the parametric function then set equal to zero. We find that

$$W_N(\mathbf{r}^N) = W_{N'}(\mathbf{r}^{N'})W_{N''}(\mathbf{r}^{N''}) + U_N(\mathbf{r}^N)$$
$$+ \text{other terms}, \quad (A.2)$$

where the "other terms" in (A.2) consist of certain products containing functions U_n with $n < N$. At least one U_n in each product has arguments drawn from both the groups $\mathbf{r}^{N'}$ and $\mathbf{r}^{N''}$. If $\mathbf{r}^{N'}$ and $\mathbf{r}^{N''}$ are now isolated from each other and the inductive hypothesis $P(N)$ is invoked, the "other terms" vanish. The validity of $P(N+1)$ follows immediately.

The extension of this proof to cases of lower symmetry requires only notational changes.

Microwave Spectra of the Tl, In, and Ga Monohalides*

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(Received July 2, 1957)

A high-temperature spectrometer has been used to study the rotational spectra of the gallium, indium, and thallium monohalides. The molecular constants are

	B_e (Mc/sec)	α_e (Mc/sec)	r_e (A)
$Tl^{205}F$	6689.97 ± 0.06	44.97 ± 0.08	2.0844 ± 0.0001
$Tl^{205}Cl^{35}$	2740.05 ± 0.02	11.90 ± 0.01	2.4848 ± 0.0001
$Tl^{205}Br^{79}$	1293.89 ± 0.01	3.927 ± 0.005	2.6181 ± 0.0001
$Tl^{205}I^{127}$	814.479 ± 0.015	1.985 ± 0.005	2.8135 ± 0.0001
$In^{115}Cl^{35}$	3269.47 ± 0.14	15.35 ± 0.15	2.4011 ± 0.0001
$In^{115}Br^{79}$	1670.14 ± 0.02	5.706 ± 0.01	2.5432 ± 0.0001
$In^{115}I^{127}$	1104.95 ± 0.45	3.117 ± 0.015	2.7539 ± 0.0009
$Ga^{69}Cl^{35}$	4493.73 ± 0.19	23.27 ± 0.12	2.2017 ± 0.0001
$Ga^{69}Br^{79}$	2481.99 ± 0.04	9.74 ± 0.03	2.3525 ± 0.0001
$Ga^{69}I^{127}$	1706.86 ± 0.04	5.67 ± 0.15	2.5747 ± 0.0001

The quadrupole coupling constants determined in the present experiment are related to the molecular bond and the role of s-p hybridization in the molecular bond is discussed.

INTRODUCTION

MICROWAVE spectroscopy of molecules in the gaseous state has provided a large amount of accurate information about molecular structure.[1,2] Of all the molecules studied, the diatomic one is the easiest to interpret in terms of a theoretical model. The number of diatomic molecules which can be studied by conventional microwave spectroscopy is severely limited by the small fraction of such molecules in the gaseous state at room temperature. The development of the high-temperature spectrometer[3,4] made it possible to observe the pure rotation spectra of most of the alkali halides[5] and its use has been extended to the molecules reported here.

Diatomic molecules in the gaseous state have been investigated by the techniques of electron diffraction,[6,7] molecular-beam magnetic and electric resonance,[8-10] and microwave spectroscopy. Electron diffraction experiments yielded internuclear distances but with an accuracy far below present standards. Early magnetic-resonance experiments gave information concerning the nuclear magnetic moments and the interaction of the electric quadrupole moment with the rotating molecule. Electric-resonance experiments have been of two kinds. In the first of these, $\Delta m_j = \pm 1$ transitions are observed; these yield, in addition to the molecular hyperfine structure, information concerning the electric dipole moment and moment of inertia of the molecule. However, the last two quantities are not determined with

[1] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955).
[2] W. Gordy, *Microwave Spectroscopy* (John Wiley and Sons, Inc., New York, 1953).
[3] Stitch, Honig, and Townes, Rev. Sci. Instr. **25**, 759 (1954).
[4] P. A. Tate and M. W. P. Strandberg, Rev. Sci. Instr. **25**, 956 (1954).

[5] Honig, Mandel, Stitch, and Townes, Phys. Rev. **96**, 629 (1954).
[6] W. Grether, Ann. Physik **26** (1936).
[7] H. Brode, Ann. Physik **37**, 344 (1940).
[8] J. B. M. Kellogg and S. Millman, Revs. Modern Phys. **18**, 323 (1946).
[9] D. R. Hamilton, Am. J. Phys. **9**, 319 (1941).
[10] H. K. Hughes, Phys. Rev. **70**, 570 (1946).

high accuracy. The second and more recent technique[11-13] employs microwave frequencies to study pure rotational transitions and is similar in scope to the work described in this paper, although the techniques are greatly different.

With the exception of GaF and InF which involved certain experimental difficulties, experimental results on all the Tl, Ga, and In halides are given here. Values of moments of inertia, internuclear distances, vibration-rotation interaction constants, quadrupole coupling constants, and mass ratios for the Cl and Br isotopes were determined. The electric dipole moment of TlF was measured.

APPARATUS AND METHOD

The apparatus for the experiments discussed here has been thoroughly described in a previous article.[3] It consists essentially of a gold-plated nickel absorption cell enclosed in a vacuum chamber. The cell is a wave guide which can be heated to a temperature of 1000°C. A thin gold-plated nickel strip, known as a Stark plate, runs the length of the cell parallel to the broad face of the wave guide. The compound to be studied is placed inside the absorption cell which is then heated until the vapor pressure of the compound is sufficiently high to produce detectable absorptions of microwave power at the resonant frequencies. An oscillating electric field, applied between the Stark plate and the wave guide, frequency-modulates the microwave resonance, which greatly increases the sensitivity of the spectrometer. The technique of observing and measuring the spectra is the same as that employed in conventional microwave spectroscopy at room temperatures and has been described elsewhere.[14]

PREPARATION OF SAMPLE

The Tl halides are stable in both the monohalide and trihalide forms and commercial samples were available. However, the In and Ga monohalides are difficult to prepare as the trihalide salts are the most stable and common.[15] Previous work on the ultraviolet absorption spectra of the monohalides[16,17] indicated that sufficient concentration of these salts in the vapor phase could be obtained by heating the trihalide salt in the presence of an excess of the metal under vacuum. The same method worked successfully to produce InCl. The heating under vacuum was done directly in the sample chamber of the spectrometer. The spectra of

InBr and InI were observed by using commerically prepared samples of the monohalide.

Attempts were made to produce GaCl by heating GaCl₃ and Ga in the spectrometer but no spectrum was observed. The high vapor pressure of GaCl₃ necessitated working at about 100°C,[18] and the spectrometer was not designed for uniform temperature control at such low temperatures. In addition, GaCl is a light molecule and a range of over 5000 Mc/sec had to be searched in order to cover all possible frequencies. Thus, GaCl might have been produced but not at a combination of frequency and temperature which we investigated.

Ga and In have similar electronic configurations and chemical properties. Since GaCl has a greater binding energy than InCl,[19] it appeared possible to produce GaCl by heating InCl₃ in the presence of Ga. Such a procedure was tried, once again directly in the apparatus, and the spectrum of GaCl was observed at a temperature of about 350°C. GaBr and GaI were made in the same way by heating Ga with InBr₃ and InI₃, respectively. It is not a very efficient method as the spectra of the In halides which could be seen at the same time were more intense than the spectra of the Ga halides. InF and GaF can be made in a similar manner by heating the metal in the presence of AlF₃.[20] The reaction requires a temperature in excess of 1000°C to obtain a sufficient yield for observation of the spectra and was not possible to achieve in the Columbia University spectrometer.

THEORY

A. Rotational Energy Levels

The theory of the molecular energy levels of a diatomic molecule is based upon the model of a rotating vibrator. If one assumes a Morse potential of the form[21]

$$V(r-r_e) = D[1 - e^{-\beta(r-r_e)}]^2,$$

where D is the dissociation energy, r_e is the equilibrium distance between nuclei, and β is a constant which relates the molecular vibration frequency ω_e and the dissociation energy D, then the solution of Schrödinger's equation gives the following energy level expansion:

$$(W_{J,v})/h = \omega_e(v+\tfrac{1}{2}) - \omega_e x_e(v+\tfrac{1}{2})^2 + B_e J(J+1)$$
$$- \alpha_e(v+\tfrac{1}{2})J(J+1) - D_e J^2(J+1)^2 + \cdots. \quad (1)$$

The above terms are related to the constants in the Morse potential and can be identified with the solutions of more specialized problems so that each can be given a physical significance. Since the Morse potential has three independent parameters, only three of the coef-

[11] Lee, Fabricand, Carlson, and Rabi, Phys. Rev. **91**, 1395 (1953).

[12] Fabricand, Carlson, Lee, and Rabi, Phys. Rev. **91**, 1403 (1953).

[13] Carlson, Lee, and Fabricand, Phys. Rev. **85**, 784 (1952).

[14] S. Geschwind, Ann. N. Y. Acad. Sci. **55**, 751 (1952).

[15] N. V. Sidgwick, *Chemical Elements and Their Compounds* (Oxford University Press, London, 1950).

[16] F. K. Levin and J. G. Winans, Phys. Rev. **84**, 431 (1951).

[17] H. M. Froslie and J. G. Winans, Phys. Rev. **72**, 481 (1947).

[18] D. R. Stull, Ind. Eng. Chem. **39**, 517 (1947).

[19] A. G. Gaydon, *Dissociation Energies* (Chapman and Hall, Ltd., London, 1953).

[20] D. Welti and R. F. Barrow, Proc. Phys. Soc. (London) **A65**, 629 (1952); R. F. Barrow and H. C. Rowlinson, Proc. Roy. Soc. (London) **A224**, 134 (1954).

[21] G. H. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (D. van Nostrand Company, Inc., New York, 1952), p. 101.

ficients of the quantum numbers in the energy expansion are independent. The agreement of the interrelations between the molecular constants with the experimental value of the constants is a measure of the validity of the Morse potential.

For a microwave rotational transition, $J+1 \leftarrow J$, the frequency of transition is given by

$$\nu = 2B_e(J+1) - 2\alpha_e(v+\tfrac{1}{2})(J+1)$$
$$-4D_e(J+1)^3 + \cdots. \quad (2)$$

The rotational constant B_e was not directly determined from the measured spectra. The experimentally determined quantities were the vibration-rotation interaction constant α_e and B_e' where

$$B_e' = B_e - 2D_e(J+1)^2.$$

The centrifugal stretching constant D_e is of order of 1 kc/sec and can be calculated from the relation

$$D_e = 4(B_e^3/\omega_e^2). \quad (3)$$

The vibration frequency ω_e is generally known from ultraviolet absorption spectroscopy. Since the D_e term represents a very small correction, B_e' can be used in Eq. (3) above.

B. Mass Ratios of Isotopes

Under the assumption that the potential function is the same for different isotopic substitutions in a given molecule, accurate mass ratios can be computed from the experimental data. If one denotes the two isotopic species of molecules by M_1M and M_2M, the ratio of the reduced masses is given by

$$\frac{M^{(1)}}{M^{(2)}} = \frac{B_e^{(2)}}{B_e^{(1)}} = \frac{M_1}{M_2}\left(\frac{M+M_2}{M+M_1}\right),$$

or

$$\frac{M_1}{M_2} = \frac{(M/M_2)B_e^{(2)}/B_e^{(1)}}{1+(M/M_2)-B_e^{(2)}/B_e^{(1)}}, \quad (4)$$

where M_1 and M_2 are the masses of the two isotopes; M is the mass of the other atom in the molecule. The mass ratio M/M_2 need be known only moderately accurately since it enters into both the denominator and numerator. A fractional error ϵ in this ratio will give a fractional error δ in the determination of M_1/M_2 which is

$$\delta = [(M_2-M_1)/(M+M_2)]\epsilon.$$

C. Dipole Moment

The energy levels for a diatomic molecule in an electric field have been discussed by Brouwer.[22] We have measured the electric dipole moment of TlF, a molecule without hyperfine structure. Here, J is a good quantum number, and the electric field splits the energy level into $J+1$ levels corresponding to M_J

[22] F. Brouwer, dissertation, Amsterdam, 1930 (unpublished).

values of $0, \pm 1, \cdots \pm J$. The expression for the energy levels so perturbed is the familiar quadratic Stark effect for molecules:

$$W = W_0 + \frac{\mu^2 E^2[J(J+1)-3M^2]}{2BJ(J+1)(2J-1)(2J+3)}. \quad (5)$$

For a $\Delta M = 0$ transition the frequency is

$$\nu = \nu_0 + \frac{3M^2(16J^2+32J+10)-8J(J+1)^2(J+2)}{J(J+2)(2J-1)(2J+1)(2J+3)(2J+5)}\left(\frac{\mu^2 E^2}{h^2 \nu_0}\right). \quad (6)$$

D. Hyperfine Structure

Most of the nuclei in the molecules studied here have $I \geq 1$ and, therefore, nonzero electric quadrupole moments. The interaction between the nuclear quadrupole moment and the gradient of the electric field at the nucleus is sufficient to account, within the experimental error, for all molecular hyperfine structure observed in the present experiments.

(1) Quadrupole Coupling for a Single Nucleus

In the case of TlCl, TlBr, and TlI only the halogen has a nonzero electric quadrupole moment and the Hamiltonian for the interaction is

$$H = \frac{-eqQ}{2I(2I-1)} \frac{[3(\mathbf{I}\cdot\mathbf{J})^2+\tfrac{3}{2}\mathbf{I}\cdot\mathbf{J}-I^2J^2]}{(2J-1)(2J+3)}, \quad (7)$$

where Q, the quadrupole moment for the particular nucleus concerned is given by

$$Q = \frac{1}{e}\int \rho(3z_n^2-r^2)dxdydz,$$

and q is defined as $(d^2V/dz^2)_{Av}$ at the same nucleus. The z direction lies along the internuclear axis and V is the electrostatic potential due to all charges outside a small sphere surrounding the nucleus.

