This requirement is satisfied if the spin of each nucleus is zero and if the molecule is in the $^1\Sigma$-state, as most molecules are in their ground states. Under these conditions, the rotational moment is the only unknown quantity and can be directly determined. If, however, the molecular rotation has a coupling with either an electron or a nucleus, or both, then the determination of the rotational moment must depend either upon the detailed knowledge of the coupled systems or some means of removing the coupling as in the Paschen-Back effect.[6]

II. EXPERIMENTAL METHOD AND APPARATUS

The measuring apparatus and experimental techniques have been described in previous papers.[5,6] The difference between the present method and other current spectroscopic arrangements lies in the use of a resonant cavity as the absorption cell. The microwave generator is simultaneously frequency modulated at two different frequencies in order for the microwave spectral lines to be observed. The higher frequency modulation is used to obtain a high signal-to-noise ratio. The lower fre-

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

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

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

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

[5] C. K. Jen, Phys. Rev. **74**, 1396 (1948).

[6] C. K. Jen, Phys. Rev. **76**. 1494 (1949).

quency modulation (actually a saw-tooth wave) is used for the spectral presentation.

A magnetic field continuously variable up to about 10,000 oersteds is used. The field strength is obtained by measurement of the flux change in a stationary coil as the direction of the magnetic field is reversed. The accuracy of the magnetic field measurement is about two percent. The measurement of small frequency differences is accurate to about 50 kc/sec. The average accuracy of a g-factor determination, with the exception of very small g-values, is thus estimated to be about ± 5 percent.

This equipment does not, in its present form, provide means for determining the sign of the magnetic moment.

III. DESCRIPTION OF THE ZEEMAN SPECTRA

It will prove useful for the following sections to describe qualitatively the characteristics of the Zeeman spectra caused by the rotational moment only. The rotational energy, W, in a magnetic sublevel, is, to the first-order approximation,

$$W = W_R - Mg\mu_0 H, \tag{1}$$

where W_R = the energy of a rotational state at $H=0$, designated by the rotational quantum numbers (J, K, etc.), M = magnetic quantum number for J along the field direction, g = g-factor for the rotational state, μ_0 = nuclear magneton, and H = magnetic field. The transition frequency for any Zeeman component is

$$\begin{aligned}\nu &= [(W_R' - W_R)/h] - (M'g' - Mg)\mu_0 H/h \\ &= \nu_R - [\Delta M g' + M(g'-g)]\mu_0 H/h, \end{aligned}\tag{2}$$

where the primed quantities refer to the upper state and the unprimed to the lower state, $\nu_R = (W_R' - W_R)/h$ is the rotational transition frequency (h = Planck's constant), and $\Delta M = M' - M$ is the change in M during transition.

For a given rotational transition, the selection rules for its Zeeman components are:

$$\Delta M = 0, \quad \text{for } \pi\text{-transitions, and}$$
$$\Delta M = \pm 1, \quad \text{for } \sigma\text{-transitions.}$$

Even without a detailed knowledge of the intensity distribution, explicit expressions for which are readily available in standard references,[7] some qualitative description of the nature of the Zeeman spectrum can be made in relation to the rotational g-factors. It can be seen from Eq. (2) that, if $g'=g$, the π-transition has no splitting and the σ-transition results in a doublet, symmetrically displaced relative to the origin (zero-field position). In case g' is not equal to g but $|(g'-g)/g'| \ll 1$, the π-transition results in a group of evenly spaced lines centered at the origin. The σ-transition results in two similar groups (each consisting of lines equally spaced as in the π-group but in general having a different intensity distribution), again symmetrically displaced relative to the origin. Each one of these groups would appear as a single broad "line" for an observation in which the spectral resolution is not sufficiently high. If, however, g' is sensibly different from g, then the lines in each group would be so far separated from one another that they should be treated as individual components.

