matrix **C** [Eq. (1)], the elements of which are listed in Table I, together with the orbital energies, ϵ. The results of the CI calculation for the singlet states are given by the matrix $^1\mathbf{U}$ [Eq. (13)], with its elements shown in Table II. The wavefunctions are classified by their symmetry types, $^1A_1$ and $^1B_2$.[16] In Table II are also recorded both calculated and observed state energies, $E-E_0$, and oscillator strengths, f.[17]

In order to apply the configuration analysis to the results of the above calculations, reference MO's are chosen which consist of the MO's localized in the benzene ring and on the oxygen atom. The elements of the matrix $\mathbf{C}^0$ [Eq. (2)][16] are given in Table III, and those of the matrix **B** [Eq. (3)] in Table IV.

Each of the singlet configurations V_σ included in the CI calculation (see Table II) is now analyzed into the $V_{\sigma'}{}^0$'s in the form of Eq. (11). The coefficients $^1l_{\sigma'\sigma}$ were computed for all the 12 singly excited configurations $V_{ik}{}^0$ and some doubly excited configurations as well as for the ground configuration $V_0{}^0$. Of these nine configurations $V_{\sigma'}{}^0$ of greater weights are here considered which are shown in Table V. In this table are given the elements of the matrix $^1\mathbf{L}$ [Eq. (14)], together with the total weight of the $V_{\sigma'}{}^0$'s, $\sum_{\sigma'} {}^1l_{\sigma'\sigma}{}^2$, for each of the V_σ's.

The elements of the matrix $^1\mathbf{U}^0$ [Eq. (15)][16] and the values of $E^0-E_0{}^0$ are shown in Table VI.[17] The Platt notation[18] is employed for classification of the states. CT means charge transfer, and S and A denote the symmetric and antisymmetric functions, respectively, with respect to σ_v. Finally, the elements of the matrix $^1\mathbf{M}$ [Eq. (16)] are shown in Table VII, where the total weight is defined as in the case of the matrix $^1\mathbf{L}$. Inspection of the weights of the individual $^1\Psi^0$'s leads to an assignment of each state wavefunction $^1\Psi$, with the results given in the table.

Analogous calculations were carried out with respect to the triplet states. The final results are summarized in Table VIII.

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Hyperfine Structure of Thallium Chloride*

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The radio-frequency spectra of TlCl at very weak electric and magnetic fields have been measured with a molecular beam electric resonance spectrometer. From these spectra the hyperfine interaction constants for the four isotopic species of the molecule were calculated. The constants for $^{205}Tl^{35}Cl$ in the $J=2$, $v=0$ state are: $eqQ=-15793.32(50)$ kHz, $c_{Cl}=1.38(10)$ kHz, $c_{Tl}=76.35(10)$ kHz, $c_3=-0.13(10)$ kHz, $c_4=-1.54(10)$ kHz. A test was made for the polarization of the chlorine nucleus in the electric field of the molecule by comparing the ratio of the quadrupole interaction constants for $^{205}Tl^{35}Cl$ and $^{205}Tl^{37}Cl$ to the ratio of the quadrupole interaction constants for the free chlorine atoms. The agreement of the two ratios is within their uncertainties, thus providing no evidence for a polarization effect. In addition, the dependence of the spin–rotation and spin–spin interaction constants on isotope was found to show good agreement with theory.

INTRODUCTION

We have measured the hyperfine structure of the thallium chloride molecule in all four of its isotopic species with a high-resolution molecular beam electric resonance (MBER) spectrometer. The spectrum of TlCl has been measured before by the methods of molecular beam electric resonance,[1] molecular beam magnetic resonance,[2] and microwave absorption.[3] The results from these earlier experiments, however, do not match the precision of the recent studies on TlF,[4] TlBr,[5] and TlI,[6] in which even the small spin–spin interactions were measured to accuracies of a few percent. With the results presented here, it is now possible to make detailed comparisons of the hyperfine interactions either among the isotopic species of a given thallium halide or among the entire family of thallium halides. For example, because of the

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similarity in the hyperfine structure for the isotopic species of TlCl, it is particularly easy to see how changes of nuclear mass and nuclear moment affect the hyperfine interactions.