First-order perturbation theory yields expressions for the energy levels given by

$$W = W_0 + (-eqQ)f(I,J,F),$$

$$f(I,J,F) = \frac{\tfrac{3}{4}C(C+1)-I(I+1)J(J+1)}{2I(2I-1)(2J-1)(2J+3)},$$

$$C = F(F+1)-I(I+1)-J(J+1),$$

where W_0 represents the unperturbed molecular energy level and $f(I,J,F)$ is Casimir's function,[23] which has been tabulated in several places.[1]

[23] H. B. G. Casimir, *On the Interaction between Atomic Nuclei and Electrons* (Tayler's Tweede Genootschap, L. F. Bohn, Haarlem, 1936).

Fig. 1 (InCl diagram):

InCl
J=3
I_1=9/2
I_2=3/2

J=3

F_1 =3/2 → F: 0, 1,3, 2

F_1 =15/2,5/2 → F: 9, 6,3, 2, 4, 8,7,1

F_1 =7/2 → F: 4, 3, 5, 2

F_1 =13/2 → F: 8,5, 7,6, 5,4

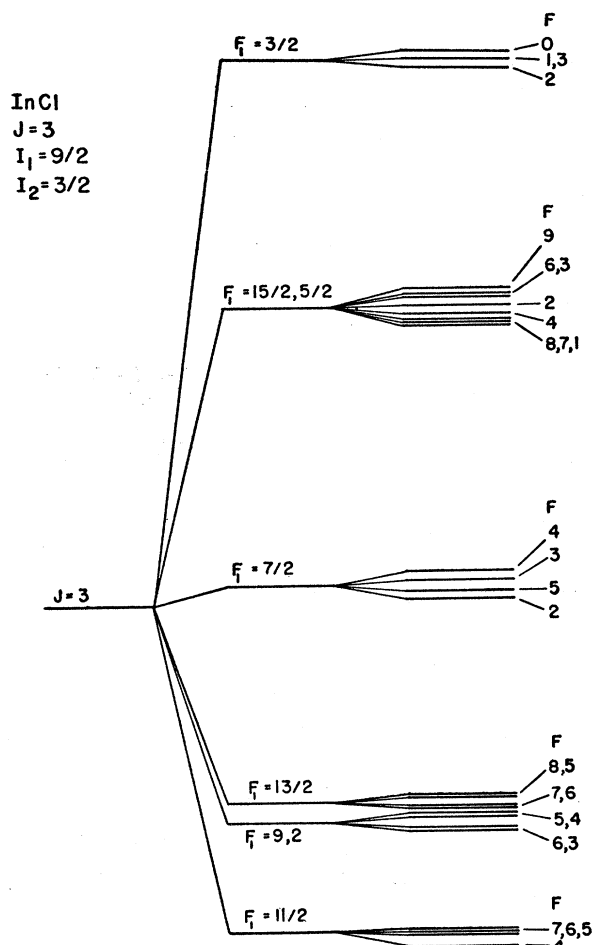F_1 =9,2 → F: 6,3

F_1 =11/2 → F: 7,6,5, 4

FIG. 1. Energy level diagram where $(eqQ)_1 \gg (eqQ)_2$. Energy levels arising from $F_1=9/2$ and $13/2$ levels are obtained by diagonalization of an energy submatrix involving these levels. The $F_1=5/2$ and $15/2$ levels are treated by ordinary perturbation theory since the matrix elements between these states are zero.

Fig. 2 (GaBr diagram):

GaBr

J=4
I_1=3/2
I_2=3/2

J=4

F_1 =5/2 → F: 3, 7, 2, 6, 4, 5

F_1 =11/2

F_1 =7/2 → F: 1, 4, 4, 3, 5

F_1 =9/2 → F: 4, 5, 2, 6, 3
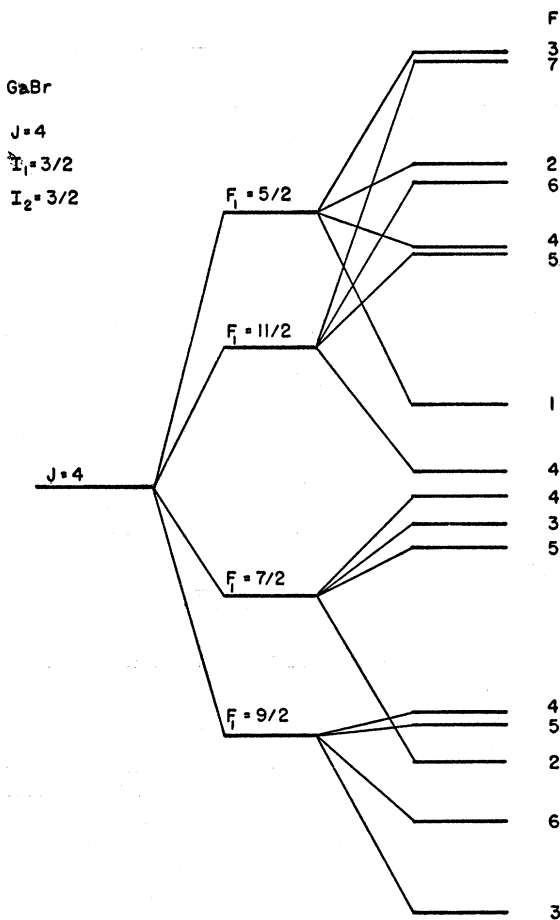
FIG. 2. Energy level diagram where $(eqQ)_1$ and $(eqQ)_2$ are both appreciable, necessitating the diagonalization of the entire energy matrix.

(2) Quadrupole Coupling for Two Nuclei

For two nuclei with angular moments I_1 and I_2 contributing to the interaction as in the Ga and In halides (except the fluorides), the Hamiltonian is a combination of functions such as expression (7),

$$H=H_1(I_1,J)+H_2(I_2,J).$$

We shall continue to represent the total angular momentum of the molecule by F and introduce F_1 as the vector sum of J and the spin I_1, and F_2 as the vector sum of J and the spin I_2.

In the $I_1JF_1I_2F$ representation the matrix elements of that part of the Hamiltonian arising from nucleus 1 are diagonal and off-diagonal elements arise from H_2. The matrix elements were calculated by the method of Bardeen and Townes.[24]

If the interaction energy of one of these, H_1, is large

[24] J. Bardeen and C. H. Townes, Phys. Rev. **73**, 97 (1948). See also, reference 1, Chap. 6.

compared to that of the other, H_2, F_1 can be considered a good quantum number and H_2 is then treated as a perturbation of the energy levels of nucleus 1 coupled to the molecule.

An energy level diagram for such a case is shown in Fig. 1 where the splitting of the $J=3$ energy level of InCl is pictured. However, in the event of degeneracies among the F_1 levels or if the separation between F_1 levels is small compared to the splitting due to H_2 it is then necessary to diagonalize the energy submatrix involving those levels. As can be seen in Fig. 1 the separation between the $F_1=9/2$ and $13/2$ levels is of the same magnitude as the splitting due to the Cl nucleus and hence these energy levels were determined by solving the secular equation. The $F_1=5/2$ and $15/2$ levels, although degenerate, can be treated by ordinary perturbation theory because the Cl quadrupole interaction has no matrix elements connecting the two levels.

If both interactions are appreciable as is the case for InBr, InI, GaCl, GaBr, and GaI, it then becomes necessary to diagonalize the complete Hamiltonian. An energy level diagram for such a case is shown in Fig. 2.

TABLE I. Molecular constants.

	B_e Mc/sec	α_e Mc/sec	D_e kc/sec	r_e angstroms	r_e (el. diff.) angstroms	eqQ Mc/sec
Tl^{205}F[a]	6689.97 ±0.06	44.975±0.08	5.91	2.0844±0.0001		
Tl^{203}F	6695.54 ±0.08					
Tl^{205}Cl^{35}	2740.05 ±0.02	11.90 ±0.01	1.1	2.4848±0.0001	2.55[b]	
Tl^{203}Cl^{35}	2743.99 ±0.03	11.96 ±0.01				
Tl^{205}Cl^{37}	2613.59 ±0.07	11.08 ±0.05				$(-15.8\pm0.5)_{Cl}$[c]
Tl^{203}Cl^{37}	2617.56 ±0.10	11.11 ±0.05				
Tl^{205}Br^{79}	1293.894±0.01	3.927±0.005		2.6181±0.0001	2.68[b]	$(130\pm10)_{Br}$
Tl^{203}Br^{79}	1297.437±0.01	3.942±0.003				
Tl^{205}Br^{81}	1270.819±0.02	3.807±0.015	0.25			
Tl^{203}Br^{81}	1274.382±0.02	3.853±0.015				
Tl^{205}I	814.479±0.015	1.985±0.005	0.11[d]	2.8135±0.0001	2.78[b]	$(-537\pm25)_{I}$
Tl^{203}I	817.570±0.015	2.003±0.001				
In^{115}Cl^{35}	3269.47 ±0.14	15.35 ±0.15	1.55	2.4011±0.0001	2.42[e]	$(-655\pm6)_{In}$, $(-18\pm2)_{Cl}$
In^{115}Br^{79}	1670.14 ±0.02	5.706±0.010	0.43	2.5432±0.0001	2.57[e]	$(-642\pm12)_{In}$, $(138\pm11)_{Br}$
In^{115}I^{127}	1104.95 ±0.45	3.117±0.015	0.19	2.7539±0.0009	2.86[e]	
Ga^{69}Cl^{35}	4493.73 ±0.19	23.27 ±0.12	2.59	2.2017±0.0001		$(-84.7\pm1.0)_{Ga}$, $(-20\pm2)_{Cl}$
Ga^{69}Br^{79}	2481.99 ±0.04	9.74 ±0.03		2.3525±0.0001		$(134\pm3)_{Br}$, $(-74\pm5)_{Ga}$
Ga^{69}Br^{81}	2453.48 ±0.03	9.613±0.02	0.74			
Ga^{71}Br^{79}	2444.65 ±0.04					
Ga^{71}Br^{81}	2416.10 ±0.04					
Ga^{69}I	1706.86 ±0.04	5.667±0.15	0.47	2.5747±0.0001		$(-549\pm31)_{I}$, $(-66\pm8)_{Ga}$
Ga^{71}I	1675.73 ±0.5	5.535±0.4				

[a] The dipole moment of TlF was found to be 7.6±0.8 Debye units.
[b] See reference 6.
[c] Lee, Carlson, Fabricand, and Rabi, Phys. Rev. 78, 340 (1950) obtained 15.79±0.04 Mc/sec.
[d] A direct measurement of the centrifugal stretching constant in the present experiment yielded a value of 0.23±0.1 kc/sec.
[e] See reference 7.

The use of second-order quadrupole interaction[25] in which the quadrupole interaction is large enough to produce a mixing of rotational states was not warranted by the experimental accuracy of the work.

(3) Intensities of Hyperfine Components

For the theoretical interpretation of the observed spectra it is necessary to know the intensities as well as the frequencies of the hyperfine components. Let us call the intensity of a molecular line with no quadrupole effects present I_0. If the quadrupole interaction of one nucleus splits this line, the intensity of each component is given by

$$I = \frac{I_0 S(I_1 J\ F_1 | I_1 J' F_1')}{\sum_{F_1} \sum_{F_1'} S(I_1 J\ F_1 | I_1 J' F_1')}, \qquad (8)$$

where

$$S(I_1 J F_1 | I_1 J' F_1')$$

is equivalent to the

$$S(SLJ | SL'J')$$

tabulated in Condon and Shortley.[26] If the second nucleus produces a quadrupole interaction, but its coupling is small compared with the coupling of the first nucleus, the tables may be again applied to find intensities of all components of the still more finely split hyperfine structure. The intensity is then given by

$$I = \frac{I_0 S(I_1 J F_1 | I_1 J' F_1') S(I_2 F_1 F | I_2 F_1' F')}{\sum_{F_1} \sum_{F_1'} \sum_{F} \sum_{F'} S(I_1 J F_1 | I_1 J' F_1') \times S(I_2 F_1 F | I_2 F_1' F')}. \qquad (9)$$

[25] J. Bardeen and C. H. Thomas, Phys. Rev. 73, 627 (1948).
[26] E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra (Cambridge University Press, New York, 1935).

If coupling of the two nuclei is not widely different, a fair approximation to the intensities may be obtained by interpolating between the two extreme cases; H_1 much greater than H_2 and H_2 much greater than H_1. This method was used for GaBr. Since Ga and Br have the same spin the intensities were given directly by expression (9).

Exact intensities may be obtained in cases of intermediate coupling or degeneracies by making use of the secular equations to obtain the correct wave function for each energy level

$$\psi(F) = \sum_{F_1} a(F_1) \psi_1(F, F_1).$$

The relative intensity for a transition from state i to state j may then be written as

$$|\sum_{F_1} \sum_{F_1'} a_i(F_1) a_j(F_1')$$
$$\times S^{\frac{1}{2}}(I_1 J F_1 | I_1 J' F_1') S^{\frac{1}{2}}(I_2 F_1 F | I_2 F_1' F')|^2. \qquad (10)$$

Careful attention must be paid to the phases (see reference 26, p. 277). This procedure was necessary for the transitions of GaI and InBr which involved near-degenerate energy levels.

