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Zeeman Effect in Rotational Spectra of Asymmetric-Rotor Molecules*

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The theory of rotational molecular magnetic moments is applied to the study of the Zeeman effect in microwave rotational spectra of asymmetric-rotor molecules. Measurements on absorption lines of H_2O, D_2O, and HDO are used to verify the theory, and the gyromagnetic tensors associated with these molecules are deduced. A discussion of electronic perturbation of rotational energy levels is appended.

I. INTRODUCTION

If a $^1\Sigma$-molecule, possessing neither intrinsic spin nor orbital electronic angular momentum, is placed in an external magnetic field, it is well known that the molecule interacts with the field, since there exists in the molecule a rotation-induced magnetic moment. The earliest experiments on rotational molecular magnetic moments were performed by Frisch and Stern[1] and Estermann and Stern[2] on the hydrogen molecule, and their results were explained theoretically by Wick.[3,4] The more refined techniques of Rabi, Millman, Kusch, and Zacharias[5] were extended to isotopic modifications of the hydrogen molecule by Ramsey.[6] In the microwave region the Zeeman effect has been studied for the special cases of linear- and symmetric-rotor molecules by Eshbach and Strandberg,[7] and Jen.[8] Some studies have also been made on asymmetric-rotor molecules,[8] but the existing data are insufficient to verify a theory for this general case. The present work concerns itself with the latter problem: The theory of the Zeeman effect in asymmetric-rotor molecules is given, and measurements made on microwave absorption spectra of the isotopic water molecules H_2O, HDO, and D_2O are used to verify the theory.

The notation and conventions used are those appearing in the King, Hainer, and Cross series of papers on the asymmetric rotor[9] in which an exhaustive treatment of much of the rigid-rotor theory involved in the following work is given.

II. THEORY

We are concerned with the first-order Zeeman effect only, for which the perturbation energy is well known. For a given magnetic moment having a component m_Z along H, the energy is given by

$$E_m^{(1)}=-(J,\tau,M|m_Z|J,\tau,M)H, \tag{1}$$

where J, τ, M are the quantum indices for the representation in which the rotational energy is diagonal.

A theory of the rotational magnetic moment of a general polyatomic $^1\Sigma$-molecule has been given by Eshbach and Strandberg.[7] The necessary apparatus for computing the Zeeman effect for asymmetric-rotor molecules is given in their paper; therefore, only a brief summary of their results will be given.

It was shown in their paper that if one starts with the defining equation for the magnetic moment of a system of charged particles,

$$\mathbf{m}=\frac{1}{2c}\sum_i e_i(\mathbf{r}_i\times\mathbf{v}_i), \tag{2}$$

e_i, $\mathbf{r}_i$, and $\mathbf{v}_i$ being charge, position, and velocity of the ith particle, the gth component of the magnetic moment in the molecule-fixed coordinate system can be expressed in terms of the angular momenta $P_{g'}$ and a quantity $G_{gg'}$ whose product with the g'th moment of inertia, $I_{g'}G_{gg'}$, transforms like a tensor under rotation:

$$m_g=\tfrac{1}{2}\sum_{g'}(G_{gg'}+G_{gg'}^*)P_{g'}. \tag{3}$$

$G_{gg'}$ is expressible as a sum of two parts, a nuclear contribution $G_{gg'}'$ and an electronic contribution $G_{gg'}''$ which can be more explicitly written

$$G_{gg'}'=G_{gg'}'^*=\frac{1}{2cI_{g'}}\sum_k e_k(|r_k|^2\delta_{gg'}-x_{kg}x_{kg'}), \tag{4a}$$

$$G_{gg'}''=-\frac{e}{mcI_{g'}}\sum_n{}'\frac{(0|L_g|n)(n|L_{g'})0)}{E_n-E_0}, \tag{4b}$$

$$G_{gg'}''^*=-\frac{e}{mcI_{g'}}\sum_n{}'\frac{(0|L_{g'}|n)(n|L_g|0)}{E_n-E_0}. \tag{4c}$$

In these expressions, e_k and r_k are charge and position of the kth nucleus (coordinates x_{kg}) in the molecule-fixed coordinate system, while $(0|L_g|n)$ and the like are matrix elements for the gth component of electronic angular momentum connecting the ground and nth electronic states, of energy E_0 and E_n, respectively. The

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

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

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

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

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

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

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

[8] C. K. Jen, Phys. Rev. **81**, 197 (1951); R. F. Schwartz, Doctoral thesis, Radcliffe College, 1952 (unpublished).