It should be specifically noted that the Zeeman pattern based on the first-order theory as in Eq. (2) would be invariant to the reversal of the signs of the two g-factors. Hence, the sign of the moment will remain indeterminate. This indeterminacy of sign can be resolved in either one of the following ways. (1) The sign can be determined experimentally with respect to the polarization of the radiation. For an absorption experiment, circularly polarized radiation can cause one branch of the Zeeman pattern or the other to disappear according to the sense of rotation. (2) In the case of a coupling with a nucleus, the sign as well as the magnitude of the rotational moment can be determined, provided the sign and the magnitude of the nuclear moment are known.[5]

IV. RESULTS OF MEASUREMENT

The Zeeman effect in the microwave rotational spectra of some polyatomic molecules has been investigated. The choice of molecules has been dictated primarily by the known presence of rotational lines in the working frequency range of the equipment. To date, measurements have been made on a few representatives of linear, symmetric, and asymmetric types of molecules. The following results refer to the σ-transitions. The g-factors are calculated by Eq. (2). The g-factor in each case is computed from the observed doublet separation and is, therefore, necessarily the average value (denoted by $\bar{g}$) between the true g-factors of two rotational states involved in the transition. The sign of any g-factor is understood to be either plus or minus, unless a definite sign is given.

OCS

Zeeman splitting in the spectra of this linear molecule was measured for OCS^{32} ($J=1\rightarrow 2$, $v=0$) line at 24,325.9 Mc/sec and for the OCS^{34} ($J=1\rightarrow 2$, $v=0$) line at 23,731.3 Mc/sec. Zeeman components were not resolvable for fields below 7000 oersteds. A completely resolved weak doublet has a separation of about 0.36 Mc/sec at $H=8000$ oersteds. Assuming the g-factors for $J=1$ and $J=2$ states are not drastically different, the calculated g-factor for these states is 0.029 ± 0.006. The difference between g-factors of OCS^{32} and OCS^{34} is not detectable in the present experiment.

N_2O

This linear molecule was previously studied with respect to the Paschen-Back effect.[6] Because of the smallness of the electric quadrupole coupling due to the

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[7] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, 1935), p. 387.

N nuclei, decoupling was almost complete at $H=10{,}000$ oersteds. The Paschen-Back components for the σ-transition of the $J=0\to 1$ rotation line were two very strong doublets. The rotational g-factor is calculated to be 0.086 ± 0.004.

NH_3

The Zeeman effect in the inversion spectra of NH_3 (symmetric top) has been studied previously perhaps more thoroughly than for any other molecule.[5,6] Since $N^{15}H_3$ does not have a nuclear quadrupole coupling, its Zeeman spectrum supplies direct information on the rotational magnetic moment. In the case of $N^{14}H_3$, the molecular rotational moment acts in conjunction with the N^{14} nuclear magnetic moment because of the electric quadrupole coupling. The rotational moment of $N^{14}H_3$ can be deduced from its Zeeman spectra with the aid of the known N^{14} nuclear moment or more directly through the Paschen-Back effect. The results for both $N^{15}H_3$ and $N^{14}H_3$ Zeeman data were found to be mutually consistent within the limits of experimental error.

Since the selection rules for the inversion spectra are $\Delta J=0$ and $\Delta K=0$, there is every reason to believe that $g'=g$. Therefore, the σ-transition for an $N^{15}H_3$ line is expected to be a strong and sharp doublet even at a very strong field strength. This expectation proved to be true. Furthermore, the Zeeman splitting at a constant field for lines bearing different J and K values did not seem to change appreciably. This fact leads to the conclusion that the dependence of the g-factor on the rotational quantum numbers is at most rather slight, and the rotational moment of NH_3 is almost exactly proportional to the total rotational angular momentum.

Although the sign of the rotational moment cannot be established through the first-order Zeeman effect in the $N^{15}H_3$ spectra, the relative sign between the nuclear and rotational moments in the $N^{14}H_3$ spectra can be determined. It turned out that the rotational moment of $N^{14}H_3$ must have the same sign as the N^{14} nuclear moment, which is known to be positive. The g-factor for $N^{15}H_3$, calculated directly from the Zeeman data, is $+0.477\pm 0.03$. The present experimental accuracy is not sufficient to differentiate between the g-factors for $N^{14}H_3$ and $N^{15}H_3$.