RESULTS

Tables listing the measured lines of the molecules whose spectra have been observed are given in Appendix I. In this section a discussion of the observed transitions and the information derived from them is given. The molecular constants determined from the data appear in Table I.
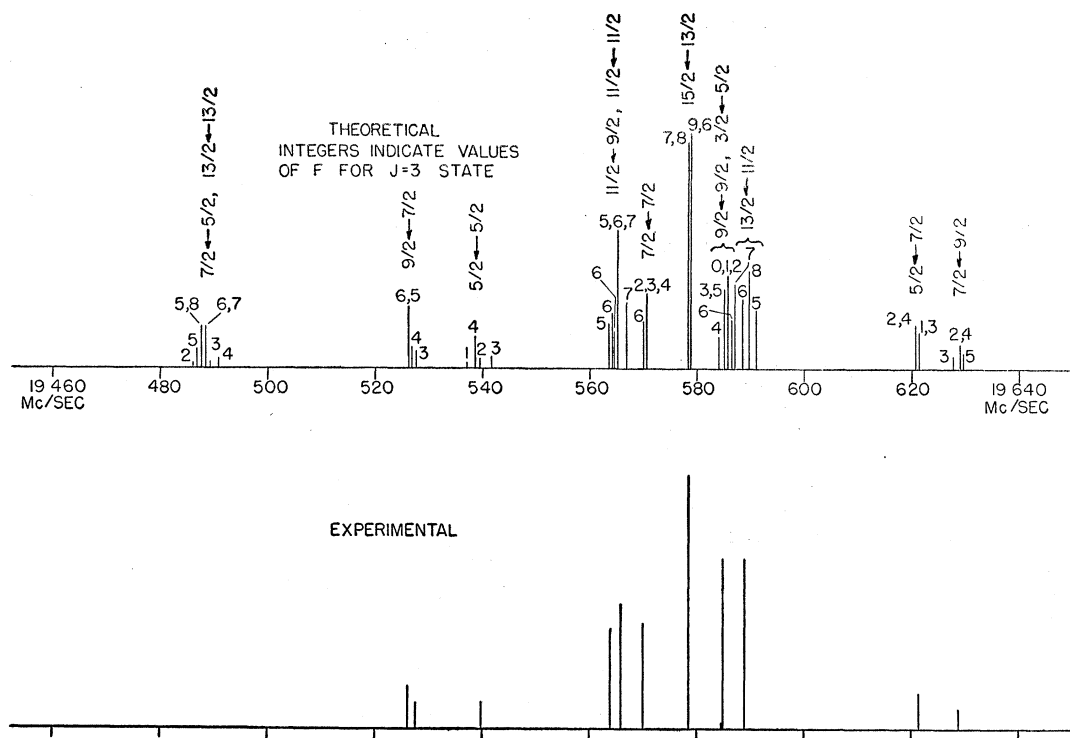
FIG. 3. Hyperfine structure of the $J=3 \leftarrow 2$ transition of In^{115}Cl^{35} (ground vibrational state) and comparison with theoretical pattern. Spins for Cl^{35} and In^{115} are 3/2 and 9/2, respectively.

TlF

The $J=2 \leftarrow 1$ transition was observed at a temperature of about 400°C. Values of B_e and α_e were determined for Tl^{205}F. A B_e value was obtained for Tl^{203}F. The electric dipole moment of Tl^{205}F was measured in the $v=0$ state.

TlCl

Lines from the $J=5 \leftarrow 4$ and $4 \leftarrow 3$ transitions for all the isotopic species of TlCl have been observed at a temperature of about 380°C and values of B_e and α_e were determined. The electric quadrupole coupling constant for Cl^{35} was calculated for the $v=0$ state of Tl^{203}Cl^{35}. The TlCl results revealed a discrepancy with the previous work on TlCl[13] where the isotope identified as Tl^{205}Cl^{35} is in reality Tl^{203}Cl^{37}. The mass ratio of the Cl isotopes was calculated.

TlBr

The $J=9 \leftarrow 8$ transition was measured at a temperature of about 400°C. From this data B_e and α_e were determined for all isotopic species. The $v=0$, $J=6 \leftarrow 5$ transition was used to determine $(eqQ)_{Br}$. The mass ratio of the Br isotopes was calculated.

TlI

The $J=17 \leftarrow 16$ transition was observed at a temperature of 400°C. Values of B_e and α_e were determined

for both Tl^{203}I and Tl^{205}I. In addition the $v=0$ lines for Tl^{205}I of the $J=10 \leftarrow 9$, $13 \leftarrow 12$ and $15 \leftarrow 14$ transitions were measured and $(eqQ)_I$ and D_e determined from this data. This value of $(eqQ)_I$ differs from a previously reported one which was based on a measurement of the $J=10 \leftarrow 9$ transition only.[27]

InCl

The $J=3 \leftarrow 2$ transition of InCl was observed at a temperature of 300°C. Values of B_e and α_e were determined for In^{115}Cl^{35}. Eleven lines were measured in the $v=0$ state and both the In^{115} and Cl^{35} electric quadrupole coupling constants were obtained.

A diagram of the theoretical and experimental spectra of the $v=0$, $J=3 \leftarrow 2$ transition is shown in Fig. 3. The $F_1=7/2 \leftarrow 5/2$ and $F_1=13/2 \leftarrow 13/2$ transitions were not observed because the strong lines of the $v=1$ hyperfine pattern obliterated them. The theoretical and experimental frequencies are given in Table II. Because of the degeneracy between the $J=2$, $F_1=9/2$ and 11/2 levels, the intensities of the transitions originating from these levels were not computed and the theoretical frequencies for these levels are missing in Table II.

The value of the Cl^{35} coupling given here differs from that reported previously.[28] The corrected value, reported

[27] M. Mandel and A. H. Barrett, Phys. Rev. 98, 1159 (1955).
[28] A. H. Barrett and M. Mandel, Phys. Rev. 99, 666 (1955).

TABLE II. Theoretical and experimental frequencies of the $v=0$, $J=3 \leftarrow 2$ transition of $In^{115}Cl^{35}$.
Experimental error is 0.20 Mc/sec.

$F_1' \leftarrow F_1$	Transition $F' \leftarrow F$	Theoretical frequency Mc/sec	Experimental frequency Mc/sec	Theoretical relative intensity
$9/2 \leftarrow 7/2$	$\begin{cases} 6 \leftarrow 5,\ 5 \leftarrow 4 \\ 4 \leftarrow 3,\ 3 \leftarrow 2 \end{cases}$	19 526.25 19 527.66	19 526.26 19 527.77	21 12
$5/2 \leftarrow 5/2$	$4 \leftarrow 4,\ 3 \leftarrow 3,\ 2 \leftarrow 2,\ 1 \leftarrow 1$	19 539.69	19 539.67	15
$11/2 \leftarrow 9/2$	$7 \leftarrow 6,\ 6 \leftarrow 5,\ 5 \leftarrow 4,\ 4 \leftarrow 3$		$\begin{cases} 19\ 563.97 \\ 19\ 565.84 \end{cases}$	
$11/2 \leftarrow 11/2$	$7 \leftarrow 7,\ 6 \leftarrow 6,\ 5 \leftarrow 5,\ 4 \leftarrow 4$			
$7/2 \leftarrow 7/2$	$5 \leftarrow 5,\ 4 \leftarrow 4,\ 3 \leftarrow 3,\ 2 \leftarrow 2$	19 570.43	19 570.25	45
$15/2 \leftarrow 13/2$	$9 \leftarrow 8,\ 8 \leftarrow 7,\ 7 \leftarrow 6,\ 6 \leftarrow 5$	19 578.41	19 578.36	100
$9/2 \leftarrow 9/2$	$6 \leftarrow 6,\ 5 \leftarrow 5,\ 4 \leftarrow 4,\ 3 \leftarrow 3$		$\begin{cases} 19\ 584.56 \\ 19\ 589.08 \end{cases}$	
$3/2 \leftarrow 5/2$	$3 \leftarrow 4,\ 2 \leftarrow 3,\ 1 \leftarrow 2,\ 0 \leftarrow 1$			
$13/2 \leftarrow 11/2$	$8 \leftarrow 7,\ 7 \leftarrow 6,\ 6 \leftarrow 5,\ 5 \leftarrow 4$			
$5/2 \leftarrow 7/2$	$4 \leftarrow 5,\ 3 \leftarrow 4,\ 2 \leftarrow 3,\ 1 \leftarrow 2$	19 621.21	19 621.36	17
$7/2 \leftarrow 9/2$	$5 \leftarrow 6,\ 4 \leftarrow 5,\ 3 \leftarrow 4,\ 2 \leftarrow 3$		19 628.75	

here, is the result of diagonalization of that portion of the Hamiltonian which enters into the $J=3$, $F_1=9/2$ levels. The original Cl^{35} coupling was based on calculations made to first order in the Cl perturbation for the $J=3$ levels, but because of the closeness of the $F_1=13/2$ level the first-order theory is not sufficient. Although the change in energy produced by diagonalization is not large, the theoretical splitting of the $F_1=9/2 \leftarrow 7/2$ transition is appreciably changed and it is this splitting on which the Cl coupling constant is based.

InBr

The $J=7 \leftarrow 6$ transition was observed at a temperature of 315°C. Values of B_e and α_e were determined for $In^{115}Br^{79}$. Sixteen lines of the $v=0$ state were measured and the In^{115} and Br^{79} quadrupole coupling constants calculated. The theoretical and experimental spectra for the $v=0$ state is shown in Fig. 4. The experimental and theoretical frequencies and intensities are given in Table III.
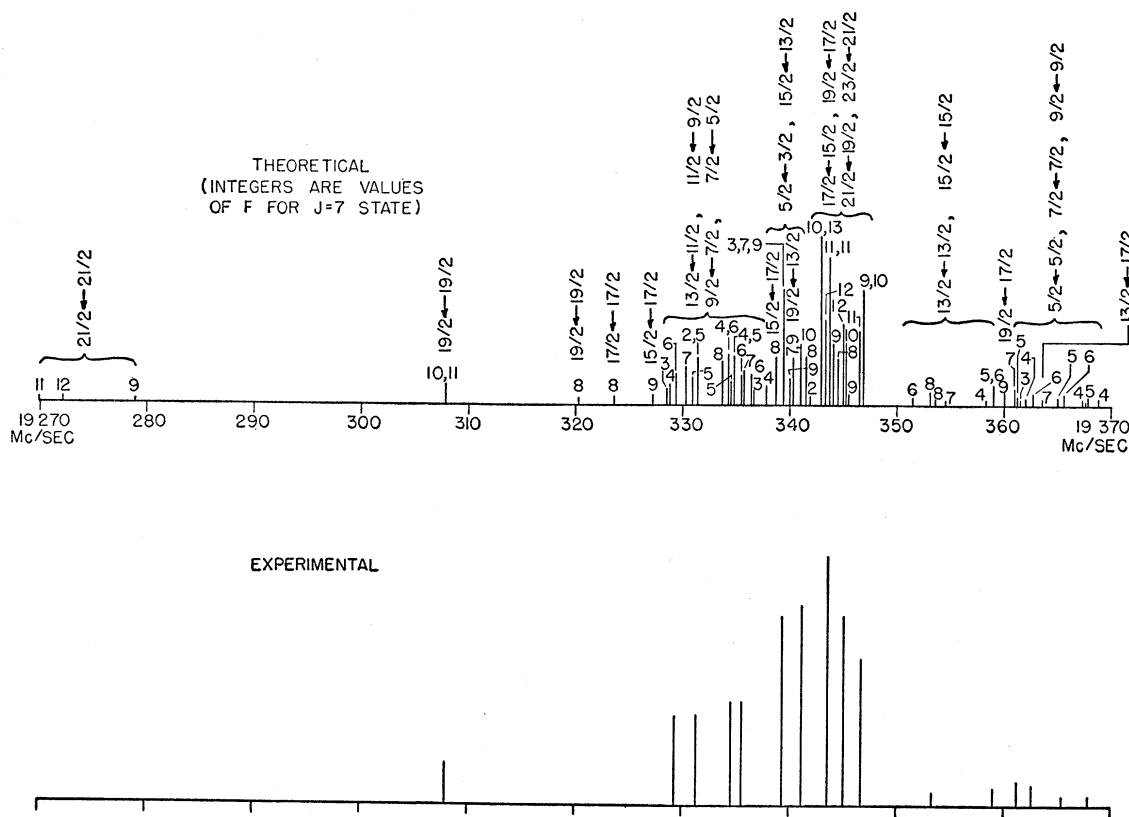

FIG. 4. Hyperfine structure of the $J=7 \leftarrow 6$ transition of $In^{115}Br^{79}$ (ground vibrational state) and comparison with theoretical pattern. Spins for Br^{79} and In^{115} are 3/2 and 9/2, respectively.

TABLE III. Theoretical and experimental frequencies of the $v=0$, $J=7 \leftarrow 6$ transition of $In^{115}Br^{79}$. Experimental error is 0.20 Mc/sec.