[9] King, Hainer and Cross, J. Chem. Phys. **11**, 27 (1943); **12**, 210 (1944).

nuclear contribution is simply that of a rigid system of rotating charges, while the electronic contribution is more complicated. This is not surprising, since the electrons are not rigidly fixed to the nuclear framework, but can precess more or less freely, subject only to the internal fields of the molecule. The net result is that the nuclear contribution is largely canceled by the precession of the electrons, a relatively small contribution remaining in most cases because not all of the electronic precession is free.

It was shown further that by utilizing the rigid-rotor direction-cosine transformations from the molecule-fixed to the space-fixed coordinate system, it is possible to express the Fth space-fixed component of the magnetic moment in terms of the $G_{gg'}$, the angular momentum matrices P_g, and the direction-cosine matrices Φ_{Fg}:

$$m_F=\tfrac{1}{2}\sum_g\sum_{g'}(G_{gg'}P_{g'}\Phi_{Fg}+G_{gg'}{}^*\Phi_{Fg}P_{g'}). \tag{5}$$

The matrix elements for this expression have been given in reference 7. In the usual J, K, M representation, the nonzero elements are $(J, K, M|J, K, M)$, $(J, K, M\mid J, K\pm 1, M)$, $(J, K, M\mid J, K\pm 2, M)$, $(J, K, M|J\pm1, K, M)$, $(J, K, M|J\pm1, K\pm1, M)$ and $(J, K, M|J\pm1, K\pm2, M)$. For the first-order Zeeman effect, we require only the diagonal elements in the J, τ, M representation, and consequently certain simplifications can be made.

The energy for an unperturbed rigid rotor can be written

$$E=\tfrac{1}{2}(a+c)J(J+1)+\tfrac{1}{2}(a-c)E(\kappa), \tag{6}$$

where

$$\kappa=(2b-a-c)/(a-c),$$
$$a=\hbar^2/2I_a,\quad b=\hbar^2/2I_b,\quad c=\hbar^2/2I_c.$$

$I_a\leqslant I_b\leqslant I_c$ are moments of inertia along principal axes in the molecule. In the J, K, M representation, the reduced energy, $E(\tau)$, possesses not only diagonal elements but $(K|K\pm2)$ elements as well. The Wang symmetrizing transformation factors this matrix into four submatrices, each of which is then diagonalized. If the magnetic perturbation is included, only the diagonal and $(J, K, M|J, K\pm2, M)$ terms of m_Z will enter in first order. The other terms will enter in second and higher order, but in most cases the perturbation energy for magnetic fields of a few thousand gauss is so small compared to the separation of the rotational energy levels that their effect is negligible.

When the Wang transformation is applied, the remaining elements are further simplified, with only the diagonal terms of the gyromagnetic tensor contributing:

$$(J, K, M|m_Z|J, K, M)=\mu_0M\left\{\frac{g_{xx}+g_{yy}}{2}+\frac{K^2}{J(J+1)}\left[g_{zz}-\frac{g_{xx}+g_{yy}}{2}\right]\right\}, \tag{7a}$$

$$(J, K, M|m_Z|J, K+2, M)=\mu_0M\frac{\{[J(J+1)-K(K+1)][J(J+1)-(K+1)(K+2)]\}^{\frac{1}{2}}}{4J(J+1)}[g_{yy}-g_{xx}], \tag{7b}$$

where $g_{ij}=\hbar G_{ij}/\mu_0$, μ_0 being the nuclear magneton. From the above matrix elements, it is seen that the first-order perturbation energy must be of the form