THE EXPERIMENT

The MBER spectrometer and the experimental procedure are described in detail elsewhere.[7] A transition region 51 cm long gives a linewidth of 500 Hz. The electric and magnetic fields in the transition region are minimal (1.5 V/cm and 0.05 Oe, respectively), so that Stark and Zeeman effects can be neglected. The oven is a stainless-steel tube with a glass test tube inside to protect the stainless steel from the corrosive effects of the molten TlCl.

Transitions for each of the four isotopic species were found, with those corresponding to the $J=2$, $v=0$ states being the most intense. $J=2$, $v=1$ and $J=1$, $v=0$ transitions were also seen in the most abundant species, $^{205}Tl^{35}Cl$. Figure 1 is an energy-level diagram for the $J=2$ state of the latter species.

INTERPRETATION

If a TlCl molecule in its $^1\Sigma$ electronic ground state is in sufficiently weak external electric or magnetic fields, its hyperfine structure can be described by a Hamiltonian containing five constants which characterize the interactions in the molecule[7]: eqQ (the electric quadrupole interaction); c_{Cl} and c_{Tl} (the spin–rotational interaction for each nucleus); c_3 and c_4 (the tensor and scalar parts of the nuclear spin–spin interaction).

The interaction constants were obtained by using a least-squares criterion for best fit between the observed spectrum and the predictions of the zero-field Hamiltonian. The calculations included the effect of the coupling between J states by the electric quadrupole interaction and the coupling between F_1 states by the magnetic hyperfine interactions.[8]

The results of this experiment are shown in Table I, where they are compared to the previous work. The accuracy of the interaction constants is limited principally by: (1) Residual electric and magnetic fields in the transition region which can cause a line to shift on the order of 100 Hz from the zero-field position; and (2) a nominal 50-Hz error in determining the line centers.

The adequacy of the zero-field approximation can be tested by using the final values of the hfs constants to fit the spectrum from the $J=1$ and $J=2$ states of $^{205}Tl^{35}Cl$. The Stark and Zeeman effects are known to depend strongly on J, yet the predictions of the zero-field Hamiltonian fit the spectra from both rotational states to within 80 Hz, so we conclude that the interactions with the external fields can be neglected safely in analyzing the spectrum from these measurements.

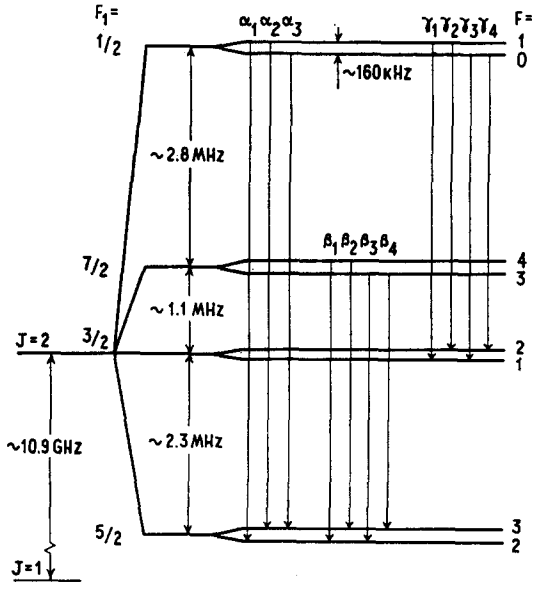

FIG. 1. Energy-level diagram for the $J=2$ state of $^{205}Tl^{35}Cl$. The frequency of the most intense transition, γ_2, is 3938.05 kHz.