$F_1' \leftarrow F_1$	Transition $F' \leftarrow F$	Theoretical frequency Mc/sec	Experimental frequency Mc/sec	Theoretical relative intensity
$19/2 \leftarrow 19/2$	$11 \leftarrow 11, 10 \leftarrow 10$	23 308.17	23 308.30	9.2
$13/2 \leftarrow 11/2$	$5 \leftarrow 4$			
$11/2 \leftarrow 9/2$	$7 \leftarrow 6, 4 \leftarrow 3$	$23\ 329.22$	23 328.97	18
$9/2 \leftarrow 7/2$	$6 \leftarrow 5, 3 \leftarrow 2$	$23\ 331.38$	23 331.51	24
$7/2 \leftarrow 5/2$	$5 \leftarrow 4, 2 \leftarrow 1$			
$15/2 \leftarrow 13/2$	$6 \leftarrow 5$			
$13/2 \leftarrow 11/2$	$8 \leftarrow 7, 7 \leftarrow 6, 6 \leftarrow 5$			
$11/2 \leftarrow 9/2$	$6 \leftarrow 5, 5 \leftarrow 4$	$23\ 334.60$	23 334.50	41
$9/2 \leftarrow 7/2$	$5 \leftarrow 4, 4 \leftarrow 3$	$23\ 335.63$	23 335.55	34
$7/2 \leftarrow 5/2$	$4 \leftarrow 3, 3 \leftarrow 2$			
$5/2 \leftarrow 3/2$	$4 \leftarrow 3$			
$15/2 \leftarrow 17/2$	$8 \leftarrow 7$			
$15/2 \leftarrow 13/2$	$7 \leftarrow 6$			
$5/2 \leftarrow 3/2$	$3 \leftarrow 2, 2 \leftarrow 1, 1 \leftarrow 0$	$23\ 339.35$	23 339.12	52
$19/2 \leftarrow 13/2$	$9 \leftarrow 8, 8 \leftarrow 7$	$23\ 341.15$	23 341.01	65
$17/2 \leftarrow 15/2$	$10 \leftarrow 9, 9 \leftarrow 8$			
$15/2 \leftarrow 17/2$	$7 \leftarrow 8$			
$23/2 \leftarrow 21/2$	$13 \leftarrow 12, 12 \leftarrow 11, 11 \leftarrow 10, 10 \leftarrow 9$	$23\ 343.55$	23 343.33	100
$21/2 \leftarrow 19/2$	$12 \leftarrow 11, 11 \leftarrow 10, 10 \leftarrow 9, 9 \leftarrow 8$	$23\ 345.06$	23 345.07	66
$19/2 \leftarrow 17/2$	$11 \leftarrow 10, 10 \leftarrow 9$	$23\ 346.57$	23 346.51	57
$17/2 \leftarrow 15/2$	$8 \leftarrow 7, 9 \leftarrow 9$			
$15/2 \leftarrow 17/2$	$9 \leftarrow 8$			
$15/2 \leftarrow 15/2$	$8 \leftarrow 8, 6 \leftarrow 6$	23 353.29	23 353.40	6.0
$13/2 \leftarrow 13/2$	$8 \leftarrow 8, 7 \leftarrow 7$			
$13/2 \leftarrow 13/2$	$6 \leftarrow 6, 5 \leftarrow 5$			
$5/2 \leftarrow 5/2$	$4 \leftarrow 4$	23 358.91	23 358.74	9.2
$19/2 \leftarrow 17/2$	$9 \leftarrow 8$			
$9/2 \leftarrow 9/2$	$6 \leftarrow 6, 3 \leftarrow 3$			
$7/2 \leftarrow 7/2$	$5 \leftarrow 5$	$23\ 361.17$	23 361.35	12
$11/2 \leftarrow 11/2$	$7 \leftarrow 7, 4 \leftarrow 4$	$23\ 362.65$	23 362.70	9.8
$13/2 \leftarrow 17/2$	$7 \leftarrow 7$			
$11/2 \leftarrow 11/2$	$6 \leftarrow 6, 5 \leftarrow 5$	23 365.37	23 365.60	6.0
$9/2 \leftarrow 9/2$	$5 \leftarrow 5, 4 \leftarrow 4$	23 367.70	23 367.97	6.0
$7/2 \leftarrow 7/2$	$4 \leftarrow 4, 3 \leftarrow 3$			

InI

The $J=9 \leftarrow 8$, $10 \leftarrow 9$, and $11 \leftarrow 10$ transitions were observed at a temperature of 370°C. Accurate frequency measurements were made only on the $v=0$, 1, and 2 states of the $J=11 \leftarrow 10$ group. Since the nuclear spins of In^{115} and I^{127} are 9/2 and 5/2, respectively, abundant hyperfine splittings of the rotational transitions were observed; in fact, twenty lines were measured in the $v=0$ state alone.

From the known quadrupole coupling constants of the other Im, Ga, and Tl monohalides, it is possible to estimate the coupling constants of InI. The In quadrupole coupling constant is expected to be of the order of 650 Mc/sec and the I coupling constant about 500 Mc/sec. Thus it is clearly not possible to regard either quadrupole interaction as a small perturbation on the other and the theoretical interpretation of the spectrum would involve the complete diagonalization of the entire Hamiltonian and the calculation of all the intensities of all possible transitions, in this case up to a ΔF_1 of ± 6. The structure of InI is expected to be very similar to that of InBr and since the quadrupole coupling constants of InBr and the Ga and Tl monohalides are known, it did not seem worthwhile to carry out the extensive calculations for InI.

The calculation of the rotational constant from the observed spectrum requires a knowledge of the transition frequency in the absence of hyperfine structure. Since this could not be obtained without extensive calculations, as discussed above, the frequency was assumed to be $24\ 279 \pm 5$ Mc/sec. This frequency range includes all the strong lines of the $J=11 \leftarrow 10$ transition and the correct center frequency is certain to lie within this range because the most intense lines of a hyperfine pattern are grouped about the undisplaced frequency. The vibration-rotation interaction constant α_e was determined by taking frequency differences between corresponding lines in the different vibrational states.

GaCl

The $J=2 \leftarrow 1$ transition was observed and measured for all the isotopic species of GaCl at a temperature of 380°C. Sufficient intensity to make an interpretation of the spectra possible was present for only the $Ga^{69}Cl^{35}$ isotope. Figure 5 shows the comparison between calculated and observed spectra and Table IV lists the measured lines, theoretical frequencies and intensities for the $v=0$ state of $Ga^{69}Cl^{35}$. Values of B_e, α_e and the quadrupole coupling constants for Ga^{69} and Cl^{35} were determined.
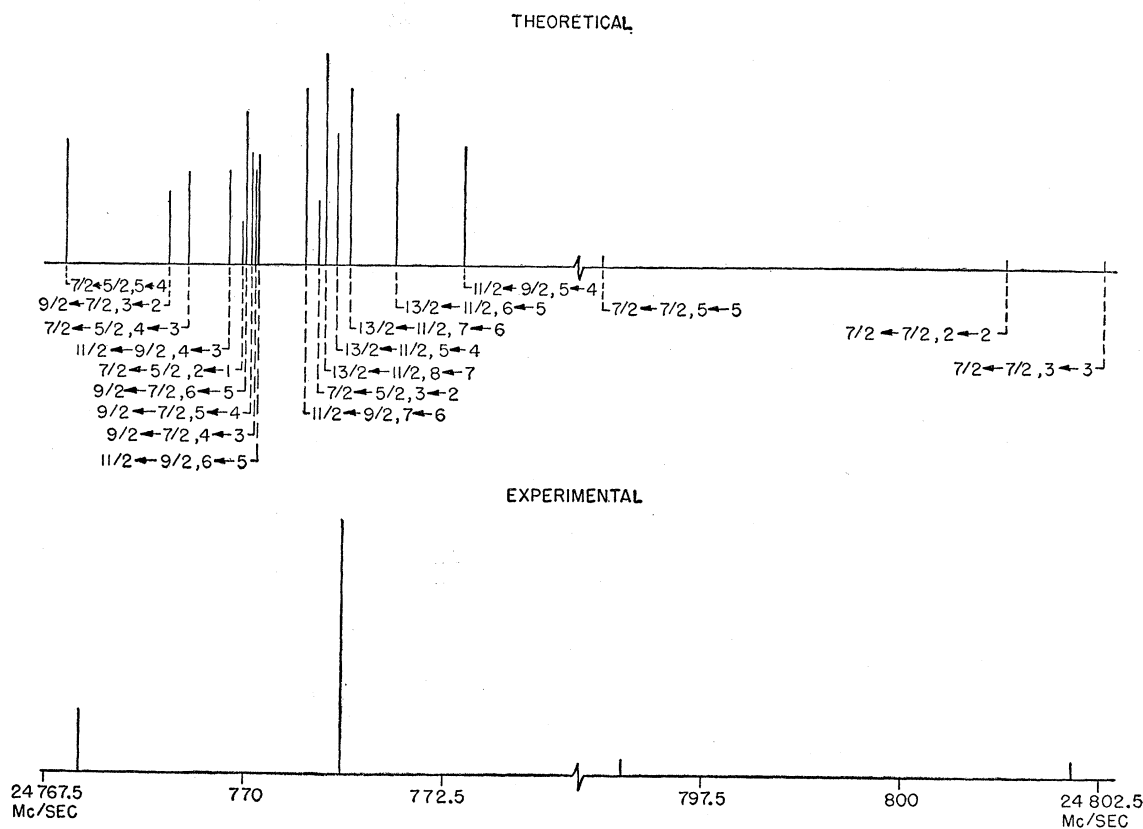
THEORETICAL

EXPERIMENTAL

FIG. 5. Hyperfine structure of the $J = 2 \leftarrow 1$ transition of $Ga^{69}Cl^{35}$ (ground vibrational state) and comparison with theoretical pattern. Spins for Ga^{69} and Cl^{35} are 3/2.

TABLE IV. Theoretical and experimental frequencies for the $v = 0$, $J = 2 \leftarrow 1$ transition of $Ga^{69}Cl^{35}$. Experimental errors are 0.20 Mc/sec unless otherwise noted.

$F_1' \leftarrow F_1$	Transition $F' \leftarrow F$	Theoretical frequency Mc/sec	Experimental frequency Mc/sec	Theoretical relative intensity
$3/2 \leftarrow 1/2$	$3 \leftarrow 2, 2 \leftarrow 2, 2 \leftarrow 1, 1 \leftarrow 1$ $\Big\}$			
$5/2 \leftarrow 5/2$	$\begin{cases} 4 \leftarrow 4, 4 \leftarrow 3, 3 \leftarrow 4, 3 \leftarrow 3, 3 \leftarrow 2 \\ 2 \leftarrow 3, 2 \leftarrow 2, 2 \leftarrow 1, 1 \leftarrow 2 \end{cases}\Big\}$	17 906.81	17 906.92	38
$1/2 \leftarrow 1/2$	$2 \leftarrow 2, 2 \leftarrow 1, 1 \leftarrow 2, 1 \leftarrow 1$ $\Big\}$			
$7/2 \leftarrow 5/2$	$4 \leftarrow 4$	17 928.37	17 928.55	50
$5/2 \leftarrow 3/2$	$3 \leftarrow 2, 2 \leftarrow 2$ $\Big\}$			
$7/2 \leftarrow 5/2$	$\begin{cases} 5 \leftarrow 4, 4 \leftarrow 3, 3 \leftarrow 3 \\ 3 \leftarrow 2, 2 \leftarrow 2, 2 \leftarrow 1 \end{cases}\Big\}$	17 930.55	17 930.57	100
$5/2 \leftarrow 3/2$	$4 \leftarrow 3, 3 \leftarrow 3, 2 \leftarrow 1, 1 \leftarrow 1, 1 \leftarrow 0$ $\Big\}$			
$3/2 \leftarrow 3/2$	$3 \leftarrow 2, 2 \leftarrow 2, 1 \leftarrow 2$	17 943.28	17 942.92±0.40	15
$3/2 \leftarrow 3/2$	$\begin{cases} 3 \leftarrow 3, 2 \leftarrow 3, 2 \leftarrow 1 \\ 1 \leftarrow 1, 1 \leftarrow 0, 0 \leftarrow 1 \end{cases}\Big\}$	17 946.52	17 946.83±0.30	33

GaBr

The $J = 5 \leftarrow 4$ transition was observed at a temperature of 360°C. Values of B_e and α_e were determined for $Ga^{69}Br^{79}$ and $Ga^{69}Br^{81}$. A B_e value was also determined for $Ga^{71}Br^{79}$ and $Ga^{71}Br^{81}$. Four lines were measured in the $v = 0$ state of $Ga^{69}Br^{79}$ and both the Ga^{69} and Br^{79} electric quadrupole coupling constants were obtained from these measurements. The observed and theoretical hyperfine patterns are shown in Fig. 6

while Table V gives the frequency and intensity of the hyperfine transitions.

GaI

Lines from the $J = 7 \leftarrow 6$ transition were measured at a temperature of about 360°. B_e and α_e were determined for both $Ga^{69}I$ and $Ga^{71}I$. The Ga^{69} and I electric quadrupole coupling constants were determined for the $v = 0$ state. Figure 7 shows the theoretical and observed hyperfine spectra. The observed frequencies and the
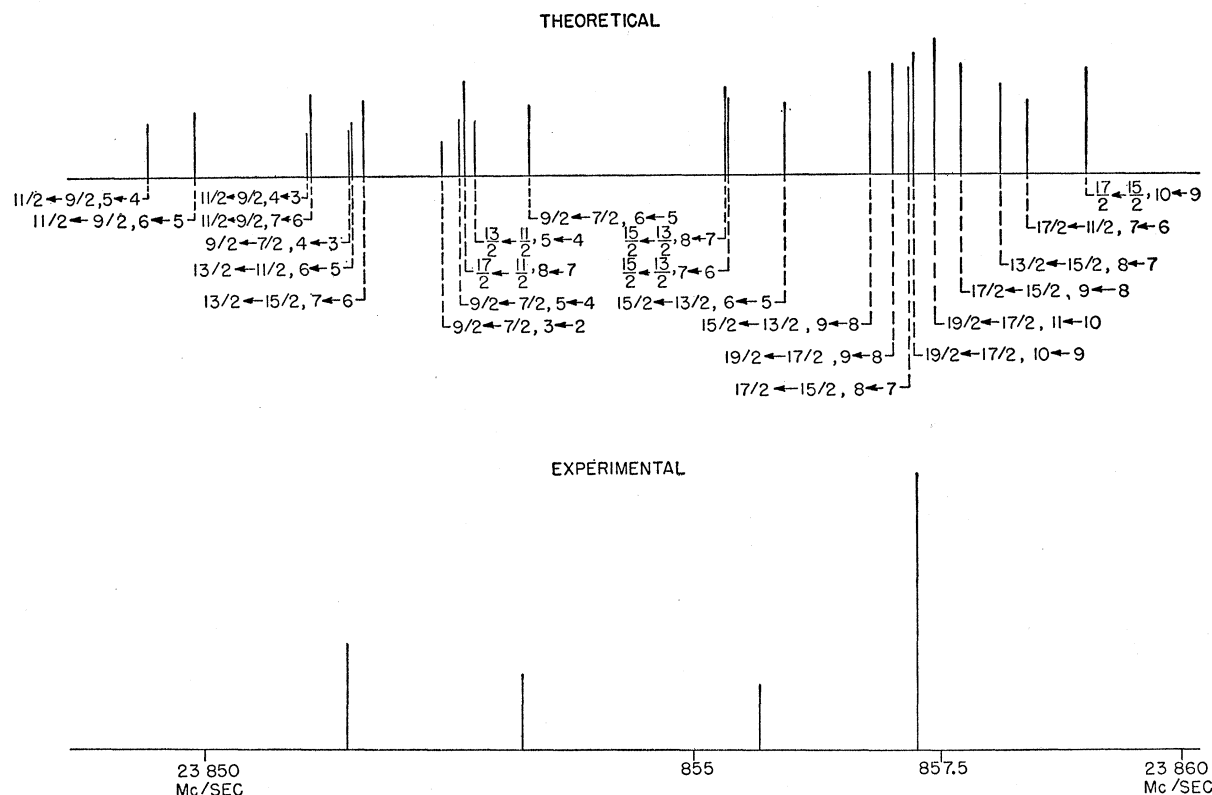
THEORETICAL

11/2←9/2,5←4
11/2←9/2,6←5   11/2←9/2,4←3
11/2←9/2,7←6
9/2←7/2,4←3
13/2←11/2,6←5
13/2←15/2,7←6

$\frac{13}{2}$←$\frac{11}{2}$,5←4
$\frac{17}{2}$←$\frac{11}{2}$,8←7
9/2←7/2,5←4
9/2←7/2,3←2

9/2←7/2,6←5
$\frac{15}{2}$←$\frac{13}{2}$,8←7
$\frac{15}{2}$←$\frac{13}{2}$,7←6
15/2←13/2,6←5
15/2←13/2,9←8
19/2←17/2,9←8
17/2←15/2,8←7

$\frac{17}{2}$←$\frac{15}{2}$,10←9
17/2←11/2,7←6
13/2←15/2,8←7
17/2←15/2,9←8
19/2←17/2,11←10
19/2←17/2,10←9

EXPERIMENTAL

23 850   855   857.5   23 860
Mc/SEC   Mc/SEC

FIG. 6. Hyperfine structure of the $J=5 \leftarrow 4$ transition of $Ga^{69}Br^{79}$ (ground vibrational state) and comparison with theoretical pattern. Spins for Ga^{69} and Br^{79} are 3/2.

