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THE HIGH FREQUENCY PARAMAGNETISM AND ELECTRONIC CONFIGURATION OF POST-TRANSITION METAL IONS IN PURE SALTS

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CONTENTS

A. INTRODUCTION

The nature of the electronic structure and bonding in transition metal compounds and complex ions has received much attention in recent years. While the general features of the bonding in these cases is reasonably well understood, a completely quantative treatment is still seriously lacking. The post-transition elements of the B-subgroups, on the other hand, have been much neglected in this regard, and only a very few attempts have been made toward a systematic approach in understanding their electronic structures and bonding.

Arguments based on statistical displacements from cubic environments, in accord with the Jahn–Teller theorem, have been advanced by Orgel[1,2] in an effort to rationalize the electronic structures of post-transition metal ions in their simple salts and complexes. Ions of the type: Cu^+, Zn^{2+}, Ag^+, Cd^{2+}, Au^+, Hg^{2+}, have $nd^{10}(n+1)s^0$ ground states, while the ions: Sn^{2+}, Sb^{3+}, Tl^+, Pb^{2+}, Bi^{3+}, have $ns^2(n+1)p^0$ configurations. If an ion having an nd^{10} configuration is subjected to antisymmetric displacements of two or more anions, the displacements will remove the centre of symmetry of the environment of the ion, thus producing an electric field which can mix d and p orbitals but not d and s orbitals. Symmetric displace-

TABLE 1

RELATIVE ONE ELECTRON ENERGY LEVELS OF POST-TRANSITION METAL IONS[a]

Ion	*Electronic configuration*	nd	$n\mathrm{d}^9(n+1)\mathrm{s}$	$n\mathrm{d}^9(n+1)\mathrm{p}$	$n\mathrm{s}^2$	$n\mathrm{s}n\mathrm{p}$	ΔE_{ds}	ΔE_{dp}	ΔE_{sp}
$\mathrm{Cu^I}$	$(\mathrm{Ar})3\mathrm{d}^{10}4\mathrm{s}^0$	20.3	17.6	12.1	—	—	2.7	8.2	—
$\mathrm{Zn^{II}}$	$(\mathrm{Ar})3\mathrm{d}^{10}4\mathrm{s}^0$	39.7	30.1	22.6	—	—	9.7	17.1	—
$\mathrm{Ag^I}$	$(\mathrm{Kr})4\mathrm{d}^{10}5\mathrm{s}^0$	21.5	16.7	11.6	—	—	4.9	9.9	—
$\mathrm{Cd^{II}}$	$(\mathrm{Kr})4\mathrm{d}^{10}5\mathrm{s}^0$	37.5	27.5	20.3	—	—	10.0	17.2	—
$\mathrm{Au^I}$	$(\mathrm{Xe})5\mathrm{d}^{10}6\mathrm{s}^0$	20.5	18.6	12.7	—	—	1.9	7.8	—
$\mathrm{Hg^{II}}$	$(\mathrm{Xe})5\mathrm{d}^{10}6\mathrm{s}^0$	34.2	28.9	19.5	—	—	5.3	14.7	—
$\mathrm{Tl^{III}}$	$(\mathrm{Xe})5\mathrm{d}^{10}6\mathrm{s}^0$	50.7	41.4	32.4	—	—	9.3	18.3	—
$\mathrm{Sn^{II}}$	$(\mathrm{Kr})4\mathrm{d}^{10}5\mathrm{s}^2 5\mathrm{p}^0$	—	—	—	30.5	21.5	—	—	9.0
$\mathrm{Sb^{III}}$	$(\mathrm{Kr})4\mathrm{d}^{10}5\mathrm{s}^2 5\mathrm{p}^0$	—	—	—	44.1	33.5	—	—	10.6
$\mathrm{Tl^I}$	$(\mathrm{Xe})5\mathrm{d}^{10}6\mathrm{s}^2 6\mathrm{p}^0$	—	—	—	20.4	11.9	—	—	8.5
$\mathrm{Pb^{II}}$	$(\mathrm{Xe})5\mathrm{d}^{10}6\mathrm{s}^2 6\mathrm{p}^0$	—	—	—	31.9	21.2	—	—	10.7
$\mathrm{Bi^{III}}$	$(\mathrm{Xe})5\mathrm{d}^{10}6\mathrm{s}^2 6\mathrm{p}^0$	—	—	—	45.3	32.5	—	—	12.8