H_2O and HDO

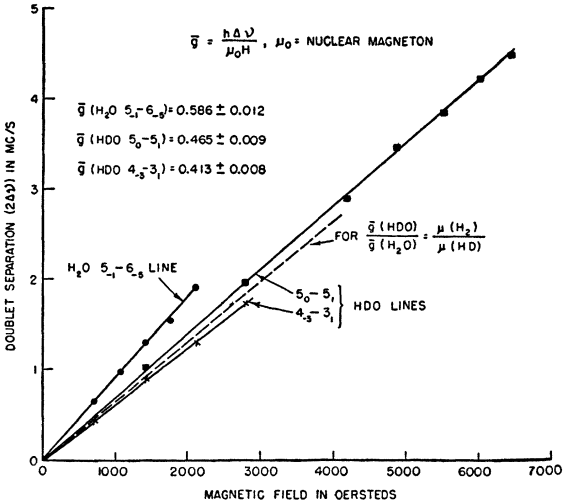

FIG. 1. Zeeman splitting of H_2O and HDO rotational lines.

These asymmetric top molecules have only three known rotational lines in the convenient range of the present apparatus, one for H_2O and two for HDO. Using the conventional designation (J_τ stands for a rotational state), the rotational frequencies are $\nu(H_2O\colon 5_{-1}-6_{-5})=22{,}235.2$ Mc/sec; $\nu(HDO\colon 5_0-5_1)=22{,}307.7$ Mc/sec; and $\nu(HDO\colon 4_{-3}-3_1)=20{,}460.4$ Mc/sec. The Zeeman splitting showed in each case a clear-cut doublet pattern at low field strengths. Figure 1 is a plot of the doublet frequency separation as a function of the magnetic field. It is seen that each of the three curves shows a linear relation between the doublet separation and the field, thus indicating a first-order perturbation effect. However, there is a large difference between one curve and the other two for the range of indicated field strengths. For the two curves ($H_2O\colon 5_{-1}-6_{-5}$ and $HDO\colon 4_{-3}-3_1$), the doublet components became rapidly weaker and broader with increasing field and could not be detected beyond the range indicated on the graph. For the curve with longer range ($HDO\colon 5_0-5_1$), the doublet components preserved their intensity and sharpness up to a much higher field. It should be noted that the "short-range" curves are associated with $\Delta J=\pm 1$ and large change in τ, while the "long-range" curve is associated with $\Delta J=0$ and a small change in τ. This evidence points to the fact that there is a definite, though probably slight, dependence on J and τ for the g-factors.

It is also worth noting that the two curves for HDO give an average g-factor, which is smaller than that for H_2O by a factor approximately equal to the inverse ratio of the reduced masses (μ) of H_2 and HD. This indicates that the rotation of the hydrogen or deuterium atoms contributes significantly to the rotational moment.

The measured g-factor for each transition, as determined by the slope of each curve in Fig. 1, represents a value between g' and g of the interacting states. The average value (denoted by $\bar{g}$) for each transition is given in the same figure.

CH_3OH

This molecule is a slightly asymmetric top. The spectral lines observed in the microwave range are attributed by Dennison and Burkhard[8] to a hindered internal

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[8] D. M. Dennison and D. G. Burkhard, Symposium on Molecular Structure and Spectroscopy, Ohio State University (June, 1948). A private communication from Professor D. M. Dennison, concerning a preliminary theory on the Zeeman effect in the CH_3OH microwave spectra, is gratefully acknowledged by the author.

rotation. A preliminary study has been made on the Zeeman effect of a few of the transitions identified by Coles[9] as those of $\Delta J=0$. These same lines have been identified theoretically by Dennison and Burkhard as $\Delta J=0$ and $K=2\rightarrow 1$. The Zeeman pattern for each of the lines studied was again a doublet, which was fairly sharp at low fields and became diffuse with increasing field. The components could not be detected beyond $H=3000$ oersteds. The observed data for σ-transitions can be fitted by the empirical formula

$$\Delta\nu=\{60+1440/J(J+1)\}H,$$

where $\Delta\nu$ = frequency displacement (in cps) of each doublet component from the zero-field line frequency, and H = field in oersteds. The corresponding g-factor, which is probably an average of the true g-factors of the interacting states, is $0.078+1.88/[J(J+1)]$.