TABLE V. Theoretical and experimental frequencies for the $v=0$, $J=5 \leftarrow 4$ transitions of $Ga^{69}Br^{79}$.

$F_1' \leftarrow F_1$	Transition $F' \leftarrow F$	Theoretical frequency Mc/sec	Experimental frequency Mc/sec	Theoretical relative intensity
7/2 ← 5/2	2 ← 1, 3 ← 2, 4 ← 3			
9/2 ← 7/2	3 ← 2, 4 ← 3, 5 ← 4, 6 ← 5	24 771.02	24 771.22±0.20	100
11/2 ← 9/2	4 ← 3, 5 ← 4, 6 ← 5, 7 ← 6			
13/2 ← 11/2	5 ← 4, 6 ← 5, 7 ← 6, 8 ← 7			
7/2 ← 5/2	5 ← 4	24 767.78	24 768.02±0.20	12
7/2 ← 7/2	5 ← 5	24 796.46	24 796.70±0.30	1
7/2 ← 7/2	2 ← 2, 3 ← 3	24 801.84	24 802.17±0.30	1.5

theoretical frequencies and intensities of the $v=0$ state are given in Table VI.

DISCUSSION OF RESULTS

A. Internuclear Distances, Rotation-Vibration Interaction Constants, Centrifugal Stretching Constants, and Mass Ratios

Internuclear distances determined by microwave spectroscopy for the alkali halides[5] are consistently lower than those obtained by electron diffraction experiments. The disagreement is of the order of 2–4%, decreasing with increasing molecular weight. The same discrepancy has been found in the Tl halides and in InI. A possible reason for this discrepancy is a small percentage of dimerization of the vapor or the formation

of Tl trihalides. This would not affect any of the spectroscopic results but would make the electron diffraction values larger.

Internuclear distances in alkali halide crystals have been accounted for by the assignment of ionic radii to the constituent atoms. The so-called "additivity rule" [29] has been investigated for the alkali halide vapors[5] and deviations have been noted. Table VII gives the internuclear distances of the Tl, In, and Ga monohalides and the differences between these values for each series. Variations in the differences $r_e(XH_1)$ minus $r_e(XH_2)$ for the metals (X's), or $r_e(X_1H)$ minus $r_e(X_2H)$ for the various halogens, indicate deviation from the additivity rule.

[29] L. Pauling, The Nature of The Chemical Bond (Cornell University Press, Ithaca, 1944).
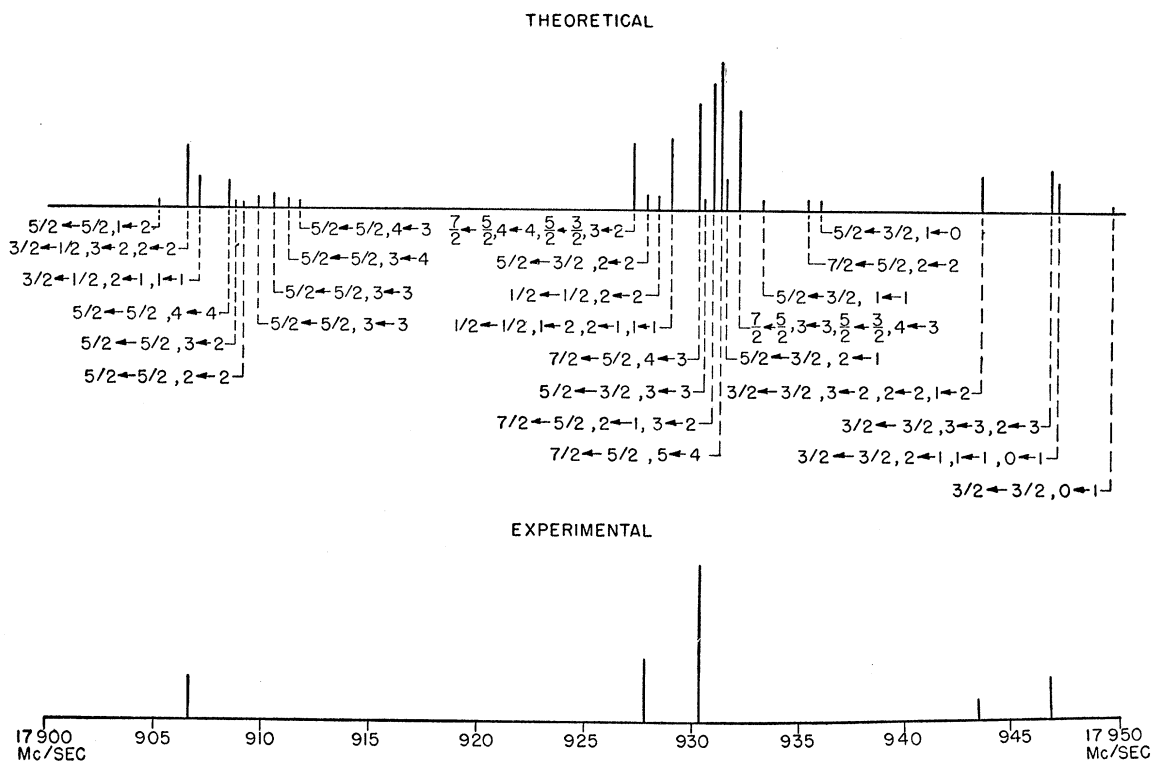
THEORETICAL

$5/2 \leftarrow 5/2, 1 \leftarrow 2$
$3/2 \leftarrow 1/2, 3 \leftarrow 2, 2 \leftarrow 2$
$3/2 \leftarrow 1/2, 2 \leftarrow 1, 1 \leftarrow 1$
$5/2 \leftarrow 5/2, 4 \leftarrow 4$
$5/2 \leftarrow 5/2, 3 \leftarrow 2$
$5/2 \leftarrow 5/2, 2 \leftarrow 2$

$5/2 \leftarrow 5/2, 4 \leftarrow 3$
$5/2 \leftarrow 5/2, 3 \leftarrow 4$
$5/2 \leftarrow 5/2, 3 \leftarrow 3$
$5/2 \leftarrow 5/2, 3 \leftarrow 3$

$\frac{7}{2} \leftarrow \frac{5}{2}, 4 \leftarrow 4, \frac{5}{2} \leftarrow \frac{3}{2}, 3 \leftarrow 2$
$5/2 \leftarrow 3/2, 2 \leftarrow 2$
$1/2 \leftarrow 1/2, 2 \leftarrow 2$
$1/2 \leftarrow 1/2, 1 \leftarrow 2, 2 \leftarrow 1, 1 \leftarrow 1$
$7/2 \leftarrow 5/2, 4 \leftarrow 3$
$5/2 \leftarrow 3/2, 3 \leftarrow 3$
$7/2 \leftarrow 5/2, 2 \leftarrow 1, 3 \leftarrow 2$
$7/2 \leftarrow 5/2, 5 \leftarrow 4$

$5/2 \leftarrow 3/2, 1 \leftarrow 0$
$7/2 \leftarrow 5/2, 2 \leftarrow 2$
$5/2 \leftarrow 3/2, 1 \leftarrow 1$
$\frac{7}{2} \leftarrow \frac{5}{2}, 3 \leftarrow 3, \frac{5}{2} \leftarrow \frac{3}{2}, 4 \leftarrow 3$
$5/2 \leftarrow 3/2, 2 \leftarrow 1$
$3/2 \leftarrow 3/2, 3 \leftarrow 2, 2 \leftarrow 2, 1 \leftarrow 2$
$3/2 \leftarrow 3/2, 3 \leftarrow 3, 2 \leftarrow 3$
$3/2 \leftarrow 3/2, 2 \leftarrow 1, 1 \leftarrow 1, 0 \leftarrow 1$
$3/2 \leftarrow 3/2, 0 \leftarrow 1$

EXPERIMENTAL

17 900 905 910 915 920 925 930 935 940 945 17 950
Mc/SEC   Mc/SEC

FIG. 7. Hyperfine structure of the $J = 7 \leftarrow 6$ transition of $Ga^{69}I^{127}$ (ground vibrational state) and comparison with theoretical pattern. Spins for Ga^{69} and I^{127} are 3/2 and 5/2, respectively.

TABLE VI. Theoretical and experimental frequencies for the $v=0$, $J=7 \leftarrow 6$ transition of $Ga^{69}I$.

$F_1' \leftarrow F_1$	Transition $F' \leftarrow F$	Theoretical frequency Mc/sec	Experimental frequency Mc/sec	Theoretical relative intensity
$17/2 \leftarrow 11/2$	$7 \leftarrow 6$			
$15/2 \leftarrow 13/2$	$9 \leftarrow 8$			
$13/2 \leftarrow 15/2$	$8 \leftarrow 7$	23 857.26	23 857.29±0.20	100
$17/2 \leftarrow 15/2$	$9 \leftarrow 8$			
$19/2 \leftarrow 17/2$	$8 \leftarrow 7, 9 \leftarrow 8, 10 \leftarrow 9, 11 \leftarrow 10$			
$15/2 \leftarrow 13/2$	$6 \leftarrow 5, 7 \leftarrow 6, 8 \leftarrow 7$	23 855.51	23 855.66±0.20	37
$9/2 \leftarrow 7/2$	$3 \leftarrow 2, 5 \leftarrow 4, 6 \leftarrow 5$			
$13/2 \leftarrow 11/2$	$5 \leftarrow 4$	23 852.84	23 853.25±0.40	40
$17/2 \leftarrow 11/2$	$8 \leftarrow 7$			
$9/2 \leftarrow 7/2$	$4 \leftarrow 3$			
$11/2 \leftarrow 9/2$	$4 \leftarrow 3, 7 \leftarrow 6$	23 851.39	23 851.47±0.20	44
$13/2 \leftarrow 11/2$	$6 \leftarrow 5$			
$13/2 \leftarrow 15/2$	$7 \leftarrow 6$			

Since these molecules are known to have a fair amount of covalent bonding, one does not expect to find constant differences. Schomaker and Stevenson[30] have modified the additivity criterion by allowing the bond distance to be sensitive to the relative amounts of ionic and covalent character present. This modification depends linearly upon the electronegativity difference, and hence does not affect the departure from additivity shown in Table VII.

The theoretical value of α_e, the rotation-vibration interaction constant, based on the assumption of a Morse potential, is[31]

$$\alpha_e = 6 \left(\frac{x_e \omega_e B_e^3}{\omega_e^2} \right)^{\frac{1}{2}} - \frac{6 B_e^2}{\omega_e}. \tag{11}$$

Values of ω_e and x_e have been determined by ultraviolet spectroscopy[32] and B_e values have been determined in the present experiment. However, the dependence of α_e on ω_e and $x_e \omega_e$ limits the accuracy of this calculation. A comparison of theoretical and experimental values of α_e is given in Table VIII. The agree-

[30] V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. 63, 37 (1941).

[31] See reference 1, p. 9.
[32] See reference 21, Appendix.

TABLE VII. Internuclear distances and additivity of ionic radii. All distances are in angstrom units.

	F inter-nuclear distance	XCl-XF difference	Cl inter-nuclear distance	XBr-XCl difference	Br inter-nuclear distance	XI-XBr difference	I inter-nuclear distance
Ga			2.2017	0.1508	2.3525	0.2220	2.5746
InH−GaH difference			0.1994		0.1907		0.1793
In			2.4011	0.1421	2.5432	0.2107	2.7539
TlH−InH difference			0.0837		0.0749		0.0598
Tl	2.0844	0.4004	2.4848	0.1333	2.6181	0.1956	2.8137

ment is quite good for the heavier molecules but becomes worse for the lighter molecules.

Table I gives the values of D_e, the centrifugal stretching constant, calculated from Eq. (3). The D_e value for TlI was determined experimentally and although much higher than the value given by Eq. (3), it was within the experimental error. The D_e values observed in the alkali halides were also consistently higher than the calculated value based on the vibration frequency ω_e obtained from ultraviolet spectroscopy.

In general, the accuracy with which D_e is determined is quite poor, and in many cases it gives rise to the principal error in B_e. In calculating the mass ratio of two isotopic species, 1 and 2, the ratio B_e^1/B_e^2 enters and this ratio is quite insensitive to the error in D_e. Hence, the error attributed to the mass ratio is considerably smaller than the error in the B_e values. The mass ratios are given in Table IX.

B. Chemical Bond

Description of a chemical bond usually involves specifying the amount of ionic character, the orbital hybridization, and the degree of bond multiplicity. In the diatomic halides we avoid the complications due to multiplicity and are thus able to obtain information about the ionic character of the bond and about hybridization.