$$E_m{}^{(1)}=-\mu_0g_{\mathrm{eff}}MH. \tag{8}$$

A simple perturbation scheme, which may be extended to higher order, can be derived by differentiating the secular determinant $\|E_{ij}-\delta_{ij}E\|$ associated with the appropriate submatrix $\|E_{ij}\|$. Since, for any determinant $\|a_{ij}\|$,

$$d\|a_{ij}\|=\sum_{i,j}\frac{\partial}{\partial a_{ij}}|a_{ij}|da_{ij}=\sum_{i,j}\Delta^{ij}da_{ij},$$

where Δ^{ij} is the i,jth cofactor of $\|a_{ij}\|$, differentiation of the rigid-rotor secular determinant yields

$$\Delta^{ij}(dE_{ij}-\delta_{ij}dE)=0.$$

We now let dE equal the perturbation energy $E_m{}^{(1)}$, and set $dE_{ij}=H(m_Z)_{ij}$, the matrix elements of which have been given in Eqs. (7a, b). After rearranging terms,

$$E_m{}^{(1)}=H\sum_{i,j}(m_Z)_{ij}\Delta^{ij}/\sum_K\Delta^{KK}, \tag{9}$$

all summations being over the indices of the submatrix appropriate to the energy level involved.

An equivalent and often more convenient formulation can be made by simplifying the basic expression (5) for m_Z. It has already been shown that only the diagonal elements of the G tensor enter in first order; so we may write, remembering that P_g commutes with Φ_{Fg},

$$(m_Z)^{(1)}=\textstyle\sum_g G_{gg}P_g\Phi_{Zg}. \tag{10}$$

The matrix elements of Φ_{Zg} diagonal in J are directly expressible in terms of those for P_g. In a representation in which the rotational energy is diagonal, we require only the diagonal elements of (m_Z), which can be written more explicitly:

$$\langle m_Z\rangle^{(1)}=\frac{M}{J(J+1)}\sum_g G_{gg}\langle P_g{}^2\rangle. \tag{11}$$

This form is convenient, since[10]

$$\langle P_g{}^2\rangle=\partial W_R/\partial\bar{g}, \tag{12}$$

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[10] J. K. Bragg and S. Golden, Phys. Rev. 75, 735 (1949).

where $\bar{g}$ is the reciprocal moment of inertia about the gth principal axis and W_R is the rotational energy. The resulting expression for $(m_Z)^{(1)}$ was given in an orally delivered paper.[11] The splitting factor may be written

$$g_{xx}=\sum_j B_{jj}g_{jj}=\frac{1}{2}\left\{1+\frac{1}{J(J+1)}\left[E(\kappa)-(\kappa+1)\frac{dE}{d\kappa}\right]\right\}g_{xx}$$

$$+\frac{1}{2}\left\{1-\frac{1}{J(J+1)}\left[E(\kappa)-(\kappa-1)\frac{dE}{d\kappa}\right]\right\}g_{yy}$$

$$+\frac{1}{2J(J+1)}\frac{dE}{d\kappa}g_{zz}. \tag{13}$$

$dE/d\kappa$ may be determined numerically, graphically (using the tables of King, Hainer, and Cross[9]), or by one of several approximate methods.[10] The derivative can also be written explicitly by utilizing a procedure similar to that used in deriving Eqs. (7a, b), in which case one obtains

$$\frac{dE}{d\kappa}=\sum_{i,j}\Delta^{ij}\frac{dE_{ij}}{d\kappa}\bigg/\sum_K \Delta^{KK}. \tag{14}$$

All summations are over the indices of the given suby matrix. The equivalence of Eq. (9) and Eq. (13) man easily be established by expanding both expressions i_j the same representation and equating coefficients of g_i-

III. AN EXAMPLE: WATER

The isotopic forms of the water molecule were chosen as a convenient series of asymmetric-rotor molecules in which the Zeeman effect might be investigated. Jen[8] has made measurements on two microwave absorption lines of HDO and on the one known line of H_2O.