SO_2

The microwave rotational spectra of this asymmetric top have been observed by other investigators.[10] Only a few out of many observed lines could be identified tentatively with quantum number specifications. The Zeeman spectra of these tentatively assigned lines were very complex. In general, each line began to show appreciable weakening at a low field (about 2000 oersteds) and split into weak components, starting from an intermediate field (about 4500 oersteds). The Zeeman components are usually too many and too weak to be measured. In one instance, however, a spectral line at about 25,392 Mc/sec (assigned as $7_{2,6}-8_{1,7}$) showed a measurable doublet-like splitting in the range from 5000 to 9000 oersteds. The doublet separation was found to be proportional to the field strength. At $H=6000$ oersteds, for example, the frequency separation between the apparent doublet components was about 0.76 Mc/sec. The approximate g-factor is 0.084 ± 0.010.

The data for $\bar{g}$ (average value of the g-factors of two rotational states described above) are summarized in Table I.

V. THEORY OF THE ROTATIONAL MAGNETIC MOMENT OF SYMMETRIC TOP MOLECULES

The quantum mechanical theory of the magnetic effect of a charged particle rigidly attached to a symmetric rotor was first derived by Condon.[1] The rigid rotor theory is certainly applicable to the effect of the nuclear charges and should be reasonably accurate for the electrons in the inner shells of atoms. Its validity, however, cannot be extended to those electrons which are loosely attached to the atoms. This fact has been clearly demonstrated by Wick's theory of the rotational moment of diatomic molecules.[3,11] For loosely attached electrons, a nonrigid rotor theory must be used to obtain agreement with experimental data. Since a polyatomic molecule has, in effect, both rigid and nonrigid constituents, a general theory will be worked out in this paper.

TABLE I. Summary of data.

Molecule	$\bar{g}$
H_2O	0.586 ± 0.012
NH_3	$+0.477\pm 0.030$
HDO[a]	0.439 ± 0.009
N_2O	0.086 ± 0.004
SO_2	0.084 ± 0.010
OCS	0.029 ± 0.006

[a] Average of two transitions.

The molecule under consideration is assumed to be a symmetric top, having two equal moments of inertia, A, about axes perpendicular to the figure axis and a third moment of inertia, C, about the figure axis. This consideration will automatically include the whole class of linear polyatomic molecules as a special case. The molecule is assumed to rotate about its center of mass as a rigid body.

Let a charge, ϵ, be rigidly attached to the molecule and thus be representative of a nuclear charge (intrinsically positive) or the charge of a firmly bound electron (intrinsically negative). Its position is described by the distance, a, measured from the figure axis and another distance, b, from the center of mass along the figure axis. In the case of a firmly bound electron, these coordinates are considered as being averaged over a static distribution function. Let there be also an electron, having charge, $-e$, and mass, m. This electron is taken to be representative of those loosely attached to the molecule. The effects of nuclear and electron spins are neglected.

Let the Cartesian coordinate system x, y, z be fixed in space and another system x', y', z' be fixed in the molecule, where z' is chosen to be coincident with the figure axis. Both systems have a common origin at the center of mass and their relative orientation is specified by the Eulerian angles (θ, ϕ, ψ) in the usual manner. The constant magnetic field H is assumed to be along the z-axis of the space-fixed system.

The Lagrangian function for the rigid body with a bound charge and a "free" electron in a magnetic field is

$$L=T_1+T_2-V+(\epsilon/c)\mathbf{v}_\epsilon\cdot\mathbf{A}_\epsilon-(e/c)\mathbf{v}_e\cdot\mathbf{A}_e, \tag{3}$$

where T_1 and T_2 are, respectively, the kinetic energies of the rigid rotor and the electron, V the total potential energy, $\mathbf{v}$ the velocity of a charged particle, and $\mathbf{A}$ the vector potential. The vector potential $\mathbf{A}$ has the components $A_x=-yH/2$, $A_y=xH/2$, and $A_z=0$ in the space-fixed system.

The Lagrangian function in Eq. (3) can be expressed in the coordinates of (θ, ϕ, ψ) and (x', y', z') and their time derivatives $(\dot{\theta}, \dot{\phi}, \dot{\psi})$ and $(\dot{x}', \dot{y}', \dot{z}')$ by an orthogonal transformation. Here, the primed quantities are

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[9] D. K. Coles, Phys. Rev. 74, 1194 (1948).