The wave function of a bonding electron the LCAO (linear combination of atomic orbitals) approximation may be written

$$\Psi = a\Psi_A + b\Psi_B,$$

where Ψ_A and Ψ_B are atomic orbitals for the halogen and metal atoms, respectively. If Ψ is normalized, $a^2 + b^2 + abS = 1$, where S is the overlap integral $\int \Psi_A\Psi_B d\tau$. The ionic character for such a heteropolar bond may be defined as $a^2 - b^2$, i.e., it is the difference between the probabilities for the electron to be found on atom A or B.

The dipole moment for a heteropolar molecule is given by

$$\mu = eR(b^2 - a^2) + \mu_{overlap} + \mu_{hybridization} + \mu_{polarization}. \quad (12)$$

The first term is called the primary moment, the second term is due to overlap of orbital wave functions from atoms of different size, the third term is due to hybridization of valence orbitals, and the fourth term is due

to the polarization of the core electrons. Because this last term is exceedingly difficult to evaluate, this equation cannot be used quantitatively to compare calculated and measured dipole moments.

In Fig. 8, μ/eR for a large number of dipole moments is plotted against electronegativity difference. Dailey and Townes[33] have pointed out that molecules with electronegativity differences > 2 are completely ionic and have $\mu/eR < 1$ because of polarization effects. We have plotted two points for TlF as there are two widely different values of the electronegativity of Tl given in the literature.[34,35] From these values it appears that TlF is completely ionic or very nearly so.

A more reliable source of information concerning molecular electronic structure is the nuclear quadrupole coupling constant eqQ. Q is a property of the nucleus but q is directly related to the electronic charge dis-

TABLE VIII. Comparison of calculated and experimental values of the vibration-rotation interaction constant α_e.

Molecule	α_e Mc/sec (calculated)	α_e Mc/sec (experimental)
Tl^{205}F	36	44.98
Tl^{205}Cl^{35}	14	11.90
Tl^{205}Br^{81}	3.4	3.807
Tl^{205}I		1.985
In^{115}Cl^{35}	13.8	15.34
In^{115}Br^{79}	6.1	5.706
In^{115}I	3.2	3.119
Ga^{69}Cl^{35}	29.8	23.30
Ga^{69}Br^{81}	9.8	9.61
Ga^{69}I	5.3	5.667

TABLE IX. Mass ratios of isotopes from microwave spectra.

	Ratio	Molecule
Cl^{35}/Cl^{37}	0.9459739±0.0000060	TlCl
	0.9459781±0.0000030	CsCl[a]
	0.9459803±0.0000015	K^{39}Cl[b, c]
Br^{79}/Br^{81}	0.9752999±0.0000050	TlBr
	0.9753068±0.0000045	CsBr[a]
	0.9752999±0.0000065	Rb^{85}Br[a]
	0.9753088±0.0000020	K^{39}Br[c, d]

a See reference 5.
b See reference 11.
c Molecular beam measurements.
d See reference 12.

[33] B. P. Dailey and C. H. Townes, J. Chem. Phys. 23, 118 (1955).
[34] M. Haissinsky, J. Chem. Phys. 46, 298 (1949).
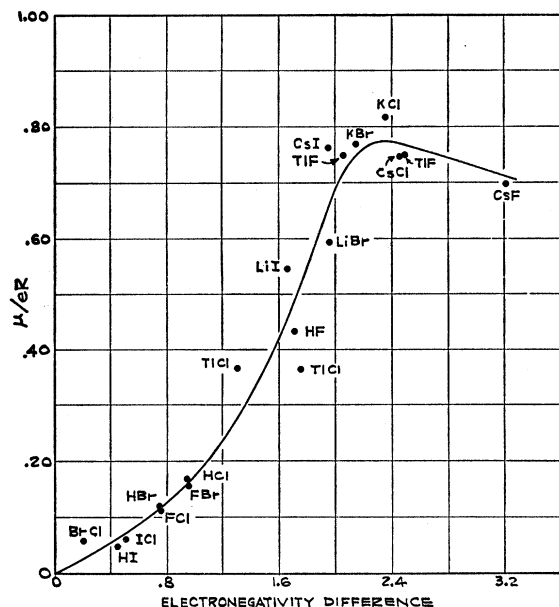[35] W. Gordy, J. Chem. Phys. 14, 305 (1946).

FIG. 8. Apparent ionic character μ/eR from molecular dipole moments (after Dailey and Townes[33]).

tribution in the molecule. For the ith electron at a distance r_i from the nucleus, we have

$$q_i = \frac{\partial^2}{\partial z^2}\left(\frac{e}{r_i}\right) = e\frac{(3\cos\theta_i - 1)}{r_i^3},$$

where θ_i is the angle between the radius vector and the molecular axis (z axis for diatomic molecules). The total q is the sum of the individual q_i's averaged over all positions of the electron in the molecule

$$q = \sum_i \int \Psi_i^* \frac{e(3\cos\theta_i - 1)}{r_i^3}\Psi_i d\tau,$$

where i is summed over all the electrons and Ψ_i is the wave function for the ith electron.

For a precise correlation of quadrupole coupling constants to the electronic structure of a molecule, it would be necessary to have accurate wave functions for each of the molecular electrons and to carry out a precise evaluation of the integrals. This has been done for the hydrogen molecule[36] but becomes too difficult for more complicated molecules.

Townes and Dailey[37] have discussed a simple semi-empirical relation between eqQ and approximate wave functions for the bonding electrons in a molecule. They point out that the magnitude of q is largely determined by the manner in which the valence electrons fill the available p orbitals of the lowest energy. An s orbital or an undisturbed closed shell of electrons make no

contribution to the energy of nuclear orientation because of their spherical symmetry. Contributions due to charges associated with neighboring atoms in the molecule or with polarization of the nonbonding closed shells of electrons can be neglected in comparison to the larger effect. For example, a negative halogen ion would have an approximately spherical distribution of charge and hence a very small value of q. The small halogen coupling constants measured in the alkali halides which are largely ionic seem to corroborate this. However a covalently bonded halogen atom, lacking one p electron in its valence shell would have a relatively large value of q and hence of the experimentally measured coupling constant eqQ.

The quadrupole coupling constants of Cl, Br, and I (F has zero eqQ) in atomic states[38] are known and therefore the contribution of an electron in a p orbit to eqQ is known independently of molecular data. However, the covalently bonded electron will not be in the same type orbit in the molecule as in the atoms. Dailey and Townes[33] write the wave function of a bonding electron in the neighborhood of the halogen atom as

$$\Psi_A = (1-s-d)^{\frac{1}{2}}\Psi_p \pm (s)^{\frac{1}{2}}\Psi_s \pm (d)^{\frac{1}{2}}\Psi_d,$$

where s is the amount of s character in the bonding orbital and d the amount of d character. Admixture of d and s character to the hybrid bonding orbital removes part of an electron from a p orbit and increases the defect of p electrons. However, the two nonbonding s electrons must take on an equivalent amount of p character; thus the defect of p electrons is decreased. Therefore the quadrupole coupling constant for a halogen forming a hybrid bond with a negative ionic character i is

$$eqQ = (-1+2s-s-d)(1-i)eqQ_{n10}.$$

For an isolated atom s, d, and i are zero and $eqQ(\text{atom}) = -eqQ_{n10}$. Thus we can write

$$(eqQ)(\text{molecule})/(eqQ)(\text{atom}) = (1-s+d)(1-i). \quad (13)$$

In Eq. (13) the effects of overlap on quadrupole coupling have been neglected. A more complete expression for eqQ would be $(-1-S^2+s-d)(1-i)eqQ_{n10}$, where S^2 is the square of the overlap integral. Allowing for the modification of the LCAO wave function associated with one atom at the nucleus of the other, Itoh[39] has shown that the contribution of overlap effects to the quadrupole coupling constant in diatomic molecules is negligible.

In order to determine the ionic character of the bond, certain assumptions concerning the role of bond hydridization have to be made. Dailey and Townes,[33] in their discussion of quadrupole coupling data for

[36] A. Nordsieck, Phys. Rev. 58, 310 (1940).
[37] C. H. Townes and B. P. Dailey, J. Chem. Phys. 17, 782 (1949).

[38] V. Jaccarino and J. G. King, Phys. Rev. 83, 471 (1951); J. G. King and V. Jaccarino, Phys. Rev. 91, 209 (1953); Jaccarino, King, Satten, and Stroke, Phys. Rev. 93, 1798 (1954).
[39] T. Itoh, Tokyo University (private communication).

diatomic halides, assume that Cl, Br, and I bonds have 15% s character when the halogen is bonded to an atom which is more electropositive than the halogen by as much as 0.25 unit. This assumption is in good agreement with the value of 10% s character for the As-bonding orbitals in AsCl[40] and the 15% s character for the S bonding orbitals in H_2S[41] found by a method which is independent of overlap effects. The setting of an upper limit to the s character would seem to limit the d character to small values since the factor $s-d$ is the one which actually enters into the equation for the quadrupole coupling constant. With $s=15\%$, $d=0$ and the atomic quadrupole coupling constants of the halogen, the ionic *character* of the Tl, In, and Ga halides has been calculated and is shown in Table X.

One can treat the electropositive atom of a diatomic halide in a similar manner. Ga and In have an $ns^2 np$ electron configuration in the bound state. Since the atomic eqQ's of Ga and In have been measured[42,43] (Tl has zero quadrupole moment), the contribution of a p electron to the eqQ is known independently of molecular data.

Under the preliminary assumption that only the covalent state contributes to the quadrupole coupling constant, we get

$$eqQ = (1+s-d)(1-i)eqQ_{n10},$$

where eqQ_{n10} equals the atomic eqQ. Since i, eqQ, and eqQ_{n10} are known, $s-d$ can be determined. This calculation yields the absurd result of 100 to 200% s character for the p bonding orbital. Apparently there is an additional contribution to the quadrupole coupling constant from the ionic state. When Ga or In is in a positively ionic state, the p subshell is vacant unless the s orbital
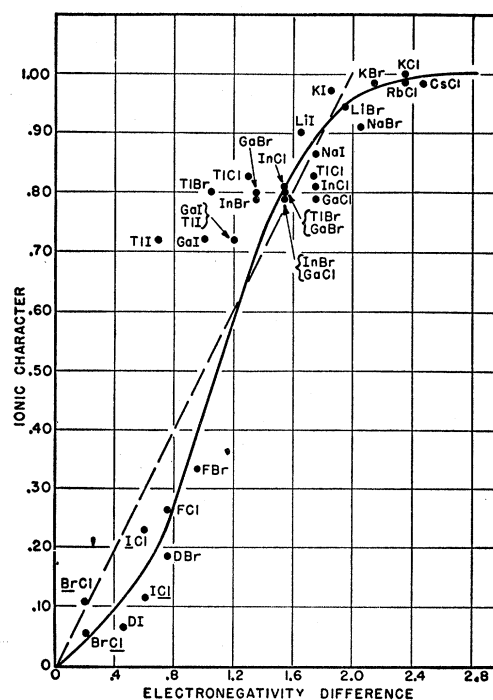

FIG. 9. Ionic character vs electronegativity difference taking hybridization into account (after Dailey and Townes[33]). Dashed line neglects hybridization (reference 45).

remains hybridized. If the two nonbonding s electrons retain their p character, the ionic state contributes $2sieqQ_{n10}$ to the total eqQ. However, this contribution must be modified because the interaction between a valence p electron and the nucleus when the atom is positively ionic is somewhat larger than for the case of the neutral atom. The ratio for the two cases may be taken as $(1+\epsilon)$ where ϵ is 0.20 for Ga and 0.25 for In[33]. The constant ϵ is estimated from the observed fine structure of the atom and ion. Thus, for a group IIIB element bonded to a halogen, the quadrupole coupling constant is

$$eqQ = [(1+s-d)(1-i)+2(1+\epsilon)si]eqQ_{n10}.$$

Since $eqQ_{n10}=eqQ(\text{atom})$, we have

$$eqQ(\text{molecule})/eqQ(\text{atom}) = (1+s-d)(1-i)$$
$$+2(1+\epsilon)si. \quad (14)$$

The $s-p$ hybridization has been assumed to be the same in both states, a condition which maximizes the resonance energy between these states. Using the values of ionic character calculated from Eq. (13), we have used Eq. (14) to determine that the $s-p$ hybridization of the Ga valence electrons in GaCl, GaBr, and GaI is 21, 18, and 13%, respectively, and of the In valence electrons in InCl and InBr is 24 and 23%, respectively. These results are included in Table X.

Dailey and Townes[33] have derived an S-shaped curve for the relation between ionicity and electronegativity differences of diatomic molecules. In Fig. 9 we have

TABLE X. Ionic character and s-p hybridization of TlCl, TlBr, TlI, IcCl, InBr, GaCl, GaBr, and GaI, obtained from nuclear quadrupole coupling data.

Molecule	Atom	Atomic eqQ Mc/sec	Molecular eqQ Mc/sec	i	s	Electro-negativity
Tl[203]Cl[35]	Cl[35]	−110	−15.8	0.83	0.15[a]	3.15
	Tl					1.9,[b] 1.4[c]
Tl[205]Br[79]	Br[79]	770	130	0.80	0.15[a]	2.95
Tl[205]I	I	−2292	−537	0.72	0.15[a]	2.6
In[115]Cl[35]	Cl[35]	−110	−18	0.81	0.15[a]	3.15
	In[115]	−899	−655		0.24	1.6,[b] 1.4[c]
In[115]Br[79]	Br[79]	770	138	0.79	0.15[a]	2.95
	In[115]	−899	−642		0.23	1.6, 1.4
Ga[69]Cl[35]	Cl[35]	−110	−20	0.79	0.15[a]	3.15
	Ga[69]	−125	−84.7		0.21	1.6,[b] 1.4[c]
Ga[69]Br[79]	Br[79]	770	134	0.80	0.15[a]	2.95
	Ga[69]	−125	−74		0.18	1.6, 1.4
Ga[69]I	I	−2292	−549	0.72	0.15[a]	2.6
	Ga[69]	−125	−66		0.13	1.6, 1.4

[a] Assumed value. See reference 33.
[b] Haissensky's value. See reference 34.
[c] Gordy's value. See reference 35.