[a] See reference 15.

ments, on the other hand, will mix d and s orbitals but not d and p. Since the d–s promotion energies (see Table 1) are considerably smaller than those of d–p, it is expected that the symmetric distortions will be of prime importance. In the case of $n\mathrm{s}^2$ ions, antisymmetric displacements will lead to mixing of s and p levels, and it is to be expected that the extent of mixing will be greatest in low centres of symmetry. Although the s–p promotion energies of these latter ions (see Table 1) are generally somewhat high in the free gaseous state, there will be a considerable energy reduction as a consequence of electrostatic polarization and crystalline field effects in the crystalline environment.

The problem of bonding hence reduces to one of evaluating the extent of d–s or s–p mixing in d^{10} and s^2 ions respectively. It has been shown that the interconfigurational mixing proposed leads to non zero high frequency paramagnetic terms in the diamagnetic susceptibilities and chemical shifts in the NMR spectra of these ions[3,4]. However, a critical examination of the magnetic susceptibility is somewhat more favorable than the chemical shift in providing a convenient probe for estimating the extent of such mixing. While NMR studies can be carried out with considerably higher precision and accuracy than conventional susceptibility measurements, the chemical shift must be evaluated relative to some reference standard. The only suitable reference for these purposes is the free gaseous ions; however, the magnetogyric ratios of the ions in question are for the most part unknown. Henceforth it is more desirable to resort to magnetic susceptibility data which are not subject to the same limitations. Even though there is some loss in accuracy the results will lead to no less certain conclusions than what the chemical shift data can provide.

A second order perturbation treatment of molecular diamagnetism leads to the expression[5]

$$\chi_M = -Ne^2/6mc^2 \sum_i \overline{r^2} + \tfrac{2}{3} N \sum_{n \neq o} \frac{|m^0(n_i;0)|^2}{E_n - E_0} = \chi_D + \chi_{HF} \tag{1}$$

where r^2 is the average value of the square of the radius of the electronic orbitals and the sum is extended over all i electrons; $|\, m^0(n;0) \,|$ are the non-diagonal matrix elements of $\sum (e/2mc)l_i$; (the total orbital angular momentum) connecting the ground state with the n^{th} excited states; $E_n - E_0$ is the energy separation between the ground and n^{th} excited states, and the other terms have their usual significance. Although the high frequency paramagnetic term, χ_{HF}, will never vanish in the case of molecules, it will be zero in centrosymmetric monoatomic ions having closed shell configurations. However, interconfigurational mixing will remove the center of symmetry thus leading to non-zero values of χ_{HF}. In characteristically ionic solids involving ions of low atomic number interconfigurational mixing is not feasible, and hence except for small covalency effects, the susceptibility is governed primarily by the diamagnetic, χ_D, terms of the respective ions. Even in molecules, χ_D may be reduced to a sum over the χ_d terms of the respective atoms[6]. For hydrogenic like wave functions, χ_d, is given by

$$\chi_d = -0.790 \sum_i \left[\frac{5n^4 - 3n^2 l(l+1) + n^2}{2(Z-\sigma)^2}\right]_i \times 10^{-6} \tag{2}$$

where the summation is over all i electrons in each of the nl orbitals. One can hope to calculate such χ_d terms with reasonable accuracy in the case of salt like systems, by incorporating Burns'[7] procedure for evaluating the effective nuclear charge of the respective ions. Thus it should be possible to deduce the value of χ_{HF} from the observed χ_M and equations (1) and (2). An alternate procedure is to evaluate χ_D from the observed static electric polarizability of the compound, and then evoking the use of equation (1) to obtain χ_{HF}. This latter procedure has not yet been thoroughly tested, although a recent study has provided considerable convincing data that the relationship is a reasonably sound one[8].