[10] B. P. Dailey, S. Golden, and E. B. Wilson, Jr., Phys. Rev. 74, 1537 (1948).

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

the coordinates of the electron alone. The nonrigid nature of the electronic motion is provided by the presence of $\dot{x}'$, $\dot{y}'$, and $\dot{z}'$. Let q_k stand for one of the coordinates θ, ϕ, ψ, x', y', z', and p_k for the generalized momentum conjugate to that coordinate. Thus, there are six such generalized momenta determined by the relation $p_k=\partial L/\partial \dot{q}_k$. The Hamiltonian of the whole system is then $\mathcal{H}=\sum_k p_k\dot{q}_k-L$. The complete result of these transformations is

$$\mathcal{H}=\frac{\mathcal{P}_\theta(\sin\theta\mathcal{P}_\theta)}{2A\sin\theta}+\frac{\mathcal{P}_\phi{}^2}{2C}+\frac{(\mathcal{P}_\phi\cos\theta-\mathcal{P}_\psi)^2}{2A\sin^2\theta}+\frac{1}{2m}\{p_{x'}{}^2+p_{y'}{}^2+p_{z'}{}^2\}+\frac{eH}{2mc}p_\psi+\frac{1}{2m}\left(\frac{eH}{2c}\right)^2\rho^2+V, \quad (4)$$

where

$\mathcal{P}_\theta=P_\theta-p_\theta-(\epsilon H/2c)[-a\cos\phi(b\cos\theta+a\sin\theta\sin\phi)]$,
$\mathcal{P}_\phi=P_\phi-p_\phi-(\epsilon H/2c)[a(a\cos\theta-b\sin\phi\sin\theta)]$,
$\mathcal{P}_\psi=P_\psi-p_\psi-(\epsilon H/2c)[a^2\cos^2\phi+(b\sin\theta-a\cos\theta\sin\phi)^2]$,
P_θ, P_ϕ, P_ψ and $p_{x'}$, $p_{y'}$, $p_{z'}$ are the generalized momenta,
$p_\theta=\cos\phi(y'p_{z'}-z'p_{y'})-\sin\phi(z'p_{x'}-x'p_{z'})$,
$p_\phi=x'p_{y'}-y'p_{x'}$,
$p_\psi=\cos\theta(x'p_{y'}-y'p_{x'})+\sin\theta\sin\phi(y'p_{z'}-z'p_{y'})+\sin\theta\cos\phi(z'p_{x'}-x'p_{z'})$,
$\rho^2=(x')^2+(y')^2+(z')^2-(x'\sin\theta\sin\phi+y'\sin\theta\cos\phi+z'\cos\theta)^2$.

Equation (4) can be expanded, noting the noncommutability of each pair of canonically conjugate variables. For simplicity, only the unperturbed Hamiltonian and those terms which will eventually contribute to the first- and second-order perturbation energies, both linear in H, will be retained. The result can be written as

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}'+\mathcal{H}''+\cdots, \quad (5)$$

where

$$\mathcal{H}_0=\frac{P_\theta(\sin\theta P_\theta)}{2A\sin\theta}+\frac{P_\phi{}^2}{2C}+\frac{(P_\phi\cos\theta-P_\psi)^2}{2A\sin^2\theta}+\frac{1}{2m}(p_{x'}{}^2+p_{y'}{}^2+p_{z'}{}^2)+V,$$

$$\mathcal{H}'=-\frac{1}{C}P_\phi p_\phi-\frac{(P_\phi\cos\theta-P_\psi)(p_\phi\cos\theta-p_\psi)}{A\sin^2\theta},$$

$$\mathcal{H}''=-\frac{\epsilon H}{2c}\left[\frac{b^2+\frac{1}{2}a^2}{A}P_\psi+\cos\theta\left(\frac{a^2}{C}-\frac{b^2+\frac{1}{2}a^2}{A}\right)P_\phi\right]+\frac{eH}{2mc}p_\psi.$$

The transcription of Eq. (5) into the quantum-mechanical expression is conveniently done by noting $P_{Q_k}=-i\hbar\partial/\partial Q_k$, where $Q_k=\theta$, ϕ, or ψ, and $\hbar=h/2\pi$,

and $\quad p_{q_k}=-i\hbar\partial/\partial q_k$, where $q_k=x'$, y', or z'. (6)

The quantities p_θ, p_ϕ, and p_ψ, known as the "internal" angular momenta, will remain unchanged.

