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The Molecular Beam Electric Resonance Method Study of Thallium Monochloride*†

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The hyperfine structure of the first rotational state of $TlCl^{35}$ and $TlCl^{37}$ was studied by the molecular beam electric resonance method. Two types of molecular transitions were observed: the conventional m_j transition in very weak and in strong Stark fields, the type previously studied in several alkali fluorides; the ΔJ transition ($J=0\rightarrow J=1$), a molecular transition observed for the first time by molecular beam methods in this experiment.

Using the m_j type transition, the electric quadrupole interactions involving the chlorine nuclei were determined for the $J=1$, $v=0$ state. The values were $eqQ(TlCl^{35})=-(15.795\pm0.004)$ Mc/sec, $eqQ(TlCl^{37})=-(12.446\pm0.003)$ Mc/sec. The ratio of quadrupole interactions, 1.2691 ± 0.0004, is in good agreement with the ratio found for other chlorine molecules and for the chlorine atoms. The quadrupole interaction increased in absolute value by $\frac{1}{2}$ percent from one vibrational state to the next higher one. The spin-rotation ($\mathbf{I}\cdot\mathbf{J}$) interaction constants in TlCl were $+(73\pm2)$ kc for Tl, $+(1.2\pm0.2)$ kc for Cl^{35}, and $+(1.0\pm0.2)$ kc for Cl^{37}. These quadrupole interaction constants and the spin-rotation interaction constants for chlorine agree with the values given by the molecular beam magnetic resonance method.

From the rotational transition data and the strong Stark field m_j transition data, the following molecular constants were evaluated for $Tl^{205}Cl^{35}$: the rotational constant $B_e=(2620.1\pm2.5)$ Mc/sec; moment of inertia $A_e=(320.2\pm0.4)\times10^{-40}$ g-cm^2, internuclear distance $r_e=(2.541\pm0.002)$A, and dipole moment for the zeroth vibrational state $\mu_0=(4.444\pm0.014)$ Debye. The internuclear distance is in very good agreement with the electron diffraction value, (2.55 ± 0.03)A, in contrast to the case of KCl and CsCl where discrepancies of 3 to 5 percent exist between electric resonance method values and the electron diffraction experiment values. Within the experimental error, the vibration-rotation interaction constant, (13 ± 1) Mc/sec, agrees with the theoretical value predicted assuming a Morse potential for this molecule.

I. INTRODUCTION

THE molecular beam electric resonance method[1] has been used to study the molecular structure of $TlCl^{35}$ and $TlCl^{37}$. This method was previously used to investigate the radiofrequency spectra of the polar diatomic molecules CsF,[2] RbF,[3] and KF.[4] Both the thallium chlorides and the alkali fluorides were studied in the $^1\Sigma$ ground states of these molecules. The thallium compounds, however, represent a somewhat different type of molecule because the thallium atom exists in a P ground state while the alkali atoms in the alkali fluorides are in S ground states.

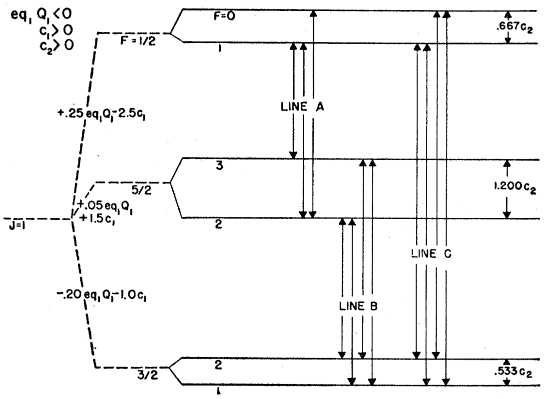

FIG. 1. The energy levels of the first rotational state of a diatomic molecule with one quadrupole moment. Observed m_j transitions are "lines A, B, and C." Arbitrary energy units. The c_2 spin-rotation splitting is greatly exaggerated in the figure relative to the quadrupole interaction splitting.

From observation of the hyperfine structure of the first rotational state of thallium chloride, it was possible to determine the electric quadrupole interactions arising from the quadrupole moments of the chlorine nuclei, and the spin-rotation ($\mathbf{I}\cdot\mathbf{J}$) interactions between the molecular angular momentum J and the chlorine or thallum nuclear spin. Other quadrupole interactions involving the chlorine nuclei have been measured in the atoms and in molecules by molecular beam magnetic resonance and microwave absorption methods.