In salts of the post-transition metal ions the high frequency term may arise not only from the orbital dependence of interconfigurational mixing localized in the metal ion, but also from terms connected with the various J multiplets wherein the L–S coupling is strong. Furthermore, weak covalency effects having overlap dependence and definable with the charge transfer between anions and cations will also make a contribution. While a completely thorough assessment of all these effects on a theoretical basis cannot be made, a reasonable evaluation of the relative importance of each of these contributions should be possible from an analysis of the electronic spectrum. Furthermore since the magnetic susceptibility and spectra (see section B) have their origins localized within the structural properties of the component ions, there is no need to treat the complete band structure of the entire crystal lattice. Admittedly, while the latter approach is more rigorous it is far more complex to handle, and the little improvement gained is hardly worth the added effort.

An attempt has been previously made to estimate the extent of sp mixing for Tl$^+$ in TlCl, TlBr and TlI salts[4]. While the conclusions reached for the chloride and bromide compounds are probably not too unreasonable, those inferred for TlI are in error owing to an incorrect analysis of the absorption spectrum. Henceforth in this study we present a more complete treatment of TlI. This particular compound provides a good model for testing the mixing hypothesis since it undergoes a reversable structural change at 175 °C from a lower symmetry orthorhombic modification to a metastable cubic form with eight fold coordination.

B. SPECTRAL PROPERTIES OF TlI

The normal absorption spectrum of TlI in both the yellow orthorhombic and red cubic modifications is presented in Fig. 1 together with the spectrum of PbI$_2$ for comparison. The TlI spectra were obtained from transmission measurements on thin film, crystalline deposits on silica substrates through the courtesy of I. Imai formerly with the University of Tokyo. The PbI$_2$ spectrum is after Fesefeldt[9] who conducted measurements in a similar manner. It is to be observed that the spectrum of yellow TlI bears a very close similarity to that of PbI$_2$. The spectra

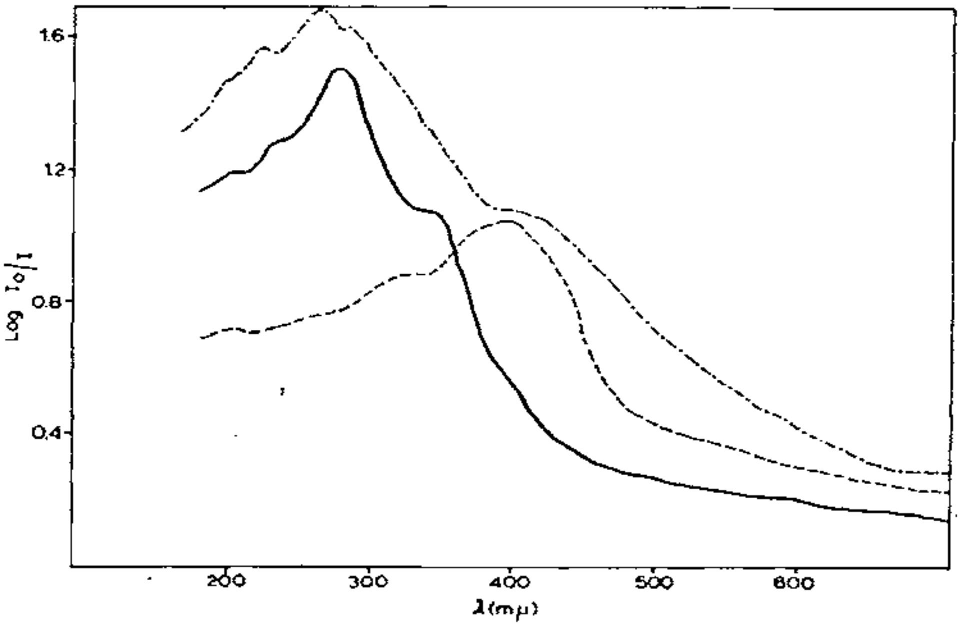

Fig. 1. Optical spectra of TlI and PbI$_2$; ———— TlI (yellow form) 20 °C; - - - - - - - TlI (red form) 180 °C; —.—.—.—.—.— PbI$_2$, 20 °C.