The solution of $\mathcal{H}\Psi=W\Psi$, where

$$\Psi=\Psi(\theta,\phi,\psi,x',y',z'),$$

is readily obtained by the perturbation method. The solution for $\mathcal{H}_0\Psi_0=W_0\Psi_0$ may be assumed to be $\Psi_0=\Theta(\theta)e^{iK\phi}e^{iM\psi}f(x',y',z')$. The first-order perturbation energy W_1 in $W=W_0+W_1+W_2+\cdots$ is (retaining only the significant terms linear in H)

$$W_1=-M\hbar\frac{\epsilon H}{2c}\left[\frac{b^2+\frac{1}{2}a^2}{A}+\frac{K^2}{J(J+1)}\left(\frac{a^2}{C}-\frac{b^2+\frac{1}{2}a^2}{A}\right)\right]+\frac{MK}{J(J+1)}\frac{eH}{2mc}(0|p_\phi|0), \quad (7)$$

where

J = total angular momentum quantum number of the molecule,
K = rotational quantum number along figure axis,
M = magnetic quantum number.

The bracketed quantity on the right-hand side of Eq. (7) represents the contribution of the bound charge ϵ to the magnetic perturbation energy. This is the result obtained by Condon for a charge rigidly attached to a symmetric rotor.[1] The second term would be the contribution due to the orbital motion of the electron, if the matrix element $(0|p_\phi|0)$ were not zero. However, for a molecule containing many electrons, it is this quantity summed over all the electrons that is of importance. This sum total is known to be zero[12] if the polyatomic molecule is in the $^1\Sigma$-state, which is the case most frequently encountered. Consequently, the second term in Eq. (7) will be dropped for the present discussion of molecules in the $^1\Sigma$-state.

The second-order perturbation gives an energy change which is, on neglecting terms in H^2,

$$W_2=M\hbar\frac{eH}{mc}\sum_{n\neq 0}\frac{1}{(E_n-E_0)}\left[\frac{\alpha_{n0}{}^2}{A}+\frac{K^2}{J(J+1)}\left\{\frac{\gamma_{n0}{}^2}{C}-\frac{\alpha_{n0}{}^2}{A}\right\}\right], \quad (8)$$

where

$\alpha_{n0}{}^2=\frac{1}{2}\{|(n|L_{x'}|0)|^2+|(n|L_{y'}|0)|^2\}$,
$\gamma_{n0}{}^2=|(n|L_{z'}|0)|^2$,
$L_{x'}=y'p_{z'}-z'p_{y'}$,
$L_{y'}=z'p_{x'}-x'p_{z'}$,
$L_{z'}=x'p_{y'}-y'p_{x'}=p_\phi$,
E_0 = energy of the electronic ground state, and
E_n = energy of the nth excited state.

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[12] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, 1932), p. 274.

Equation (8) represents the contribution from a nonrigid electron in a symmetric top molecule to the magnetic perturbation energy. When applied to the special case of a linear or diatomic molecule, Eq. (8) is reduced to a form in exact agreement with that derived by Wick.[3,11]

For a molecule, it is necessary to sum W_1 in Eq. (7) over all bound charges (nuclear charges and bound electrons) and W_2 in Eq. (8) for all "free" electrons. Let

$$W_H=\sum_i^N (W_1)_i+\sum_j^n (W_2)_j.$$

W_H represents the total contribution of all charged particles in the molecule to the part of the magnetic perturbation energy that is proportional to the magnetic field. Such a procedure is valid only under the assumption that each particle behaves as if it is in a field specified by its space coordinates alone. Then it is possible to express the result in terms of the magnetic moment of the molecule through the equation $W_H=-\mu_H H$, where μ_H is the component of the magnetic moment $\boldsymbol{\mu}$ along the magnetic field. Or the result can be even more conveniently expressed in terms of the g-factor in the equation $W_H=-Mg\mu_0 H$, where M is, again, the magnetic quantum number, μ_0 is equal to $e\hbar/2M_p c$ (the nuclear magneton in terms of the proton mass M_p). The final expression for the g-factor is