The three isotopic modifications of water, H_2O, HDO, and D_2O were chosen, not only because lines and structures were known for these molecules, but also because it was felt that the three isotopic variations of the same molecule would provide a convenient check for the theory. As has been pointed out previously,[2] the product $I_{g'}G_{gg'}$ transforms like a tensor under rotation. In the molecules H_2O and D_2O, the principal axes of this tensor must coincide with the principal inertial axes because of charge symmetry, so this tensor must be diagonal for these molecules. Furthermore, it is possible to rotate coordinates to obtain the complete tensor for HDO, and since the moments of inertia are well known for all three molecules, the splitting factor g_{eff} can be calculated for all, using three parameters only. (A small correction arises from translation of the center of mass in the direction of the dipole moment, but this correction is of the order of 0.5 percent or less and can be neglected.)

The measurements were made on a slow-sweep microwave spectrograph employing Stark modulation, the output of the phase detector being recorded on an Esterline-Angus recorder. Linearly polarized microwave radiation was employed, and since the absorptions observed are all electric dipole transitions, the orientation of the wave guide with respect to the magnetic field determines the type of transition observed.

Both $\pi(\Delta M=0)$ and $\sigma(\Delta M=\pm1)$ transitions were observed. If g_1 and g_2 are the splitting factors of the lower and higher rotational levels involved in the transition, respectively, the perturbation energies, expressed as frequencies, will be

$$\upsilon_\pi=\upsilon_0-(\mu_0 M/h)(g_2-g_1)H, \tag{15a}$$

$$\upsilon_\sigma=\upsilon_\pi\mp(\mu_0/h)g_2H \quad (\text{for } \Delta M=\pm1). \tag{15b}$$

If g_1 and g_2 are equal, it is seen that there will be no splitting of the π-components, while there will be two σ-components, one on each side of the original line. If the splitting factors are unequal but the difference is not great enough to effect the resolution of the individual components, the line shapes will be distorted, and adequate interpretation of the data requires further consideration. The exact nature of the line distortion may be determined if one knows the relative intensities of the individual components, which are known to be directly proportional to the square of the direction-cosine matrix element for the transition involved.

For $\Delta J=0$ transitions, the intensities of the individual σ-components are proportional to $(J\mp M)\times(J\pm M+1)$. The resulting unresolved pattern is symmetrical about a frequency

$$\Delta\upsilon=\pm\tfrac{1}{2}(\mu_0/h)(g_1+g_2)H. \tag{16}$$

In this case, therefore, σ-Zeeman measurements yield an average value for the splitting factors of the two levels involved.

If $\Delta J=\pm1$, $\Delta M=\pm1$, we are not so fortunate, since the components are arranged in an asymmetric pattern with intensities proportional to $(J\pm M+1)(J\pm M+2)$, for example, if $\Delta J=+1$. The intensity maximum for the unresolved components has no simple interpretation, unless g_1-g_2 is also known. While it is possible, in principle, to obtain this by a process of curve fitting, it was felt that some check should be made, in the case of the single H_2O $5_{23}-6_{16}$ line. This was accomplished by observing the simultaneous Stark-Zeeman effect with parallel electric and magnetic fields. For this case, the two fields commute, and the Hamiltonian is still diagonal in M, the perturbation energy being simply the sum of the electric and magnetic contributions. The Stark effect for an asymmetric-rotor molecule is second order, and partially removes the M degeneracy, although an M^2 degeneracy remains. The Zeeman effect is first-order and, hence, removes the degeneracy completely, if the difference between g_1 and g_2 is sufficiently great. In the present case, the $M=\pm5$ π-components were resolved, and the result is

$$|g_1-g_2|=0.036\pm0.002.$$

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[11] Gokhale, Johnson, and Strandberg, Phys. Rev. **83**, 881 (1951).

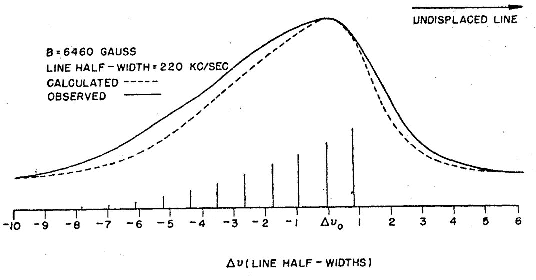

FIG. 1. Low frequency σ-components of $5_{23}-6_{16}$ H_2O line, compared with expected line shape calculated from measured value for $|g_1-g_2|$.