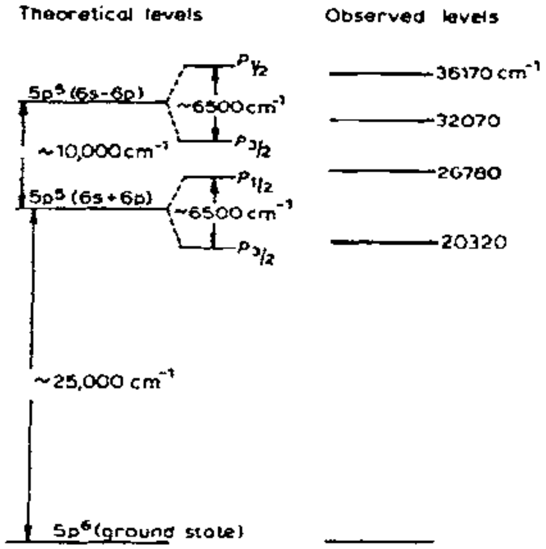

Fig. 2. Energy level of the iodide ion in PbI_2 according to Tubbs (see reference 13). The theoretical scheme is for allowed transitions only.

of Tl^+ and Pb^{2+} ions in alkali iodide solid solutions have been studied in considerable detail, and at least the gross features of these spectra are reasonably well understood[10,11,12]. Although the pure iodide spectra show some unique features not present in the solid solutions, the positions and relative intensities of certain bands can be assigned with reasonable assurance. Tubbs[13] has recently made a very careful study of the PbI_2 spectrum, and has proposed for the very broad, intense UV-visible band a reasonable interpretation which is in good agreement with the experimental results shown in Fig. 2. The normal, incompletely resolved spectrum of PbI_2 exhibits intense maxima at 410 and 290 mμ, which according to Tubbs have their origin localized in the I^- ion. Another maximum at 275 mμ is most likely attributed to both the ${}^1S_0 \rightarrow {}^3P_1$ transition of the Pb^{2+} ion and the higher spin-orbit component of the I^- ion, while the 230 mμ band is associated with the ${}^1S_0 \rightarrow {}^1P_1$ transition of Pb^{2+}. Finally a shoulder appearing in the 200 mμ region is probably of charge transfer origin, but exhibiting a relatively low resolution because of the overlapping with the intense 230 mμ band.

The observed spectra of both the yellow and red modifications of TlI were interpreted on the basis of that rationalized for PbI_2. However, the main features in the spectrum of the red form are a general shift of all bands to lower energy, an overall reduction in intensity, and the maxima associated with the I^- ion which were resolved into two separate components are now contained under one broad envelope. The results of the analysis are presented in Table 2 together with the relative oscillator strengths, f_r. These latter values were assigned only on a relative basis, since the actual thickness of the absorbing medium was known only

TABLE 2

OPTICAL SPECTRUM OF SOLID TlI

Absorption (mμ)	*Energy* (*ev.*)	*Assignment*	f_r*
Orthorhombic (yellow) form (20 °C)			
210	5.90	*C.T.* ($I^- \rightarrow Tl^+$)	0.19
240	5.17	${}^1P_1(Tl^+)$	0.28
—	—	${}^3P_2(Tl^+)$	0.01
290	4.27	${}^3P_1(Tl^+)$	0.05
—	—	I; $5p^6 \rightarrow (6s-6p)^1$	0.30
350	3.54	I; $5p^6 \rightarrow (6s+6p)^1$	0.27
Cubic (red) form (180 °C)			
212	5.85	*C.T.* ($I^- \rightarrow Tl^+$)	0.12
245	5.06	${}^1P_1(Tl^+)$	0.19
—	—	${}^3P_2(Tl^+)$	0.02
335	3.70	${}^3P_1(Tl^+)$	0.04
—	—	I; $5p^6 \rightarrow (6s-6p)^1$	0.46
395	3.14	I; $5p^6 \rightarrow (6s+6p)^1$	0.34

* $f_r = 4.32 \times 10^{-9}$ (A) ($\nu_{\frac{1}{2}}$); $\log I_{1/0} = At$ ($t \approx 10^{-4}$ cm)

within an order of magnitude, and no corrections were made for reflectance, scattering, etc. Fortunately because of the manner in which the spectral data enter into the calculation of the high frequency paramagnetic terms only a knowledge of the relative intensities are required, as shown later. Again because of the qualitative value of the spectra, both the maxima and f_r values of various ${}^3P$ terms were assigned relative to that obtained in alkali halide solutions[10].