[40] P. Kusliuk, J. Chem. Phys. 22, 86 (1954).
[41] G. R. Bird and C. H. Townes, Phys. Rev. 94, 1203 (1954).
[42] R. T. Daly and J. H. Holloway, Phys. Rev. 96, 539 (1954).
[43] P. Kusch and T. G. Eck, Phys. Rev. 94, 1799 (1954).

redrawn their curve to include the Tl, In, and Ga halides. The electronegativities used are those of Huggins,[44] except for Tl, In, and Ga which he does not give. Two different values of the electronegativity for Tl, In, and Ga have been given by Haissensky[34] and Gordy.[35] Points representing both values are included in Fig. 9.

The above interpretation of quadrupole coupling constants is not unique. Gordy[45] has proposed a simple relation between ionicity and the quadrupole coupling constants in which s character is neglected completely. Using it he obtains as the relation between ionic character and electronegativity difference for a bond $A - B$:

$$i = \tfrac{1}{2}|X_A - X_B|.$$

This is shown as a dashed line in Fig. 9. Recently Gordy[46] has modified his straight-line relationship in the region $|\Delta X| > 2$ to conform with the known data for the alkali halides.

CONCLUSIONS

The present experiment has yielded accurate information concerning the internuclear distances, rotational constants, vibration-rotation interaction constants, and the quadrupole coupling constants of the Tl, In, and Ga monohalides.

The ionic character for diatomic halides involving Group IIIB elements is less than that for the alkali halides, in keeping with their greater electronegativity. The values of s character found for the Ga and In bonding orbitals, which are fairly independent of the assumed s character of the halogen bonding orbitals, argue strongly for the presence of s-p hybridization in the ionic state.

The quadrupole coupling data presented here show that the electronegativities of Tl, In, and Ga are the same and approximately equal to 1.4 which is in agreement with Gordy's values.

APPENDIX I. MEASURED FREQUENCIES IN Mc/sec FOR MICROWAVE TRANSITIONS OF THE Tl, In, AND Ga HALLIDES

TlF: $J = 2 \leftarrow 1$

	$v = 0$	$v = 1$
Tl²⁰³F	26 291.86+0.10	
Tl²⁰⁵F	26 669.76±0.10	26 489.86±0.20

TlCl

Rotational transition	Hyperfine transition	$v = 0$	$v = 1$	$v = 2$
		Tl²⁰³Cl³⁵		
$J = 5 \leftarrow 4$	$F = 13/2 \leftarrow 11/2, 11/2 \leftarrow 9/2, 9/2 \leftarrow 7/2,$ $7/2 \leftarrow 5/2$	27 379.49±0.10	27 260.18±0.10	27 140.35±0.10
	$F = 11/2 \leftarrow 11/2$	27 376.62±0.10		
$J = 4 \leftarrow 3$		21 903.16±0.20		
		Tl²⁰³Cl³⁷		
$J = 5 \leftarrow 4$		26 119.36±0.10		
$J = 4 \leftarrow 3$		20 895.33±0.10	20 806.64±0.30	
		Tl²⁰⁵Cl³⁵		
$J = 5 \leftarrow 4$		27 340.51±0.10	27 221.30±0.10	27 102.42±0.10
$J = 4 \leftarrow 3$		21 872.16±0.10		
		Tl²⁰⁵Cl³⁷		
$J = 5 \leftarrow 4$		26 079.87±0.10	25 969.04±0.20	
$J = 4 \leftarrow 3$		20 864.11±0.20	20 776.20±0.20	

[44] M. J. Huggins, J. Am. Chem. Soc. **75**, 4123 (1953).
[45] See reference 2, p. 284.
[46] W. Gordy, Discussions Faraday Soc. **19**, 14 (1955).

APPENDIX I—*Continued.*

TlBr

Rotational transition	Hyperfine transition	$v=0$	$v=1$	$v=2$	$v=3$
		$Tl^{205}Br^{79}$			
$J=6 \leftarrow 5$	$F=15/2 \leftarrow 13/2, 13/2 \leftarrow 11/2$	$15\ 502.55 \pm 0.10$[a]			
	$11/2 \leftarrow 9/2, 9/2 \leftarrow 7/2$	$15\ 503.79 \pm 0.20$[a]			
$J=9 \leftarrow 8$		$23\ 254.06 \pm 0.05$	$23\ 183.49 \pm 0.10$	$23\ 112.80 \pm 0.10$	$23\ 042.54 \pm 0.10$
		$Tl^{205}Br^{81}$			
$J=9 \leftarrow 8$		$22\ 839.75 \pm 0.10$	$22\ 771.22 \pm 0.20$		
$J=10 \leftarrow 9$		$25\ 377.53 \pm 0.05$			
		$Tl^{203}Br^{79}$			
$J=9 \leftarrow 8$		$23\ 317.65 \pm 0.10$	$23\ 246.83 \pm 0.20$	$23\ 175.68 \pm 0.20$	
		$Tl^{203}Br^{81}$			
$J=9 \leftarrow 8$		$22\ 903.48 \pm 0.10$	$22\ 834.13 \pm 0.20$		

TlI

Rotational transition	Hyperfine transition	$v=0$	$v=1$	$v=2$
		$Tl^{205}I$		
$J=17 \leftarrow 16$		$27\ 655.37 \pm 0.10$	$27\ 588.22 \pm 0.20$	$27\ 520.39 \pm 0.20$
$J=16 \leftarrow 15$		$26\ 029.54 \pm 0.30$		
$J=15 \leftarrow 14$	$F=35/2 \leftarrow 33/2, 33/2 \leftarrow 31/2, 31/2 \leftarrow 29/2$	$24\ 403.14 \pm 0.10$[a]		
	$29/2 \leftarrow 27/2, 27/2 \leftarrow 25/2, 25/2 \leftarrow 23/2$	$24\ 402.36 \pm 0.10$[a]		
$J=13 \leftarrow 12$	$F=31/2 \leftarrow 29/2, 29/2 \leftarrow 27/2, 27/2 \leftarrow 25/2$	$21\ 149.81 \pm 0.10$[a]		
	$25/2 \leftarrow 23/2, 23/2 \leftarrow 21/2, 21/2 \leftarrow 19/2$	$21\ 148.78 \pm 0.05$[a]		
$J=10 \leftarrow 9$	$F=25/2 \leftarrow 23/2, 23/2 \leftarrow 21/2, 21/2 \leftarrow 19/2$	$16\ 270.38 \pm 0.10$[a]	$16\ 230.50 \pm 0.10$[a]	
	$19/2 \leftarrow 17/2, 17/2 \leftarrow 15/2, 15/2 \leftarrow 13/2$	$16\ 268.26 \pm 0.10$[a]	$16\ 228.26 \pm 0.10$[a]	
		$Tl^{203}I$		
$J=17 \leftarrow 16$		$27\ 760.25 \pm 0.30$	$27\ 692.01 \pm 0.40$	$27\ 624.02 \pm 0.20$

InCl: $J=3 \leftarrow 2$

Hyperfine transition		$v=0$	$v=1$
		$In^{115}Cl^{35}$	
$F_1=9/2 \leftarrow 7/2;$	$F=3 \leftarrow 2, 4 \leftarrow 3$	$19\ 527.77 \pm 0.20$[a]	
$F_1=9/2 \leftarrow 7/2;$	$F=5 \leftarrow 4, 6 \leftarrow 5$	$19\ 526.26 \pm 0.20$[a]	
$F_1=5/2 \leftarrow 5/2;$	$F=1 \leftarrow 1, 2 \leftarrow 2, 3 \leftarrow 3, 4 \leftarrow 4$	$19\ 539.67 \pm 0.20$[a]	
$F_1=11/2 \leftarrow 9/2;$	$F=4 \leftarrow 3, 5 \leftarrow 4, 6 \leftarrow 5, 7 \leftarrow 6$	$\{19\ 563.97 \pm 0.20$[a]	
$F_1=11/2 \leftarrow 11/2;$	$F=4 \leftarrow 4, 5 \leftarrow 5, 6 \leftarrow 6, 7 \leftarrow 7$	$\{19\ 565.84 \pm 0.20$[a]	
$F_1=7/2 \leftarrow 7/2;$	$F=2 \leftarrow 2, 3 \leftarrow 3, 4 \leftarrow 4, 5 \leftarrow 5$	$19\ 570.25 \pm 0.20$[a]	
$F_1=15/2 \leftarrow 13/2;$	$F=6 \leftarrow 5, 7 \leftarrow 6, 8 \leftarrow 7, 9 \leftarrow 8$	$19\ 578.36 \pm 0.20$[a]	$19\ 486.10 \pm 0.20$[a]
$F_1=9/2 \leftarrow 9/2;$	$F=3 \leftarrow 4, 4 \leftarrow 4, 5 \leftarrow 5, 6 \leftarrow 6$		
$F_1=3/2 \leftarrow 5/2;$	$F=0 \leftarrow 1, 1 \leftarrow 2, 2 \leftarrow 3, 3 \leftarrow 4$	$19\ 584.56 \pm 0.20$[a]	$19\ 491.88 \pm 0.20$[a]
$F_1=13/2 \leftarrow 11/2;$	$F=7 \leftarrow 6$		
$F_1=13/2 \leftarrow 11/2;$	$F=5 \leftarrow 4, 6 \leftarrow 5, 8 \leftarrow 7$	$19\ 589.08 \pm 0.20$[a]	$19\ 496.29 \pm 0.20$[a]
$F_1=5/2 \leftarrow 7/2;$	$F=1 \leftarrow 2, 2 \leftarrow 3, 3 \leftarrow 4, 4 \leftarrow 5$	$19\ 621.36 \pm 0.20$[a]	
$F_1=7/2 \leftarrow 9/2;$	$F=2 \leftarrow 3, 3 \leftarrow 4, 4 \leftarrow 5, 5 \leftarrow 6$	$19\ 628.75 \pm 0.20$[a]	
		$In^{115}Cl^{37}$	
$F_1=15/2 \leftarrow 13/2;$	$F=6 \leftarrow 5, 7 \leftarrow 6, 8 \leftarrow 7, 9 \leftarrow 8$	$18\ 768.93 \pm 0.20$[a]	

$In^{115}Br^{79}$ $J=7 \leftarrow 6$

Hyperfine transition		$v=0$	$v=1$
$F_1=19/2 \leftarrow 19/2;$	$F=10 \leftarrow 10, 11 \leftarrow 11$	$23\ 308.30 \pm 0.20$[a]	$23\ 228.68 \pm 0.20$[a]
$F_1=13/2 \leftarrow 11/2;$	$F=5 \leftarrow 4$	$23\ 328.97 \pm 0.20$[a]	
$F_1=11/2 \leftarrow 9/2;$	$F=4 \leftarrow 3, 7 \leftarrow 6$		
$F_1=9/2 \leftarrow 7/2;$	$F=6 \leftarrow 5, 3 \leftarrow 2$	$23\ 331.51 \pm 0.20$[a]	
$F_1=7/2 \leftarrow 5/2;$	$F=2 \leftarrow 1, 5 \leftarrow 4$		
$F_1=15/2 \leftarrow 13/2;$	$F=6 \leftarrow 5$		
$F_1=13/2 \leftarrow 11/2;$	$F=8 \leftarrow 7, 7 \leftarrow 6, 6 \leftarrow 5$		$\{23\ 334.50 \pm 0.20$[a]
$F_1=11/2 \leftarrow 9/2;$	$F=6 \leftarrow 5, 5 \leftarrow 4$		
$F_1=9/2 \leftarrow 7/2;$	$F=5 \leftarrow 4, 4 \leftarrow 3$		$\{23\ 335.55 \pm 0.20$[a]
$F_1=7/2 \leftarrow 5/2;$	$F=4 \leftarrow 3, 3 \leftarrow 2$		
$F_1=5/2 \leftarrow 3/2;$	$F=4 \leftarrow 3$		

APPENDIX I—*Continued.*

$In^{115}Br^{79}$ $J = 7 \leftarrow 6$

Hyperfine transition		$v=0$	$v=1$	$v=2$
$F_1 = 15/2 \leftarrow 17/2$;	$F = 8 \leftarrow 7$			
$F_1 = 15/2 \leftarrow 13/2$;	$F = 7 \leftarrow 6$			
$F_1 = 5/2 \leftarrow 3/2$;	$F = 3 \leftarrow 2, 2 \leftarrow 1, 1 \leftarrow 0$	$23\ 339.12 \pm 0.20^a$		
$F_1 = 19/2 \leftarrow 13/2$;	$F = 9 \leftarrow 8, 8 \leftarrow 7$			
$F_1 = 17/2 \leftarrow 15/2$;	$F = 10 \leftarrow 9, 9 \leftarrow 8$	$23\ 341.01 \pm 0.20^a$		
$F_1 = 15/2 \leftarrow 17/2$;	$F = 7 \leftarrow 8$			
$F_1 = 23/2 \leftarrow 21/2$;	$F = 13 \leftarrow 12, 12 \leftarrow 11, 11 \leftarrow 10, 10 \leftarrow 9$			
$F_1 = 21/2 \leftarrow 19/2$;	$F = 12 \leftarrow 11, 11 \leftarrow 10, 10 \leftarrow 9, 9 \leftarrow 8$	$23\ 343.33 \pm 0.20^a$	$23\ 263.76 \pm 0.20^a$	
$F_1 = 19/2 \leftarrow 17/2$;	$F = 11 \leftarrow 10, 10 \leftarrow 9$	$23\ 345.07 \pm 0.20^a$		
$F_1 = 17/2 \leftarrow 15/2$;	$F = 8 \leftarrow 7, 9 \leftarrow 9$	$23\ 346.51 \pm 0.20^a$		
$F_1 = 15/2 \leftarrow 17/2$;	$F = 9 \leftarrow 8$			
$F_1 = 15/2 \leftarrow 15/2$;	$F = 8 \leftarrow 8, 6 \leftarrow 6$			
$F_1 = 13/2 \leftarrow 13/2$;	$F = 8 \leftarrow 8, 7 \leftarrow 7$	$23\ 353.40 \pm 0.20^a$		
$F_1 = 13/2 \leftarrow 13/2$;	$F = 6 \leftarrow 6, 5 \leftarrow 5$			
$F_1 = 5/2 \leftarrow 5/2$;	$F = 4 \leftarrow 4$	$23\ 358.74 \pm 0.20^a$	$23\ 279.09 \pm 0.20^a$	
$F_1 = 19/2 \leftarrow 17/2$;	$F = 9 \leftarrow 8$			
$F_1 = 13/2 \leftarrow 13/2$;	$F = 4 \leftarrow 4, 3 \leftarrow 3$			
$F_1 = 7/2 \leftarrow 7/2$;	$F = 5 \leftarrow 5$	$23\ 361.35 \pm 0.20^a$		
$F_1 = 11/2 \leftarrow 11/2$;	$F = 7 \leftarrow 7, 4 \leftarrow 4$		$23\ 282.61 \pm 0.20^a$	
$F_1 = 13/2 \leftarrow 17/2$;	$F = 7 \leftarrow 7$	$23\ 362.70 \pm 0.20^a$		
$F_1 = 11/2 \leftarrow 11/2$;	$F = 6 \leftarrow 6, 5 \leftarrow 5$	$23\ 365.60 \pm 0.20^a$	$23\ 285.37 \pm 0.20^a$	
$F_1 = 9/2 \leftarrow 9/2$;	$F = 5 \leftarrow 5, 4 \leftarrow 4$			
$F_1 = 7/2 \leftarrow 7/2$;	$F = 4 \leftarrow 4, 3 \leftarrow 3$	$23\ 367.97 \pm 0.20^a$	$23\ 287.37 \pm 0.20^a$	