Since we know the line breadth, it is now possible to plot the expected line shape. A comparison of expected and observed intensity for the H_2O $5_{23}-6_{16}$ transition is shown in Fig. 1, for a typical field and line breadth. Table I includes a summary of observed data at various line breadths and fields.

The difference in g's for Q-branch ($\Delta J=0$) transitions belonging to HDO was found to be so small, in general, that no appreciable effect could be observed when the orientation of the wave guide was such as to allow π-transitions. In all cases, this means that the difference $|g_1-g_2|$ is of the order of 0.001 or less, except for the $2_{20}-2_{21}$ transition, for which no π-measurement was made. The various g factors determined for these lines appear in Table II.

The $4_{14}-3_{21}$ line of HDO exhibited a considerable difference in g factors, however, and since $\Delta J=-1$, the true values of g_1 and g_2 could not be measured directly. A direct determination of the difference $|g_1-g_2|$ was not possible, because of the unfortunate Stark pattern associated with this line.[12] The difference was predicted, by utilizing the data obtained from the other lines of HDO and H_2O. The set of linear equations for the effective g factor appears in Table III, expressed in terms of the gyromagnetic tensor of HDO. The set of g factors obtained from a least-square fit of Eqs. (a) to (g) (Table III) was used to calculate the difference $|g_1-g_2|$ for the $4_{14}-3_{21}$ transition, and the expected line shape for given magnetic field and line breadth compared with the observed line shape. As can be seen in Fig. 2, the agreement is sufficiently good to justify determination of the true g's. The results are listed in Table I.

A least-squares fit for equations (a) to (i) was then made, the results being compared with experimental splitting factors in Table III. It will be noted that all values lie well within the experimental inaccuracy, which is necessarily larger for the $\Delta J=\pm 1$ transitions because of the fitting process. The diagonal elements of the gyromagnetic tensors of H_2O, HDO, and D_2O are given in Table IV, the transformations being derived from the following values of molecular constants:

TABLE I. Results of curve fitting for unresolved absorption lines.

Molecule	Level	Line frequency (Mc/sec)	Field (gauss)	Line breadth (Mc/sec)	g_{eff}
H_2O	5_{23}	22 235.22	6050	0.212	0.684±0.012
			6390	0.205	0.696±0.012
			6100	0.290	0.678±0.012
			3400	0.220	0.698±0.015
	6_{16}		6050	0.212	0.648±0.012
			6390	0.205	0.642±0.012
			6100	0.290	0.653±0.012
			3400	0.220	0.662±0.015
HDO	4_{14}	20 460.40	6000	0.220	0.453±0.010
			6050	0.252	0.453±0.010
			3400	0.195	0.441±0.015
	3_{21}		6000	0.220	0.496±0.010
			6050	0.252	0.495±0.010
			3400	0.195	0.485±0.015
	6_{24}[a]	26 880.40	6100	0.446	0.449±0.012
	7_{17}[a]		6100	0.446	0.449±0.012
D_2O	2_{20}	10 919.44	4010	0.252	0.350±0.010
			3850	0.296	0.343±0.010
	3_{13}		4010	0.252	0.339±0.010
			3850	0.296	0.332±0.010

[a] Identification not certain

H_2O:[13] $\kappa=-0.436$, $a=27.33\ \text{cm}^{-1}$, $b=14.57\ \text{cm}^{-1}$, $c=9.49\ \text{cm}^{-1}$.

HDO:[12] $\kappa=-0.696$, $a=23.38\ \text{cm}^{-1}$, $b=8.97\ \text{cm}^{-1}$, $c=6.39\ \text{cm}^{-1}$.

D_2O:[14] $\kappa=-0.543$, $a=15.38\ \text{cm}^{-1}$, $b=7.25\ \text{cm}^{-1}$, $c=4.84\ \text{cm}^{-1}$.