$$g=\sum_i \frac{\epsilon_i}{e}\left[\frac{b_i^2+\frac{1}{2}a_i^2}{\mathcal{A}}+\frac{K^2}{J(J+1)}\left(\frac{a_i^2}{\mathcal{C}}-\frac{b_i^2+\frac{1}{2}a_i^2}{\mathcal{A}}\right)\right]$$

$$-\frac{2}{m}\sum_j \sum_{n\neq 0}\frac{1}{(E_n-E_0)_j}\left[\frac{\alpha_{n0}{}^2}{\mathcal{A}}+\frac{K^2}{J(J+1)}\left(\frac{\gamma_{n0}{}^2}{\mathcal{C}}-\frac{\alpha_{n0}{}^2}{\mathcal{A}}\right)\right]_j, \quad (9)$$

where $\mathcal{A}=A/M_p$ and $\mathcal{C}=C/M_p$.

VI. DISCUSSION OF RESULTS

Although it is seen from the preceding section that it is theoretically possible to calculate the rotational magnetic moment of any linear or symmetric molecule, yet, in practice, only the contribution from the nuclear charges can be handled without difficulty. It is true that a reasonably good approximation should be possible for the effect of inner shell electrons which are tightly bound to an atom in the molecule; but the problem concerning the loosely bound electrons cannot be solved quantitatively unless one has extensive knowledge concerning the electronic wave functions. As such knowledge is still lacking for the molecules under consideration, only a qualitative discussion of the experimental results will be made.

There is, in general, no apparent contradiction between the theory and experiment as regards the order of magnitude of the molecular rotational magnetic moment and its dependence upon the parameters such as the moments of inertia, charge distribution, internal angular velocity, and rotational quantum numbers. According to the theory, the nuclear charges always contribute to a positive g-factor, whose value ranges from about unity for molecules made up of light atoms to approximately one-half for molecules made up of medium heavy atoms. This is primarily due to the smaller charge-to-mass ratio of the heavier nuclei for comparable internuclear distances. This trend of generally descending g-factor for heavier molecules is quite apparent from the experimental data. The theory further asserts that the electronic contribution to the g-factor is a variable quantity depending principally upon the interaction between the electron and the electric field due to the rest of the molecule. If the electron is very tightly bound to the molecule, then its effect could amost completely compensate that of an equal and opposite charge in the neighboring nucleus. If the charge distribution is farther away from the center of mass than the corresponding nuclear charge, the net g-factor could be negative. Experimentally, the linear molecules N_2O and OCS have g-factors which are respectively about seven and seventeen times smaller than the nuclear contributions. The effect of bound charges is evidently very large in both cases. In fact, there is some grounds for believing that the g-factor of OCS may be negative from some recent data on the OCS[33] Zeeman spectra.

If, however, an electron is loosely bound in the molecule, the theory predicts, as first pointed out by Wick, a considerably smaller effect for its magnetic contribution relative to the effect of the nuclear charges. The electron is, to use a physical picture, "slipping" behind the rigid rotation of the nuclei. The slip could be one hundred percent if the nondiagonal matrix elements of $L_{x'}$, $L_{y'}$, and $L_{z'}$ were all zero for a symmetric top molecule. Under this condition, the nuclear charges would produce their full effects in the rotational moment. While in practice such complete slip has never been known to exist in a molecule, the case of the H_2 molecule comes remarkably close to the condition. In the present experiment, the g-factors of H_2O, HDO, and NH_3 have been found to be large. To interpret this result as due to a rigid rotation of electrons would necessitate some distribution of electronic charges abnormally close to the center of mass. It seems much more plausible to picture the electrons associated with the hydrogen atoms in these molecules as being similar to those in the hydrogen molecule. Wick's interpretation of nonrigid rotation of electrons is thus supported by the present evidence.