C. ANALYSIS OF MAGNETIC SUSCEPTIBILITY DATA

On the basis of the spectral properties it is apparent that the total high frequency paramagnetism will be a composite of the various contributing effects, and may be expressed as follows:

$$\chi_{hf} = \sum_i C_i \chi_{hf}{}^i \tag{3}$$

where $\chi_{hf}{}^1$ is associated with the charge transfer from I^- to Tl^+ and is overlap dependent; $\chi_{hf}{}^2$ is the contribution from the interconfigurational sp mixing on the Tl^+ ion; $\chi_{hf}{}^3$ and $\chi_{hf}{}^4$ are both attributed to the "exciton like" transition localized in the I^- ion[13]; lastly $\chi_{hf}{}^5$ and $\chi_{hf}{}^6$ are associated with the various J multiplets of the Tl^+ ion as a consequence of the strong L–S coupling. The various C_i coefficients merely adjust the relative amounts that each of the matrix elements $\langle n \,|\, L \,|\, 0 \rangle / E_n - E_0$ contributes to χ_{hf}, and are directly determinable from the f_r values[4]. We shall now proceed to treat each of these terms in detail.

(i) Charge transfer

The general expression for $\chi_{\mathrm{hf}}{}^{1}$ is

$$\chi_{\mathrm{hf}} = \tfrac{4}{3}N\beta^2 \frac{|\langle\psi_{\mathrm{E}}|L|\psi_{\mathrm{N}}\rangle|^2}{\Delta E_{\mathrm{CT}}} \tag{4}$$

where ψ_{N} is the highest occupied orbital of the I^- donor and ψ_{E} the lowest unoccupied orbital of the Tl^+ acceptor, L is the total orbital angular momentum operator, ΔE_{CT} is the energy of the observed charge transfer transition, and β the Bohr magneton. The crystal structure of yellow TlI indicates that there are five near neighbor Tl^+ ions coordinated about each I^- ion having an average bond distance of 3.46 Å. On allowing for interconfigurational mixing in the Tl^+ ion (since this is the spectral region in which such an effect is realizable), the appropriate orthonormalized function for the "inert" electron pair can be written as

$$\begin{aligned} \phi_0 &= \alpha(6\mathrm{s})+(1-\alpha^2)^{\frac{1}{2}}(6\mathrm{p}) \\ \phi_1 &= (1-\alpha^2)^{\frac{1}{2}}(6\,\mathrm{s})-\alpha(6\mathrm{p}) \end{aligned} \tag{5}$$

from whence it follows that $\psi_{\mathrm{E}} = 5/\sqrt{5}[(1-\alpha^2)_{\frac{1}{2}}(6\mathrm{s})-\alpha(6\mathrm{p})]$ and ψ_{N} is the 5p orbital of I^-. After substituting into (4) and expanding, the result is

$$\chi_{\mathrm{hf}}{}^{1} = \tfrac{4}{3}N\beta^2 \frac{10\alpha^2 S^2}{\Delta E_{\mathrm{CT}}} \tag{6}$$

where S is the two center overlap integral between the $5\mathrm{p}_\sigma$ orbital of I^- and the $6\mathrm{p}_\sigma\mathrm{Tl}^+$ orbital. The overlap was computed directly by employing hydrogenic like functions with effective nuclear charges obtained according to Burns' improved procedure[7].

A similar approach was also applied to the red, cubic form, however, in this case there are eight Tl^+ ions in a cubic array about each I^- at a distance of 3.63 Å. The resulting expression for $\chi_{\mathrm{hf}}{}^{1}$ is

$$\chi_{\mathrm{hf}}{}^{2} = \tfrac{4}{3}N\beta^2 \frac{16\alpha^2 S^2}{\Delta E_{\mathrm{CT}}} \tag{7}$$

Values of the various pertinent quantities involved in equations (6) and (7), and all succeeding equations (8)–(15) are presented in Tables 4 and 5.