As a third check, an extension was made to the completely deuterated molecule D_2O, one line of which was known.[15,16] From Stark-effect data, the line appeared to be the $2_{20}-3_{13}$ transition of D_2O. The frequency of the line lies well outside the range of thermally tuned klystrons and could not be measured by the slow-sweep spectrograph; hence, the conventional method in which the measurement is made visually had to be employed. The difference in g factors was again determined by a simultaneous Stark-Zeeman observation, but in this case the component of highest M, namely, 2, could not be resolved at the fields used. The line broadening was

TABLE II. Results of Zeeman measurements on Q-branch lines ($\Delta J=0$) of HDO.

Transition	Frequency (Mc/sec)	g_{eff}	$\lvert g_1-g_2\rvert$
$7_{44}-7_{43}$	8 577.7	0.477±0.005	<0.001
$2_{21}-2_{20}$	10 278.99	0.551±0.006	
$5_{33}-5_{32}$	22 307.67	0.485±0.005	<0.001

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[12] M. W. P. Strandberg, J. Chem. Phys. **17**, 901 (1949).

[13] G. Herzberg, *Molecular Structure and Molecular Spectra* (D. Van Nostrand Company, Inc., New York, 1945), Vol. 2, p. 488.

[14] Fuson, Randall, and Dennison, Phys. Rev. **56**, 982 (1939).

[15] D. W. Posener, Quarterly Progress Report, Research Laboratory of Electronics, Massachusetts Institute of Technology, p. 28, July 15, 1952 (unpublished).

[16] C. R. Beard and D. R. Bianco, J. Chem. Phys. **20**, 1488 (1952).

TABLE III. Results of least-squares fit for magnetic splitting factor, g_{eff}. (g_{aa}, g_{bb}, g_{cc} are diagonal elements of g_{ij} for HDO.)

Molecule	Level	Equation $\Sigma_j B_{jj}g_{jj}=(g_{\text{eff}})_{\text{obs}}$	Calculated g_{eff}, using best values of g_{ij}
H_2O	5_{23}	$0.0756\,g_{aa}+1.2680\,g_{bb}+0.2888\,g_{cc}=0.689\pm0.012$	0.690 (a)
	6_{16}	$0.0349\,g_{aa}+0.2414\,g_{bb}+1.2278\,g_{cc}=0.653\pm0.012$	0.658 (b)
HDO	5_{33}	$0.2972\,g_{aa}+0.3892\,g_{bb}+0.3136\,g_{cc}=0.485\pm0.005$	0.481 (c)
	5_{32}	$0.2945\,g_{aa}+0.4160\,g_{bb}+0.2895\,g_{cc}=0.485\pm0.005$	0.480 (d)
	2_{20}, 2_{21} (Av)	$0.6651\,g_{aa}+0.1878\,g_{bb}+0.1471\,g_{cc}=0.551\pm0.006$	0.555 (e)
	7_{44}	$0.2818\,g_{aa}+0.4066\,g_{bb}+0.3116\,g_{cc}=0.477\pm0.005$	0.478 (f)
	7_{43}	$0.2811\,g_{aa}+0.4137\,g_{bb}+0.3053\,g_{cc}=0.477\pm0.005$	0.478 (g)
	4_{14}	$0.0522\,g_{aa}+0.1962\,g_{bb}+0.7516\,g_{cc}=0.449\pm0.010$	0.442 (h)
	3_{21}	$0.3255\,g_{aa}+0.4352\,g_{bb}+0.2394\,g_{cc}=0.492\pm0.010$	0.485 (i)
D_2O	2_{20}	$0.6586\,g_{aa}+0.2338\,g_{bb}+0.1076\,g_{cc}=0.357\pm0.010$	0.347 (j)
	3_{13}	$0.0855\,g_{aa}+0.1898\,g_{bb}+0.7247\,g_{cc}=0.338\pm0.010$	0.336 (k)

measured, however; and for the measured line breadth, 140 kc/sec, a 6100 gauss field gave a line breadth of 240 kc/sec, which yields for the difference

$$|g_1-g_2|=0.011\pm0.004.$$

Using this difference, the necessary corrections to the observed maximum of the σ-pattern were calculated, and thus, the splitting factors for the two levels were measured. The results are shown in Table I, and compared with the least-squares fit in Table III.