The molecular transitions which were observed for thallium monochloride were of two types. One type of transition was between two states with the same rotational quantum number J but different values of the electric quantum number m_j, the projection of $\mathbf{J}$ in the direction of the applied electric field. This m_j transition has been used to study the $J=1$ and $J=2$ states of the alkali fluorides. A description of the apparatus and the techniques used to obtain a refocused beam in these states is given in the papers on the fluorides. The specific transition which was observed in TlCl by similar techniques was the $(1,0)-(1,\pm1)$ transition.

The second type of transition observed for $Tl^{205}Cl^{35}$ was between two energy levels in different rotational states. Such molecular transitions have been observed by microwave absorption methods for many molecules. An absorption method, however, is very difficult to use for most diatomic molecules because of the high temperatures required to form a vapor of these molecules and the consequent difficulty of keeping the absorbing wave guide hot enough to prevent excessive condensation on its walls. Neither thallium nor alkali halide molecules have as yet been studied by absorption methods.

This experiment marks the first time that a rotational

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[1] H. K. Hughes, Phys. Rev. **72**, 614 (1947).

[2] J. W. Trischka, Phys. Rev. **74**, 718 (1948).

[3] V. Hughes and L. Grabner, Phys. Rev. **79**, 314 (1950).

[4] L. Grabner and V. Hughes, Phys. Rev. **79**, 819 (1950).

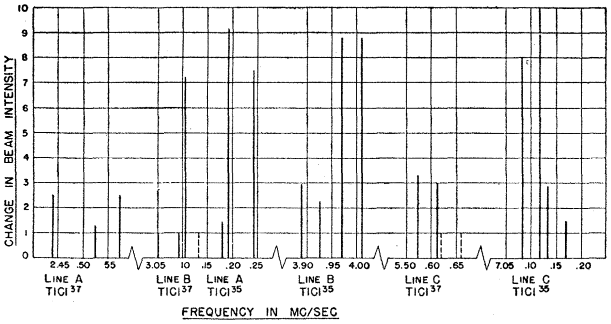

FIG. 2. Schematic plot of very weak field spectrum of $TlCl^{35}$ and $TlCl^{37}$. Zero vibrational state lines only. Dotted lines indicate predicted lines not distinguishable because of overlap with higher vibrational state lines.

transition in a molecule has been observed by a molecular beam method.[5] The entire group of alkali and thallium halides is now open to systematic study by this rotational transition method for the determination of such molecular data as the moment of inertia, internuclear distance, dipole moment, and quadrupole interactions.

Since for the rotational transition the observed energy level differences will have a dependence on the moment of inertia and hence reduced mass of the molecule, the spectral patterns for isotopic molecules will be separated from one another. In addition, because of the vibration-rotation interaction, the transition frequency which corresponds to a certain energy level separation will be appreciably different for molecules in different vibrational states.

II. THEORY AND DATA

1. The m_j Transition

The m_j transition ($\Delta J=0$) in a diatomic molecule is strictly forbidden in the absence of a static electric field. An applied Stark field superimposed on the radio-frequency C-field makes the transitions possible but splits the energy levels of the molecule and complicates the spectrum. To obtain the hyperfine structure pattern of the $J=1$ state of TlCl, the Stark field was made as small as possible consistent with observability of the transition so that the field corrections would be small. It was found possible to observe all the lines at fields of less than 5 v/cm. Corrections of less than 2 kc were then necessary to find the zero field spectrum.

The energy levels and selection rules for m_j transitions in the alkali fluorides are discussed in detail in an earlier paper.[6] This description of the energy levels is directly applicable to thallium chloride. The thallium nucleus takes the place of the fluorine nucleus since both nuclei have a spin of $\frac{1}{2}$ and hence no quadrupole moment. The chlorine nucleus has a spin of $\frac{3}{2}$ and replaces the alkali nucleus which has a quadrupole moment. The subscript 1 in this paper will apply to the chlorine nucleus and subscript 2 to the thallium nucleus.