(ii) Interconfigurational mixing

Configuration interaction in the ground state of the Tl^+ ion is represented by the ϕ_0 function of equation (5). Thus this contribution to χ_{HF} may be written as

$$\begin{aligned}\chi_{\mathrm{hf}}{}^2 &= \tfrac{2}{3}N\beta^2\,\frac{|\langle n\,|\,L\,|\,\phi_0\rangle\,|^2}{E_n-E_0}\\ &= \tfrac{2}{3}N\beta^2\,\frac{4(1-\alpha^2)}{E_n-E_0}\end{aligned} \tag{8}$$

where the n excited states are the singlet transitions to the vacant 6p orbitals, and thus E_n-E_0 is identifiable with the energy of the ${}^1S_0 \rightarrow {}^1P_1$ transition.

(iii) "Exciton-like" effects localized on I^-

These contributions give rise to the $\chi_{\mathrm{hf}}{}^3$ and $\chi_{\mathrm{hf}}{}^4$ terms of equation (3), and are respectively associated with the processes: $5p^6 \rightarrow 5p^5[\delta(6s)+(1-\delta^2)^{\frac{1}{2}}6p]$ and $5p^6 \rightarrow 5p^5[(1-\delta^2)^{\frac{1}{2}}6s-\delta(6p)]$ in the I^- ion. The former transition is some 11,000 cm^{-1} lower than the latter in PbI_2, and about 23,000 cm^{-1} above the $5p^6$ ground state[13]. In the yellow form of TlI the 290 and 350 mμ bands can be assigned to these transitions, while in the red form they are shifted to 335 and 395 mμ respectively (see Table 2). The corresponding high frequency paramagnetic terms are thus

$$\begin{aligned}\chi_{\mathrm{hf}}{}^3 &= \tfrac{2}{3}N\beta^2\,\frac{|\langle\psi_0\,|\,L\,|\,5p\rangle\,|^2}{\Delta E_0}\\ &= \tfrac{2}{3}N\beta^2\,\frac{4(1-\delta^2)}{\Delta E_0}\end{aligned} \tag{9}$$

where $\psi_0 = \delta(6\,s)+(1-\delta^2)^{\frac{1}{2}}6\,p$, ΔE_0 is the average energy of the $5\,p \rightarrow \psi_0$ transition, and

$$\begin{aligned}\chi_{\mathrm{hf}}{}^4 &= \tfrac{2}{3}N\beta^2\,\frac{|\langle\psi_1\,|\,L\,|\,5p\rangle\,|^2}{\Delta E_1}\\ &= \tfrac{2}{3}N\beta^2\,\frac{4\delta^2}{\Delta E_1}\end{aligned} \tag{10}$$

where $\psi_1 = (1-\delta^2)^{\frac{1}{2}}(6s)-\delta(6p)$, and ΔE_1 is the average energy of the $5p \rightarrow \psi_1$ transition. However, before equations (9) and (10) can be employed the unknown δ parameters must be evaluated.

Since both ψ_0 and ψ_1 are properly orthonormalized functions the standard procedure of minimizing the energy gives (see Table 3).

$$E = \delta^2(H_{6s6s}-H_{6p6p})+H_{6p6p}+2\delta(1-\delta^2)^{\frac{1}{2}}H_{6s6p} \tag{11}$$

It must further be reconciled that neither the iodide nor the thallium ion will bear a full unit of electrostatic charge. The actual charge, q, on the iodide will be reduced to something less than -1 as a consequence of polarization, and may be estimated from the expression[14]

$$q = 1 - \left[(e/4\pi)\frac{2\alpha_-}{\alpha_M}(1-1/n_0)\right] \tag{12}$$

where α_- and α_M are the polarizabilities of the I^- and TlI respectively, and n_0 is the refractive index of the crystal. These quantities are readily obtainable from the literature[4], and when substituted into (12) the charges obtained are -0.67 and -0.65 on iodide in the yellow and red forms of TlI respectively. The average value -0.66 was employed in both cases.