From a comparison of all values of effective g factors in Table III, it can be seen that without exception all observed g's agree with the least-squares fit to within the experimental error. The magnitude of the terms in the gyromagnetic "tensor" G_{ij} is interesting, since they are somewhat larger than one would expect from a simple calculation such as that given in reference 7 for the positive limits of the rotation g factor. The order of magnitude is approximately what would be expected, however, and it will be noted that no term in G_{ij} is larger than $+0.878$, which is the observed value of g_{eff} for the hydrogen molecule. In this sense, the terms are less than the maximum positive limit, since H_2 probably represents the most extreme case.

A comment may be made concerning the use of magnetic splitting factors in identifying isotopic species in a given molecular spectrum. From the diagonal terms of the gyromagnetic tensors of H_2O, HDO, and D_2O, it is easily seen that an unambiguous assignment of a line can be made for these three molecules if g_{eff} is measured, since in the equation $g_{\text{eff}}=\sum_j B_{jj}g_{jj}$ the condition $\sum B_{jj}=1$ always holds. Consequently, since the ranges of g_{jj}'s of the respective molecules do not overlap, no two levels belonging to spectra of different modifications of water can possess the same g_{eff}. As an example, in addition to the $2_{20}-3_{21}$ D_2O line, whose identity was confirmed by this method, the line at 26 880 Mc/sec, first observed by McAfee,[17] was studied. The results were

$$|g_1-g_2|\leqslant 0.001, \quad g_2=0.449.$$

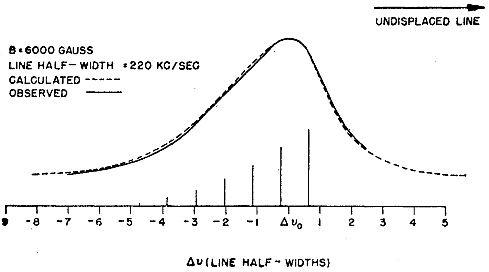

FIG. 2. Low frequency σ-components of $4_{14}-3_{21}$ HDO line, compared with calculated line shape, based on Zeeman measurements of other lines.

This precludes the possibility that the absorption is due to D_2O, which was the original identification, and requires instead that the line belong to the spectrum of HDO. Observations of the Stark effect[18] indicate that the line may be the $6_{24}-7_{17}$ transition in HDO, an identification which is consistent with the Zeeman data.

APPENDIX. CONTRIBUTION OF ELECTRONS TO MOLECULAR ROTATIONAL ENERGY

It seems worth while to correlate information contained in the present paper and published elsewhere,[7, 11, 19] concerning electronic effects in a rotating molecule. The resulting corrections, which are usually ignored, are small but not negligible, and should be considered.

It has been shown[11, 19] that the contribution of the electrons to the molecular rotational energy may be written

$$H^e=\sum_g\sum_{g'}\frac{P_gP_{g'}}{I_gI_{g'}}A_{gg'}, \tag{17}$$

where

$$A_{gg'}=-(mc/e)G_{gg'}{}''I_{g'}.$$

$G_{gg'}{}''$ is the electronic contribution to the molecular magnetic moment tensor, defined by Eq. (4b) of the present paper. A treatment similar to that given for the rotational magnetic moment shows that only the diagonal elements of the tensor A_{ij} will affect first-order corrections. Hence,

$$\langle H^e\rangle=\sum_g\frac{A_{gg}}{I_g{}^2}\langle P_g{}^2\rangle=-\frac{mc}{e}\sum\frac{G_{gg}{}''\langle P_g{}^2\rangle}{I_g}. \tag{18}$$

TABLE IV. Diagonal elements of g_{ij} determined by least-squares fit of equations in Table III.

Molecule	g_{aa}	g_{bb}	g_{cc}
H_2O	0.645	0.707	0.650
HDO	0.623	0.408	0.438
D_2O	0.363	0.352	0.332

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[17] K. B. McAfee, *A Study of the Absorption of Some Gases at Microwave Frequencies*, Doctoral thesis, Harvard, 1949 (unpublished).

[18] D. W. Posener, Quarterly Progress Report, Research Laboratory of Electronics, Massachusetts Institute of Technology, Jan. 15, 1953 (unpublished).