The zero field energy levels and observable frequency pattern for a diatomic molecule in the first rotational state and with $I_1=\frac{3}{2}$, $I_2=\frac{1}{2}$, eq_1Q_1 negative, c_1 and c_2 positive, is shown in Fig. 1. The chlorine spin I_1 is coupled to J through the quadrupole interaction and the chlorine spin-rotation interaction and splits the $J=1$ rotational level into three F_1 levels where $\mathbf{F}_1=\mathbf{I}_1+\mathbf{J}$. Further splitting of the F_1 levels, caused by the coupling of the thallium spin and J through the thallium spin-rotation interaction, gives rise to the $\mathbf{F}=\mathbf{F}_1+\mathbf{I}_2$ levels. The latter splitting is much smaller than the quadrupole splitting. To show the splitting clearly in Fig. 1, however, the F levels are drawn much further apart than they would be if the figure were to scale. In the case of TlCl, the quadrupole splitting is of the order of several megacycles while the thallium spin-rotation splitting is less than 100 kc.

Transitions are observed between F states subject to various selection rules and the observability criterion.[6] The latter criterion requires that m_j change by unity in the C-field region for a transition to be observable as a defocusing of the molecular beam. Figure 2 is a schematic plot of the spectrum of $TlCl^{35}$ and $TlCl^{37}$ observed under very weak field conditions. These transitions were for zeroth vibrational state molecules only. Molecules in higher vibrational states have a spectrum slightly shifted from the frequency positions shown because of the dependence of quadrupole interaction on vibration.

The resolution[2] of the observed pattern at very weak fields is determined by the line width arising from the uncertainty relation $\Delta\nu\Delta t\sim 1$, where Δt is the time during which a transition can occur, that is, the time a molecule spends in the 4 cm wide C-field region. The oven source for a TlCl beam is at approximately 600°K. This means that the average velocity of a molecule in the beam is 2.5×10^4 cm/sec. $\Delta\nu$ is then about 6 kc. The full width at half-maximum of the observed lines was 5 to 6 kc for the narrowest lines.

When the Stark field is made very large, the field splitting becomes much larger than the quadrupole interaction splitting and the predicted pattern of observable lines becomes a known function of dipole

TABLE I. Internal interactions in TlCl for the observed line groups; $J=1$, $v=0$ state.

Molecule	Line group	$+C_2/h$ kc	$-eqQ/h$ Mc/sec Before C_1 correction	$-eqQ/h$ Mc/sec After C_1 correction
$TlCl^{35}$	A	74 ± 1	15.7697	15.7937 ± 0.015
	B	71 ± 2	15.8021	15.7901 ± 0.010
	C	74 ± 3	15.7939	15.7979 ± 0.005
$TlCl^{37}$	A	73 ± 2	12.4272	12.4474 ± 0.015
	B	75 ± 5	12.4596	12.4496 ± 0.010
	C	73 ± 3	12.4401	12.4434 ± 0.005

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[5] A complete description of the apparatus and the techniques used for the rotational transition data will be given in a forthcoming paper by us on potassium chloride.

[6] V. Hughes and L. Grabner, Phys. Rev. **79**, 829 (1950).

TABLE II. Internal interactions in TlCl; $J=1$, $v=0$ state.

Molecule	$+C_1{}^a/h$ kc	$H_1{}^a$ gauss	Average $+C_2{}^b/h$ kc	$H_2{}^b$ gauss	$-eqQ/h$ Mc/sec weighted average	Ratio of quadrupole interactions
$TlCl^{35}$	1.2 ± 0.2	2.9 ± 0.5	73 ± 2	29.6 ± 0.9	15.7950 ± 0.004	1.2691 ± 0.0004
$TlCl^{37}$	1.0 ± 0.2	2.9 ± 0.6	73 ± 2	29.6 ± 0.9	12.4458 ± 0.003	

[a] Subscript 1 = Cl.
[b] Subscript 2 = Tl.

moment μ, moment of inertia A, and the static field E.[7] A plot of the energy levels of a diatomic molecule *vs* the square of the applied electric field is given in the KF paper[4] as Fig. 2(a). The pattern of observable lines consists of seven lines separated by known fractions of the quadrupole interaction. Line 1, the lowest frequency line of the pattern, was observed in $Tl^{205}Cl^{35}$ for Stark fields between 600 and 800 v/cm. The line 1 frequencies were in the range 100 to 200 Mc/sec. Only zeroth vibrational state lines were resolved since higher vibrational state lines overlap other lines in the pattern.