$In^{115}I^{127}$ [a]: $J = 11 \leftarrow 10$

$v=0$	$v=1$	$v=2$
$24\ 275.39 \pm 0.20$	$24\ 206.89 \pm 0.20$	
$24\ 278.01 \pm 0.20$	$24\ 209.36 \pm 0.20$	$24\ 140.91 \pm 0.20$
$24\ 279.23 \pm 0.20$	$24\ 210.68 \pm 0.20$	
$24\ 280.42 \pm 0.20$	$24\ 211.78 \pm 0.20$	$24\ 143.30 \pm 0.20$
$24\ 282.48 \pm 0.20$	$24\ 213.78 \pm 0.20$	

[a] Hyperfine structure was not worked out.

GaCl: $J = 2 \leftarrow 1$

Hyperfine transition		$v=0$	$v=1$	$v=2$	$v=3$
		$Ga^{69}Cl^{35}$			
$F_1 = 3/2 \leftarrow 1/2$;	$F = 3 \leftarrow 2, 2 \leftarrow 2, 2 \leftarrow 1, 1 \leftarrow 1, 4 \leftarrow 4, 4 \leftarrow 3, 3 \leftarrow 4, 3 \leftarrow 3$	$17\ 906.92 \pm 0.20$			
$F_1 = 5/2 \leftarrow 5/2$;	$F = 3 \leftarrow 2, 2 \leftarrow 3, 2 \leftarrow 2, 2 \leftarrow 1, 1 \leftarrow 2$				
$F_1 = 1/2 \leftarrow 1/2$;	$F = 2 \leftarrow 2, 2 \leftarrow 1, 1 \leftarrow 2, 1 \leftarrow 1$				
$F_1 = 7/2 \leftarrow 5/2$;	$F = 4 \leftarrow 4$	$17\ 928.55 \pm 0.20$			
$F_1 = 5/2 \leftarrow 3/2$;	$F = 3 \leftarrow 2, 2 \leftarrow 2$				
$F_1 = 7/2 \leftarrow 5/2$;	$F = 5 \leftarrow 4, 4 \leftarrow 3, 3 \leftarrow 3, 3 \leftarrow 2, 2 \leftarrow 2, 2 \leftarrow 1$	$17\ 930.57 \pm 0.20$	$17\ 837.00 \pm 0.50$	$17\ 743.96 \pm 0.50$	$17\ 650.97 \pm 0.50$
$F_1 = 5/2 \leftarrow 3/2$;	$F = 4 \leftarrow 3, 3 \leftarrow 3, 2 \leftarrow 1, 1 \leftarrow 1, 1 \leftarrow 0$				
$F_1 = 3/2 \leftarrow 3/2$;	$F = 3 \leftarrow 2, 2 \leftarrow 2, 1 \leftarrow 2$	$17\ 942.92 \pm 0.40$			
$F_1 = 3/2 \leftarrow 3/2$;	$F = 3 \leftarrow 3, 2 \leftarrow 3, 2 \leftarrow 1, 1 \leftarrow 1, 1 \leftarrow 0, 0 \leftarrow 1$	$17\ 946.83 \pm 0.30$			
		$Ga^{71}Cl^{35}$			
$F_1 = 7/2 \leftarrow 5/2$;	$F = 5 \leftarrow 4, 4 \leftarrow 3, 3 \leftarrow 3, 3 \leftarrow 2, 2 \leftarrow 2, 2 \leftarrow 1$	$17\ 759.09 \pm 0.50$	$17\ 666.88 \pm 0.50$	$17\ 573.70 \pm 0.50$	
$F_1 = 5/2 \leftarrow 3/2$;	$F = 4 \leftarrow 3, 3 \leftarrow 3, 2 \leftarrow 1, 1 \leftarrow 1, 1 \leftarrow 0$				
		$Ga^{69}Cl^{37}$			
$F_1 = 7/2 \leftarrow 5/2$;	$F = 5 \leftarrow, 4\ 4 \leftarrow 3, 3 \leftarrow 3, 3 \leftarrow 2, 2 \leftarrow 2, 2 \leftarrow 1$	$17\ 289.15 \pm 0.50$			
$F_1 = 5/2 \leftarrow 3/2$;	$F = 4 \leftarrow 3, 3 \leftarrow 3, 2 \leftarrow 1, 1 \leftarrow 1, 1 \leftarrow 0$				
		$Ga^{71}Cl^{37}$			
$F_1 = 7/2 \leftarrow 5/2$;	$F = 5 \leftarrow 4, 4 \leftarrow 3, 3 \leftarrow 3, 3 \leftarrow 2, 2 \leftarrow 2, 2 \leftarrow 1$	$17\ 118.24 \pm 0.50$			
$F_1 = 5/2 \leftarrow 3/2$;	$F = 4 \leftarrow 3, 3 \leftarrow 3, 2 \leftarrow 1, 1 \leftarrow 1, 1 \leftarrow 0$				

APPENDIX I—*Continued.*

GaBr: $J = 5 \leftarrow 4$

Hyperfine transition		$v = 0$	$v = 1$	$v = 2$
		Ga^{69}Br^{79}		
$F_1 = 7/2 \leftarrow 5/2$;	$F = 2 \leftarrow 1, 3 \leftarrow 2, 4 \leftarrow 3$ ⎫			
$F_1 = 9/2 \leftarrow 7/2$;	$F = 3 \leftarrow 2, 4 \leftarrow 3, 5 \leftarrow 4, 6 \leftarrow 5$ ⎪	24 771.22±0.20	24 673.55±0.20	24 576.08±0.20
$F_1 = 11/2 \leftarrow 9/2$;	$F = 4 \leftarrow 3, 5 \leftarrow 4, 6 \leftarrow 5, 7 \leftarrow 6$ ⎬			
$F_1 = 13/2 \leftarrow 11/2$;	$F = 5 \leftarrow 4, 6 \leftarrow 5, 7 \leftarrow 6, 8 \leftarrow 7$ ⎭			
$F_1 = 7/2 \leftarrow 5/2$;	$F = 5 \leftarrow 4$	24 768.02±0.20[a]		
$F_1 = 7/2 \leftarrow 7/2$;	$F = 5 \leftarrow 5$	24 796.70±0.30		
$F_1 = 7/2 \leftarrow 7/2$;	$F = 2 \leftarrow 2, 3 \leftarrow 3$	24 802.17±0.30		
		Ga^{69}Br^{81}		
$F_1 = 7/2 \leftarrow 5/2$;	$F = 2 \leftarrow 1, 3 \leftarrow 2, 4 \leftarrow 3$ ⎫			
$F_1 = 9/2 \leftarrow 7/2$;	$F = 3 \leftarrow 2, 4 \leftarrow 3, 5 \leftarrow 4, 6 \leftarrow 5$ ⎪	24 486.56±0.20	24 390.37±0.20	24 294.26±0.20
$F_1 = 11/2 \leftarrow 9/2$;	$F = 4 \leftarrow 3, 5 \leftarrow 4, 6 \leftarrow 5, 7 \leftarrow 6$ ⎬			
$F_1 = 13/2 \leftarrow 11/2$;	$F = 5 \leftarrow 4, 6 \leftarrow 5, 7 \leftarrow 6, 8 \leftarrow 7$ ⎭			
$F_1 = 7/2 \leftarrow 5/2$;	$F = 5 \leftarrow 4$	24 483.58±0.20		
		Ga^{71}Br^{79}		
$F_1 = 7/2 \leftarrow 5/2$;	$F = 2 \leftarrow 1, 3 \leftarrow 2, 4 \leftarrow 3$ ⎫			
$F_1 = 9/2 \leftarrow 7/2$;	$F = 3 \leftarrow 2, 4 \leftarrow 3, 5 \leftarrow 4, 6 \leftarrow 5$ ⎪	24 399.00±0.20		
$F_1 = 11/2 \leftarrow 9/2$;	$F = 4 \leftarrow 3, 5 \leftarrow 4, 6 \leftarrow 5, 7 \leftarrow 6$ ⎬			
$F_1 = 13/2 \leftarrow 11/2$;	$F = 5 \leftarrow 4, 6 \leftarrow 5, 7 \leftarrow 6, 8 \leftarrow 7$ ⎭			
		Ga^{71}Br^{81}		
$F_1 = 7/2 \leftarrow 5/2$;	$F = 2 \leftarrow 1, 3 \leftarrow 2, 4 \leftarrow 3$ ⎫			
$F_1 = 9/2 \leftarrow 7/2$;	$F = 3 \leftarrow 2, 4 \leftarrow 3, 5 \leftarrow 4, 6 \leftarrow 5$ ⎪	24 114.08±0.20		
$F_1 = 11/2 \leftarrow 9/2$;	$F = 4 \leftarrow 3, 5 \leftarrow 4, 6 \leftarrow 5, 7 \leftarrow 6$ ⎬			
$F_1 = 13/2 \leftarrow 11/2$;	$F = 5 \leftarrow 4, 6 \leftarrow 5, 7 \leftarrow 6, 8 \leftarrow 7$ ⎭			

GaI: $J = 7 \leftarrow 6$

Hyperfine transition		$v = 0$	$v = 1$	$v = 2$
		Ga^{69}I		
$F_1 = 17/2 \leftarrow 11/2$;	$F = 7 \leftarrow 6$ ⎫			
$F_1 = 15/2 \leftarrow 13/2$;	$F = 9 \leftarrow 8$ ⎪			
$F_1 = 13/2 \leftarrow 15/2$;	$F = 8 \leftarrow 7$ ⎬	23 857.29±0.20[a]	23 778.29±0.20[a]	23 698.78±0.30[a]
$F_1 = 17/2 \leftarrow 15/2$;	$F = 9 \leftarrow 8$ ⎪			
$F_1 = 19/2 \leftarrow 17/2$;	$F = 8 \leftarrow 7, 9 \leftarrow 8, 10 \leftarrow 9, 11 \leftarrow 10$ ⎭			
$F_1 = 15/2 \leftarrow 13/2$;	$F = 6 \leftarrow 5, 7 \leftarrow 6, 8 \leftarrow 7$	23 855.66±0.20[a]		
$F_1 = 9/2 \leftarrow 7/2$;	$F = 3 \leftarrow 2, 5 \leftarrow 4, 6 \leftarrow 5$ ⎫			
$F_1 = 13/2 \leftarrow 11/2$;	$F = 5 \leftarrow 4$ ⎬	23 853.25±0.40[a]		
$F_1 = 17/2 \leftarrow 11/2$;	$F = 8 \leftarrow 7$ ⎭			
$F_1 = 9/2 \leftarrow 7/2$;	$F = 4 \leftarrow 3$ ⎫			
$F_1 = 11/2 \leftarrow 9/2$;	$F = 4 \leftarrow 3, 7 \leftarrow 6$ ⎪	23 851.47±0.20[a]		
$F_1 = 13/2 \leftarrow 11/2$;	$F = 6 \leftarrow 5$ ⎬			
$F_1 = 13/2 \leftarrow 15/2$;	$F = 7 \leftarrow 6$ ⎭			
		Ga^{71}I		
$F_1 = 17/2 \leftarrow 11/2$;	$F = 7 \leftarrow 6$ ⎫			
$F_1 = 15/2 \leftarrow 13/2$;	$F = 9 \leftarrow 8$ ⎪			
$F_1 = 13/2 \leftarrow 15/2$;	$F = 8 \leftarrow 7$ ⎬	23 421.95±0.20[a]	23 344.45±0.30[a]	
$F_1 = 17/2 \leftarrow 15/2$;	$F = 9 \leftarrow 8$ ⎪			
$F_1 = 19/2 \leftarrow 17/2$;	$F = 8 \leftarrow 7, 9 \leftarrow 8, 10 \leftarrow 9, 11 \leftarrow 10$ ⎭			

[a] Owing to overlap of neighboring lines, the foregoing figures do not necessarily represent true line positions, but rather maxima corresponding to the designated transition.

APPENDIX II. DATA FOR DETERMINATION OF TlF DIPOLE MOMENT

Data on $J = 2 \leftarrow 1$, $v = 0$ line.

Voltage (volts)	Frequency (Mc/sec), $M = 1$ component
0	26 669.76±0.10
18.5	26 670.83±0.10