

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

EDWARD A. BOUDREAUX

*Department of Chemistry, Louisiana State University in New Orleans,  
New Orleans, La. (U.S.A.)*

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### 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 quantitative 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<sup>1,2</sup> 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<sup>a</sup>

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

<sup>a</sup> 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  $ns^2$  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 inter-configurational mixing proposed leads to non zero high frequency paramagnetic terms in the diamagnetic susceptibilities and chemical shifts in the NMR spectra of these ions<sup>3,4</sup>. 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<sup>5</sup>

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

where  $\overline{r^2}$  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  $n^{\text{th}}$  excited states;  $E_n - E_0$  is the energy separation between the ground and  $n^{\text{th}}$  excited states, and the other terms have their usual significance. Although the high frequency paramagnetic term,  $\chi_{HF}$ , 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  $\chi_{HF}$ . 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,  $\chi_D$ , terms of the respective ions. Even in molecules,  $\chi_D$  may be reduced to a sum over the  $\chi_d$  terms of the respective atoms<sup>6</sup>. For hydrogenic like wave functions,  $\chi_d$ , is given by

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

where the summation is over all  $i$  electrons in each of the  $nl$  orbitals. One can hope to calculate such  $\chi_d$  terms with reasonable accuracy in the case of salt like systems, by incorporating Burns'<sup>7</sup> procedure for evaluating the effective nuclear charge of the respective ions. Thus it should be possible to deduce the value of  $\chi_{HF}$  from the observed  $\chi_M$  and equations (1) and (2). An alternate procedure is to evaluate  $\chi_D$  from the observed static electric polarizability of the compound, and then evoking the use of equation (1) to obtain  $\chi_{HF}$ . 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<sup>8</sup>.

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<sup>4</sup>. 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 reversible 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<sup>9</sup> 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

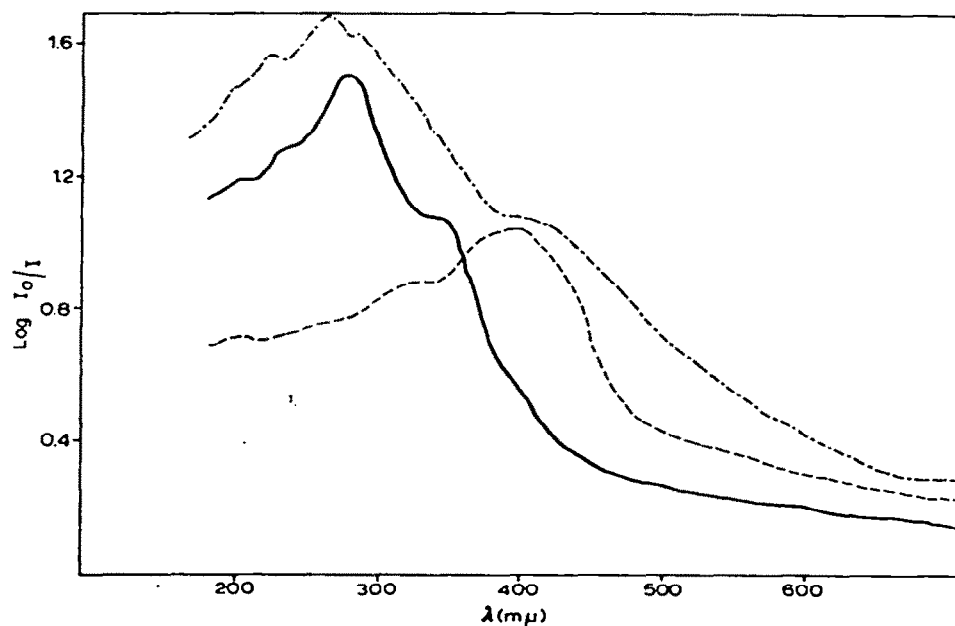


Fig. 1. Optical spectra of  $TlI$  and  $PbI_2$ ; ———  $TlI$  (yellow form) 20 °C; - - - -  $TlI$  (red form) 180 °C; - · - · -  $PbI_2$ , 20 °C.

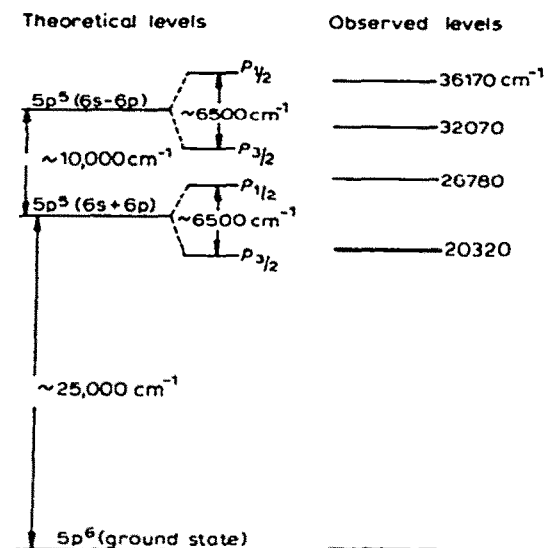


Fig. 2. Energy level of the iodide ion in  $\text{PbI}_2$  according to Tubbs (see reference 13). The theoretical scheme is for allowed transitions only.