Under strong field conditions, the line width is principally determined by the nonuniformity of the C-field gap.[2] For the field values used in these experiments the line widths were more than 100 kc so that the spin-rotation interaction splittings could be neglected. To find the position of the unperturbed Stark line, that is, the position in the absence of quadrupole interaction splitting, corrections were made to the observed line 1 frequencies for both the diagonal and off-diagonal matrix elements of the quadrupole operator in the suitable strong field representation.[6] The effect of mixing of J states by the applied static field was also taken into account in the calculations.

2. The Rotational Transition

The rotational energy levels of a vibrating rotator model diatomic molecule in zero field, exclusive of hyperfine structure, are given by[8] $W=B_eJ(J+1)-\alpha_e(v+\frac{1}{2})J(J+1)+\cdots$ where $B_e=\hbar^2/2A$ is the rotational constant of the molecule and α_e is the vibration-rotation interaction constant. The rotational transition, in contrast to the m_j transitions, can be observed at zero Stark field, and all runs in TlCl were made under this condition.

The spectrum of the $J=0$ to $J=1$ transition will consist of a series of lines, with a spacing of $2\alpha_e$ between adjacent vibrational state lines. Since the zeroth rotational state has negligible hyperfine structure, the transition pattern for a given vibrational state will be further split only by the hyperfine structure of the $J=1$ state. The spectral patterns for $Tl^{205}Cl^{35}$ and $Tl^{203}Cl^{35}$ do not coincide in frequency for the rotational transition whereas they do for the very weak field m_j transition because their quadrupole interactions are identical.

The most intense line of the observed rotational transition spectrum of $Tl^{205}Cl^{35}$ was located at 5228 Mc/sec. The hyperfine structure of this $v=0$ line was only partially resolved because excessive power from a 2K43 klystron was fed into the C-field region. Several other lines were observed so that a definite assignment of this line to one of the four isotopic species of TlCl could be made. The peak of a power-broadened line corresponding to the $v=2$ state line of $Tl^{205}Cl^{35}$ was located at 5176 Mc/sec, and from the difference in frequency of this vibrational state line and the zeroth vibrational state line, the value of α_e was computed.

III. RESULTS

From the splitting of line groups A, B, and C into three or four components (see Fig. 2), we could calculate the value of c_2 and the positions of the F_1 levels after small corrections were made to account for the dipole-dipole interaction, the second-order $\mathbf{I}_2\cdot\mathbf{J}$ interaction, and the second-order quadrupole interaction coupling the $J=1$ and $J=3$ states. The quadrupole interaction constants were then computed for the three line groups as tabulated in Table I. Finally the value of c_1 was chosen which gave best agreement for the eq_1Q_1 values of a given isotope.

The averaged values of c_1, c_2, and eq_1Q_1 are listed in Table II, together with the ratio of the eq_1Q_1's for the two chlorine isotopes. H_1 and H_2 are the magnetic fields per unit rotational quantum number at the chlorine and thallium nuclei produced by the molecular rotation as computed from the equation $H=hc/\mu_Ng$. The errors listed for each quantity in the table take account of the estimated accuracy of measurement of frequency and the line position centers.

In Table III are listed the molecular constants for $Tl^{205}Cl^{35}$ as determined from a combination of the rotational transition data and the strong field m_j transition data. Only the $\mu_0{}^2A_0$ product was used from the latter set of data although the moment of inertia and dipole moment were also calculated from this data. The values were $A_0=(331\pm16)\times10^{-40}$ g-cm^2 and $\mu_0=(4.38\pm0.15)\times10^{-18}$ esu. The $\mu_0{}^2A_0$ product can be determined from the m_j transition data to a much higher precision than either A_0 or μ_0 separately. The coefficient of the quadratic term in the expression[7] for the dependence of frequency of the m_j transition on electric field contains $\mu_0{}^2A_0$. The A_0 and μ_0 are calculable

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[7] H. K. Hughes, Phys. Rev. 76, 1675 (1949).

[8] G. Herzberg, *Molecular Spectra and Molecular Structure, I. Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950), second edition, p. 106 ff.

only by observing the departure of the frequency from an E^2 field dependence.