The absolute energy, E, in (11) is established by fixing the energy of the

TABLE 3

DATA FOR ESTIMATING δ

Energy (ev)						
Integral	*TlI (yellow)*			*TlI (red)*		
	I^-	I^0	$I^{-0.66}$	I^-	I^0	$I^{-0.66}$
$^aH_{5p5p}$	-3.23	-10.45	-5.60	-3.23	-10.45	-5.80
H_{6s6s}	-0.94	-2.71	-1.46	-0.84	-2.71	-1.50
H_{6p6p}	-0.55	-1.78	-0.96	-0.55	-1.78	-0.98
$^bH_{6s6p}$	-0.70	-2.25	-1.21	-0.70	-2.25	-1.24
^cE	—	—	-2.06	-	—	-2.66

[a] Orbital ionization energies. [b] Taken as $\frac{1}{2}(H_{6s6s}+H_{6p6p})$. [c] Obtained from the observed spectra by fixing the position of the 6s6p mixed state relative to the 5p state.

TABLE 4

HIGH FREQUENCY PARAMAGNETIC CONTRIBUTIONS TO TlI

Orthorhombic (yellow) form (20° C)

C_i	*Other parameters*	*Energy (ev.)*	*Susceptibility* $(\times 10^{6-}$ emμ$)$
$C_1 = 0.633$	$S(5p, 6p)_\sigma = 0.390$	$\Delta E_{CT} = 5.90$	$\chi_{hf}{}^1 = 3.5\,\alpha^2$
$C_2 = 0.933$	—	$2(^1P_1 - {}^1S_0) = 5.17$	$\chi_{hf}{}^2 = 15.6\,(1-\alpha^2)$
$C_3 = 0.900$	$(1-\delta^2) = 0.786$	$\Delta E_0 = 3.54$	$\chi_{hf}{}^3 = 17.2$
$C_4 = 1.000$	$\delta^2 = 0.214$	$\Delta E_1 = 4.27$	$\chi_{hf}{}^4 = 4.3$
$C_5 = 0.167$	—	$(^3P_1 - {}^1S_0) = 4.27$	$\chi_{hf}{}^5 = 1.7$
$C_6 = 0.033$	—	$(^3P_2 - {}^1S_0) = 5.17$	$\chi_{hf}{}^6 = 0.3$

TABLE 5

HIGH FREQUENCY PARAMAGNETIC CONTRIBUTIONS TO TlI

Cubic (red) form (180 °C)

$C_{i\sigma}$	*Other parameters*	*Energy (ev.)*	*Susceptibility* $(\times 10^{-6}$ emμ$)$
$C_1 = 0.261$	$S(5p, 6p)_\sigma = 0.387$	$\Delta E_{CT} = 5.85$	$\chi_{hf}{}^1 = 2.4\,\alpha^2$
$C_2 = 0.431$	—	$(^1P_1 - {}^1S_0) = 5.06$	$\chi_{hf}{}^2 = 7.3\,(1-\alpha^2)$
$C_3 = 0.739$	$(1-\delta^2) = 0.633$	$\Delta E_0 = 3.14$	$\chi_{hf}{}^3 = 12.8$
$C_4 = 1.000$	$\delta^2 = 0.367$	$\Delta E_1 = 3.70$	$\chi_{hf}{}^4 = 8.6$
$C_5 = 0.087$	—	$(^3P_1 - {}^1S_0) = 3.70$	$\chi_{hf}{}^5 = 1.0$
$C_6 = 0.043$	—	$(^3P_2 - {}^1S_0) = 5.06$	$\chi_{hf}{}^6 = 0.5$

$I^{-0.66}$ ground state on interpolating monotonically between the ionization potentials of I^- and I^0, and then using the observed spectrum to fix the positions of the ψ_0 and ψ_1 levels. Similarly the diagonal elements, H_{6s6s} and H_{6p6p}, were assigned as the average orbital ionization energies (adjusted for charge) obtainable from atomic spectra tables[15]. The H_{6sp} terms were then simply set equal to $\frac{1}{2}(H_{6s6s}+H_{6p6p})$. The values of these various quantities are presented in Table 3 while the resulting δ values are given in Tables 4 and 5.