DISCUSSION

It is reasonable to suppose that strong electric fields and field gradients from surrounding electrons are capable of deforming, or polarizing, nuclei within the molecule. In particular, it has been suggested that the apparent dependence on environment of the ratio of quadrupole coupling constants for the chlorine isotopes was evidence for nuclear polarization.[9] To compare the ratio of the quadrupole interactions of the two chlorine isotopes as measured in TlCl, we form the ratio

$$R_Q=[eq(r_e)Q]^{205}Tl^{35}Cl/[eq(r_e)Q]^{205}Tl^{37}Cl,$$

where r_e is the equilibrium internuclear separation.[10] Since r_e is the same for both species of the molecule,[3] it is reasonable to assume that $q(r_e)$ is the same for both. Then R_Q is equal to the ratio of nuclear quadrupole moments, $Q^{35}Cl/Q^{37}Cl$, and, in the absence of nuclear polarization, it should be equal to the ratio of quadrupole interactions measured in free atoms. For TlCl we find $R_Q=1.26895(8)$ which may be compared to the value 1.2688773(15) measured in atomic

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[10] $eq(r_e)Q$ was calculated from the equation $eq(r)Q=eq(r_e)Q+aJ(J+1)+b(v+\frac{1}{2})$ where a is negligibly small. Since only $v=0$ states were measured in $^{205}Tl^{37}Cl$, to evaluate b it was necessary to assume that the percentage change in $eq(r)Q$ between the $v=0$ and the $v=1$ states is the same for both $^{205}Tl^{35}Cl$ and $^{205}Tl^{37}Cl$. We know from TlBr data that this assumption is reasonable.

TABLE I. Hyperfine-structure constants (in kilohertz).

Molecule	J	v	eqQ	c_{Cl}	c_{Tl}	c_3	c_4
Present work:							
$^{205}Tl^{35}Cl$	1	0	−15 793.29(50)	1.39(15)	76.36(15)	−0.15(15)	−1.57(15)
	2	0	−15 793.32(50)	1.38(10)	76.35(10)	−0.13(10)	−1.54(10)
	2	1	−15 873.87(50)	1.37(10)	75.98(10)	−0.10(10)	−1.55(10)
$^{203}Tl^{35}Cl$	2	0	−15 793.31(50)	1.40(10)	75.77(10)	−0.09(10)	−1.52(10)
$^{205}Tl^{37}Cl$	2	0	−12 445.94(50)	1.10(15)	72.82(15)	−0.13(15)	−1.28(15)
$^{203}Tl^{37}Cl$	2	0	−12 446.64(20)	1.21(50)	71.80(50)	−0.56(50)	−1.11(50)
Previous results:							
Zeiger and Bolef[a]							
$Tl^{35}Cl$	...	0	−15 788(20)	1.4(1)			
	...	1	−15 884(20)				
$Tl^{37}Cl$	...	0	−12 425(20)	1.1(1)			
	...	1	−12 501(20)				
Carlson, Lee, and Fabricand[b]							
$Tl^{35}Cl$	1	0	−15 795(4)	1.2(2)	73(2)		
$Tl^{37}Cl$	1	0	−12 446(3)	1.0(2)	73(2)		

[a] See Ref. 2. [b] See Ref. 1.

chlorine.[11] Thus there is no evidence that the chlorine nucleus is polarized in the TlCl molecule.

We may also use the measured interaction constants to test some general concepts of the magnetic hyperfine structure in molecules. Consider, for example, ratios of the type,

$$(c_{Cl})_X/(c_{Cl})_Y, \quad (c_{Tl})_X/(c_{Tl})_Y,$$
$$(c_3)_X/(c_3)_Y, \quad \text{or} \quad (c_4)_X/(c_4)_Y, \quad X \neq Y,$$

where X and Y each denote one of the four isotopic species of TlCl. Reasonable theories of the spin–rotational interaction[12] predict that when considering only isotopic substitution, the spin–rotational constant of a nucleus is proportional to its magnetic dipole moment, and to the rotational constant of the molecule. Similarly, a theory of the spin–spin interactions[13] predicts that under isotopic substitution, the spin–spin interaction constants, c_3 and c_4, are proportional to the product of the dipole moments of both nuclei. The hyperfine constants measured in this experiment on thallium chloride show excellent agreement with these expected proportionalities.

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