[19] H. R. Johnson and M. W. P. Strandberg, J. Chem. Phys. **20**, 687 (1952).

If atomic rather than nuclear masses are used to calculate the molecular moments of inertia, Eq. (18) may be rewritten[11, 19]

$$\langle H^e\rangle = \frac{mc}{e}\sum_g \frac{G_{gg}\langle P_g^2\rangle}{I_g}. \tag{19}$$

The fractional correction, owing to electronic precession, to the reciprocal moment of inertia I_g^{-1} is evidently $(mc/e)G_{gg}$. From an analysis of Zeeman observations, the three G_{gg}'s can be determined for the molecule considered, enabling one to calculate the electronic correction to the molecular rotational constants.

As an example of the order of magnitude of this correction, let us consider the molecule H_2O. The previously calculated values of $G_{gg'}$, Table IV, yield the following corrections to the rotational constants: A_0, 0.0049 cm^{-1}; B_0, 0.0028 cm^{-1}; C_0, 0.0017 cm^{-1}. It will be noted that these corrections are all approximately 0.02 percent, which is greater than, or of the same order of magnitude as the accuracy often assigned to rotational constants determined by microwave absorption methods.

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High Energy Gamma-Gamma Cross Section of In^{115}

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Several photonuclear reactions induced in indium by the x-rays from a 25-Mev betatron have been measured. Special attention has been given to the reaction $In^{115}(\gamma,\gamma')In^{115*}$. Applying proper corrections, it was found that this reaction has a shape similar to the shape found in the usual photonuclear reactions. This experiment shows that 1 in 7 de-excitations of an excited indium nucleus decays by γ-emission. The (γ,n) reaction in In^{115} has been measured and was found to have 0.42 Mev-barn for the integrated cross section, in good agreement with theoretical predictions. The ratio of the cross sections for production of the isomeric and ground states of In^{114} has also been studied. It was found that transitions to the isomeric state of In^{114} are highly favored, as would be expected from an analysis of the spin changes involved. The cross section for the reaction $In^{115}(\gamma,2n)In^{113*}$ has been measured and the ratio of this cross section to the (γ,n) reaction is compared with that predicted by statistical theory.

I. INTRODUCTION

An investigation of the reactions induced by photons in indium has the possibility of giving considerable information about the nature of the interaction of high energy photons with nuclei. A preliminary investigation of the activities induced in indium by an irradiation with a betatron[1] showed that it is possible to resolve the contributions from the following reactions:

	Reaction	Half-life
(a)	$In^{115}(\gamma,n)In^{114*}$	50 days
(b)	$In^{115}(\gamma,n)In^{114}$	72 sec
(c)	$In^{115}(\gamma,\gamma')In^{115*}$	4.5 hours
(d)	$In^{115}(\gamma,2n)In^{113*}$	1.7 hours

Besides these half-lives a strong activity from neutron capture in In^{115} (half-life = 54 min) was observed. Other activities which perhaps could be expected, such as $In^{113}(\gamma,np)Cd^{111}$—49-min half-life—and the end products of (γ,n) reactions in In^{113} have not been observed or could not be separated by counting; the first alternative is probably correct since In^{113} is only a 4.2 percent isotope.

A careful investigation of the activities listed above, as a function of the maximum energy of the betatron, can give information on four kinds of problems.

1. Characteristics of the (γ,n) processes in In^{115}.
2. Ratio of the cross section for production of the ground and isomeric states of In^{115}.
3. (γ,γ') reaction in In^{115} by production of the isomeric state in In^{115}.
4. The ratio between the $(\gamma,2n)$ and (γ,n) reactions in In^{115} and an analysis of this ratio in the light of statistical theory of nuclei.

The ratio of the cross sections for production of the ground and isomeric states is of special interest, since in the two cases previously investigated[2,3] the parent nucleus had small spin whereas in this case the parent nucleus In^{115} has a large spin (9/2). The spins of the ground and isomeric states of the residual nucleus are 1 and 5, respectively.

The (γ,γ') reaction in In^{115} which is studied by detection of the isomeric state in this isotope is of special interest since the excitation function for this

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