(iv) Contributions from JJ′ multiplets

The final contributions to χ_{HF} are $\chi_{hf}{}^5$ and $\chi_{hf}{}^6$ which are given in terms of the general expression

$$\tfrac{2}{3}N\beta^2 \sum_{J'\neq J} \frac{|(L+2S)(J;J')|^2}{E_{J'}-E_J} \tag{13}$$

associated with the various JJ' multiplets of Tl^+. Only the $^1S_0 \rightarrow {}^3P_1$ and $^1S_0 \rightarrow {}^3P_2$ states lead to non-vanishing elements in (13*), thus

$$\chi_{hf}{}^5 = N\frac{\beta^2}{3}\frac{(4)}{\Delta E(^3P_1 - {}^1S_0)} \tag{14}$$

$$\chi_{hf}{}^6 = N\frac{\beta^2}{3}\frac{(5)}{\Delta E(^3P_2 - {}^1S_0)} \tag{15}$$

However, since the C_5 and C_6 of equation (3) are small equations (14) and (15) will make only very small contributions to χ_{HF}. This is fortunate since the $^3P_1$ and $^3P_2$ states cannot be located unambigously in the absence of a much more thorough spectral study than that presented in Fig. 1; nor can their contributions to χ_{HF} be rigorously justified.

D. RESULTS AND CONCLUSIONS

The experimental susceptibilities of both the yellow and the higher temperature red forms were determined by the standard Gouy technique, and are given in Table 6. The maximum error due to packing, weighing, etc. was found to be 2.9 per cent, while the average error was no more than 1 per cent, and is the best that can be obtained experimentally. Consequently the value of χ_{HF} was obtained from equation (1) after calculating χ_D according to equation (2). In calculating χ_D, allowance was made for reduced charges of +0.66 and −0.66 on

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* It is assumed that the intercombination singlet–triplet bands become allowed because of the significant departure from Russell–Saunders coupling.

TABLE 6

ESTIMATED VALUES OF α IN TlI

TlI	*Susceptibility* ($\times 10^{-6}$ *emμ*)				
	$\chi_{M(obs)}$	χ_D	χ_{HF}	$\Delta\chi_{HF}$[a]	α[b]
Orthorhombic	-69.2	-105	$+36$	-3	0.5
Cubic	-75.0	-105	$+30$	-0.2	$0.0 < \alpha \leqslant 0.2$

[a] $\Delta\chi_{HF} = \chi_{HF} - \sum_i C_i \chi_{hf}^i$. [b] See equation (5) in text.

the thallium and iodide ions respectively (see section C (*iii*)). The procedure is the same in principle as that employed by Gray and Cruikshank[16] in calculating the diamagnetism of organic molecules. Finally equation (3) makes it possible to compute the mixing parameter α, and the values so obtained are presented in Table 6.

It must be realized that in calculating α the pertinent equations lead to a small difference of two quantities to which it is not possible to assign any absolute limits of error. Thus the reported values should not be interpreted with a high degree of accuracy. Nonetheless, the order of magnitude is correct, and if the experimental error of the measured susceptibility is accepted as an over-all index, then the actual α values should not differ by more than 50 per cent from those given in Table 6. There is good reason to suspect that if anything the actual value should be lower than that obtained. Furthermore since the magnitude of α in the red cubic form is much smaller than that for the yellow orthorhombic form, only the range of upper and lower limits are given for the former.

The results suggest that the upper limit to sp mixing in the Tl^+ ion is about 71 per cent complete in the less symmetrical, yellow form of TlI and not more than 28 per cent complete in the red, cubic form. These limits are inferred relative to the maximum allowable value of $\alpha = 2^{-1/2}$ for complete mixing. It should be emphasized that these findings are indeed consistent with Orgel's proposal that sp mixing should be greatest in sites of lower symmetry.

A similar, though not yet complete, treatment of PbI_2 indicates that the sp mixing in the Pb^{2+} ion is roughly the same order of magnitude as that found for Tl^+ in the orthorhombic form of TlI. The investigation is also currently being extended to post-transition metal halides and oxides where in sp mixing and/or ds mixing is a possibility.

One of the most significant aspects of this study is the demonstration of the potentially powerful role that diamagnetism can play as an aid to the elucidation of structure and bonding in those cases for which established physical techniques and theoretical principles specifically for transition metal ions cannot be made.

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