IV. DISCUSSION

The quadrupole interactions in thallium chloride are about forty times those for an alkali chloride[9] and one-seventh that found for the chlorine atoms.[10] The negative signs of both quadrupole interactions, as determined by the observability criterion for the m_j transitions, is the same as that given for eqQ in all chlorine molecules previously investigated by microwave absorption methods.[11] The ratio of the eqQ's in $TlCl^{35}$ and $TlCl^{37}$ is in excellent agreement with other recent measurements on chlorine compounds.[10,12]

Higher vibrational state lines in the very weak Stark field m_j transition spectrum were found to be displaced to slightly higher frequencies than the corresponding $v=0$ lines. To account for this pattern, the absolute value of quadrupole interaction constant must increase by about $\frac{1}{2}$ percent for an increase of unity in the vibrational quantum number. This shift is in the opposite direction to the case of the alkali fluorides[3,4] where a decrease of about 1 percent in eqQ was observed on going to the next higher vibrational state.

A study of thallium chloride has been made simultaneously with this investigation by Zeiger and Bolef[13] using the molecular beam magnetic resonance method. The quadrupole interaction constants and the c_1 constant can be determined from their zero magnetic field spectrum. Their numerical values are in agreement with the electric resonance method results listed in Table II. This agreement provides a strong check on the validity of the analysis of the observed spectra in the two methods.

The value of the spin-rotation interaction constant, c_2, is much larger than any spin-rotation interaction constants previously reported.[2,3] Both the sign and magnitude of c_2 are definitely established by the close fit of observed and theoretical spectral patterns. The positive sign of c_2 is predicted by Foley's theory and model of the spin-rotation interaction,[14] and is the same sign as that reported for all other molecules in which this type of interaction has been observed.

It is of interest to note[15] that the ratio of the spin-rotation interactions for the thallium and chlorine nuclei, $c_2/c_1(Cl^{35})$, is equal to $73/1.2=61$, which is approximately the same as the ratio of the hyperfine structure splittings,

$$\Delta\nu(Tl)/\Delta\nu(Cl^{35})=21300^{16}/410^{10}=52.$$

TABLE III. Molecular constants of $Tl^{205}Cl^{35}$.

Quantity	Value	Units
A_e	320.2 ± 0.4	10^{-40} g-cm^2
B_e	2620.1 ± 2.5 874.0 ± 0.8	Mc/sec 10^{-4} cm^{-1}
r_e	2.541 ± 0.002	10^{-8} cm
μ_0	4.444 ± 0.014	10^{-18} esu
$\mu_0{}^2A_0$	63.4 ± 0.3	10^{-74} g-cm^2-esu
α_e	13 ± 1	Mc/sec

The internuclear distance, r_e which is tabulated in Table III, is in very good agreement with less accurate results obtained by two other methods.[17] An electron diffraction experiment gave a value of (2.55 ± 0.03)A, while band spectroscopy gave a value of 2.53A. This excellent agreement of the present experimental value and the electron diffraction value for TlCl is in marked contrast to the case of KCl[9] and CsCl.[18] In KCl, the electric resonance rotational transition value was about 3 percent less than the electron diffraction value,[19] while for CsCl the electric resonance m_j transition value was about 5 percent less than the electron diffraction value.[19]

If the percent of ionic character be defined as the ratio of the dipole moment to the product of internuclear distance and electronic charge, then the value for TlCl is 37 percent.

Within its rather large experimental error, the vibration-rotation interaction constant, α_e, which is (13 ± 1) Mc/sec, agrees with the theoretical value[20] of 13.2 Mc/sec computed from the assumption of a Morse potential for the TlCl molecule. Thallium chloride, in this respect, is radically different from the case of potassium chloride[9] where the experimental value of α_e and the Morse potential calculated value differ by about 30 percent.

We wish to express our thanks to Professor I. I. Rabi for his valuable suggestions on experimental techniques and his continued aid in the interpretation of observed spectral patterns. We have benefited from discussions with Professor H. M. Foley concerning the spin-rotation interactions. Professor Foley suggested the use of the term spin-rotation interaction rather than the previously used term spin-orbit interaction for the **I·J** interaction in a molecule. The apparatus on which the rotational transition was observed was constructed by Dr. V. W. Hughes.

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[19] Maxwell, Hendricks, and Mosley, Phys. Rev. **52**, 968 (1937).

[20] See reference 8, p. 108.