of  $\text{TI}^+$  and  $\text{Pb}^{2+}$  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<sup>10, 11, 12</sup>. 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<sup>13</sup> has recently made a very careful study of the  $\text{PbI}_2$  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  $\text{PbI}_2$  exhibits intense maxima at 410 and 290  $\text{m}\mu$ , which according to Tubbs have their origin localized in the  $\text{I}^-$  ion. Another maximum at 275  $\text{m}\mu$  is most likely attributed to both the  $^1S_0 \rightarrow ^3P_1$  transition of the  $\text{Pb}^{2+}$  ion and the higher spin-orbit component of the  $\text{I}^-$  ion, while the 230  $\text{m}\mu$  band is associated with the  $^1S_0 \rightarrow ^1P_1$  transition of  $\text{Pb}^{2+}$ . Finally a shoulder appearing in the 200  $\text{m}\mu$  region is probably of charge transfer origin, but exhibiting a relatively low resolution because of the overlapping with the intense 230  $\text{m}\mu$  band.

The observed spectra of both the yellow and red modifications of  $\text{TI}$  were interpreted on the basis of that rationalized for  $\text{PbI}_2$ . 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  $\text{I}^-$  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 (m $\mu$ )	Energy (ev.)	Assignment	$f_r^a$
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
—	—	$I; 5p^5 \rightarrow (6s-6p)^4$	0.30
350	3.54	$I; 5p^5 \rightarrow (6s+6p)^4$	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
—	—	$I; 5p^5 \rightarrow (6s-6p)^4$	0.46
395	3.14	$I; 5p^5 \rightarrow (6s+6p)^4$	0.34

<sup>a</sup>  $f_r = 4.32 \times 10^{-8} (A) (\nu_{\frac{1}{2}})$ ;  $\log I_{t/0} = At$  ( $t \approx 10^{-4}$  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<sup>10</sup>.

### 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:

$$\chi_{hf} = \sum_i C_i \chi_{hf}^i \quad (3)$$

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<sup>13</sup>; 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  $\chi_{hf}$ , and are directly determinable from the  $f_r$  values<sup>4</sup>. We shall now proceed to treat each of these terms in detail.

*(i) Charge transfer*

The general expression for  $\chi_{\text{bf}}^1$  is

$$\chi_{\text{bf}} = 3N\beta^2 \frac{|\langle \psi_E | L | \psi_N \rangle|^2}{\Delta E_{\text{CT}}} \quad (4)$$

where  $\psi_N$  is the highest occupied orbital of the  $\text{I}^-$  donor and  $\psi_E$  the lowest unoccupied orbital of the  $\text{Tl}^+$  acceptor,  $L$  is the total orbital angular momentum operator,  $\Delta E_{\text{CT}}$  is the energy of the observed charge transfer transition, and  $\beta$  the Bohr magneton. The crystal structure of yellow TII indicates that there are five near neighbor  $\text{Tl}^+$  ions coordinated about each  $\text{I}^-$  ion having an average bond distance of 3.46 Å. On allowing for interconfigurational mixing in the  $\text{Tl}^+$  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

$$\begin{aligned} \phi_0 &= \alpha(6s) + (1 - \alpha^2)^{1/2}(6p) \\ \phi_1 &= (1 - \alpha^2)^{1/2}(6s) - \alpha(6p) \end{aligned} \quad (5)$$

from whence it follows that  $\psi_E = 5/\sqrt{5}[(1 - \alpha^2)^{1/2}(6s) - \alpha(6p)]$  and  $\psi_N$  is the 5p orbital of  $\text{I}^-$ . After substituting into (4) and expanding, the result is

$$\chi_{\text{bf}}^1 = 3N\beta^2 \frac{10\alpha^2 S^2}{\Delta E_{\text{CT}}} \quad (6)$$

where  $S$  is the two center overlap integral between the  $5p_z$  orbital of  $\text{I}^-$  and the  $6p_z \text{Tl}^+$  orbital. The overlap was computed directly by employing hydrogenic like functions with effective nuclear charges obtained according to Burns' improved procedure<sup>7</sup>.

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

$$\chi_{\text{bf}}^2 = 3N\beta^2 \frac{16\alpha^2 S^2}{\Delta E_{\text{CT}}} \quad (7)$$

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  $\text{Tl}^+$  ion is represented by the  $\phi_0$  function of equation (5). Thus this contribution to  $\chi_{\text{HF}}$  may be written as

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

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  $\chi_{\text{hf}}^3$  and  $\chi_{\text{hf}}^4$  terms of equation (3), and are respectively associated with the processes:  $5p^6 \rightarrow 5p^5[\delta(6s) + (1-\delta^2)^{1/2}6p]$  and  $5p^6 \rightarrow 5p^5[(1-\delta^2)^{1/2}6s - \delta(6p)]$  in the  $I^-$  ion. The former transition is some 11,000  $\text{cm}^{-1}$  lower than the latter in  $\text{PbI}_2$ , and about 23,000  $\text{cm}^{-1}$  above the  $5p^6$  ground state<sup>13</sup>. In the yellow form of TII the 290 and 350  $m\mu$  bands can be assigned to these transitions, while in the red form they are shifted to 335 and 395  $m\mu$  respectively (see Table 2). The corresponding high frequency paramagnetic terms are thus