The theory is also explicit concerning the dependence of the rotational g-factor on the rotational quantum numbers for a symmetric top molecule. The available experimental evidence cannot be said to have established this dependence unambiguously. The only symmetric top molecule dealt with here is the NH_3 molecule. It has just been shown that the nuclear charge rotation is the principal contributor to the magnetic moment because of the electronic slippage. Calculation shows that the coefficient of the $K^2/J(J+1)$ term in the first summation in Eq. (9) is indeed very small, thus making the g-factor essentially independent of the quantum numbers. However, this situation should be regarded as somewhat accidental. In a more general case, a dependence of the g-factor on rotational quantum numbers is to be expected. The case of the water molecule, discussed in Sec. IV, indirectly supports this viewpoint.

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Radioactivities of Ru^{105}, Rh^{105}, Br^{84}, and Br^{83}

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A lens spectrometer was used to study the disintegrations of Ru^{105} (4.5 hr), Rh^{105} (36.2 hr), Br^{84} (32 min), and Br^{83} (2.4 hr). Ru^{105} emits a simple beta-spectrum with an end-point energy of 1.150±0.006 Mev. This is followed by a 0.726-Mev gamma-ray to a metastable level in Rh^{105}. The decay to the ground state of Rh^{105} proceeds with a gamma-ray of about 0.1 Mev, with a half-life of 45 seconds. The ground state of Rh^{105} emits a simple beta-spectrum of 0.570±0.005 Mev. No gamma-ray appears to be associated with this decay. Br^{84} emits a complex beta-spectrum which can be resolved into at least four groups with end points and relative intensities of 4.679 Mev (40 percent), 3.56 Mev (9 percent), 2.53 Mev (16 percent), and 1.72 Mev (35 percent). The 4.679-Mev group, which goes directly to the ground state of Kr^{84}, does not have a forbidden spectrum shape. It is suggested that the 32-minute half-life may be associated with an isomeric level above the ground state of Br^{84}. The decay of Br^{83} consists of a single beta-ray group with a maximum energy of 0.940±0.010 Mev.

I. INTRODUCTION

THE availability of a large magnetic lens spectrometer, located close to a nuclear reactor, suggested the possibility of a more detailed investigation of the disintegration of Ru^{105} (4.5 hr), Rh^{105} (36.2 hr), Br^{84} (32 min), and Br^{83} (2.4 hr). The spectrometer measurements have been supplemented by coincidence and absorption studies.

Ru^{105} decays by negatron emission to Rh^{105}, which in turn goes to Pd^{105}. Earlier investigations,[1–3] using absorption techniques, report values for the beta-ray end point of 1.3, 1.4, and 1.5 Mev, and values for the energy of a gamma-ray of 0.7 and 0.76 Mev. The Rh^{105} activity was reported[1,2,4,5] again by absorption methods, to have a beta-ray of end-point energy between 0.5 and 0.78 Mev. A weak gamma-ray of 0.3 Mev has also been reported.[1,5]

In addition to yielding more precise values of the beta- and gamma-ray energies, the present investigation has revealed the existence of a 45-second metastable level located about 0.1 Mev above the ground state of Rh^{105}. The 0.3-Mev gamma-ray previously associated with the Rh^{105} activity was not observed. An energy level scheme for the $Ru^{105}-Rh^{105}-Pd^{105}$ transitions is suggested, which is not inconsistent with the predictions of the nuclear shell model.[6,7]

The investigation of the Br^{84} activity was instituted mainly because earlier considerations, based on the available data and on the predictions of the nuclear shell model,[6,8] suggested that the high energy beta-transition should, if it were between the ground states of Br^{84} and Kr^{84}, exhibit a spectrum shape characteristic of a forbidden transition. Earlier absorption work[9,10] reports values of 5.3 and 4.5 Mev for the maximum energy of the beta-rays. The results of the present investigation show that the Br^{84} beta-decay is complex, consisting of at least four groups. Moreover, the highest energy group, with end-point energy of 4.679±0.010 Mev is found to have an allowed shape. Since coincidence experiments indicate that this transition is directly to the ground state of Kr^{84}, the absence of a forbidden shape is inconsistent with what appear to be very reasonable predictions of the nuclear shell model.

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