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

where  $\psi_0 = \delta(6s) + (1-\delta^2)^{1/2}6p$ ,  $\Delta E_0$  is the average energy of the  $5p \rightarrow \psi_0$  transition, and

$$\begin{aligned}\chi_{\text{hf}}^4 &= \frac{1}{3}N\beta^2 \frac{|\langle \psi_1 | L | 5p \rangle|^2}{\Delta E_1} \\ &= \frac{1}{3}N\beta^2 \frac{4\delta^2}{\Delta E_1}\end{aligned}\quad (10)$$

where  $\psi_1 = (1-\delta^2)^{1/2}(6s) - \delta(6p)$ , and  $\Delta E_1$  is the average energy of the  $5p \rightarrow \psi_1$  transition. However, before equations (9) and (10) can be employed the unknown  $\delta$  parameters must be evaluated.

Since both  $\psi_0$  and  $\psi_1$  are properly orthonormalized functions the standard procedure of minimizing the energy gives (see Table 3).

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

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<sup>14</sup>



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

where  $\alpha_-$  and  $\alpha_M$  are the polarizabilities of the  $I^-$  and TII respectively, and  $n_0$  is the refractive index of the crystal. These quantities are readily obtainable from the literature<sup>4</sup>, and when substituted into (12) the charges obtained are  $-0.67$  and  $-0.65$  on iodide in the yellow and red forms of TII 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  $\delta$

Integral	TII (yellow)			TII (red)		
	$I^-$	$I^0$	$I^{-0.66}$	$I^-$	$I^0$	$I^{-0.66}$
<sup>a</sup> $H_{spsp}$	-3.23	-10.45	-5.60	-3.23	-10.45	-5.80
$H_{ssss}$	-0.94	-2.71	-1.46	-0.84	-2.71	-1.50
$H_{spsp}$	-0.55	-1.78	-0.96	-0.55	-1.78	-0.98
<sup>b</sup> $H_{sssp}$	-0.70	-2.25	-1.21	-0.70	-2.25	-1.24
<sup>c</sup> $E$	—	—	-2.06	—	—	-2.66

<sup>a</sup> Orbital ionization energies. <sup>b</sup> Taken as  $\frac{1}{2}(H_{ssss} + H_{spsp})$ . <sup>c</sup> 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 TII  
Orthorhombic (yellow) form (20° C)

$C_i$	Other parameters	Energy (ev.)	Susceptibility ( $\times 10^{-6}$ emu)
$C_1 = 0.633$	$S(5p, 6p)_\sigma = 0.390$	$\Delta E_{CT} = 5.90$	$\chi_{bf}^1 = 3.5 \alpha^2$
$C_2 = 0.933$	—	$2(^1F_1 - ^1S_0) = 5.17$	$\chi_{bf}^2 = 15.6 (1 - \alpha^2)$
$C_3 = 0.900$	$(1 - \delta^2) = 0.786$	$\Delta E_o = 3.54$	$\chi_{bf}^3 = 17.2$
$C_4 = 1.000$	$\delta^2 = 0.214$	$\Delta E_1 = 4.27$	$\chi_{bf}^4 = 4.3$
$C_5 = 0.167$	—	$(^3P_1 - ^1S_0) = 4.27$	$\chi_{bf}^5 = 1.7$
$C_6 = 0.033$	—	$(^3P_2 - ^1S_0) = 5.17$	$\chi_{bf}^6 = 0.3$

TABLE 5  
HIGH FREQUENCY PARAMAGNETIC CONTRIBUTIONS TO TII  
Cubic (red) form (180 °C)

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

$I^{-0.66}$  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  $\psi_0$  and  $\psi_1$  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<sup>15</sup>. 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  $\delta$  values are given in Tables 4 and 5.

(iv) *Contributions from  $JJ'$  multiplets*

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

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

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

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

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

However, since the  $C_5$  and  $C_6$  of equation (3) are small equations (14) and (15) will make only very small contributions to  $\chi_{HF}$ . This is fortunate since the  $^3P_1$  and  $^3P_2$  states cannot be located unambiguously in the absence of a much more thorough spectral study than that presented in Fig. 1; nor can their contributions to  $\chi_{HF}$  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  $\chi_{HF}$  was obtained from equation (1) after calculating  $\chi_D$  according to equation (2). In calculating  $\chi_D$ , allowance was made for reduced charges of +0.66 and -0.66 on

\* 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  $\alpha$  IN TII

TII	Susceptibility ( $\times 10^{-6}$ emu)				$\alpha^b$
	$\chi_{M(obs)}$	$\chi_D$	$\chi_{HF}$	$\Delta\chi_{HF}^a$	
Orthorhombic	-69.2	-105	+36	-3	0.5
Cubic	-75.0	-105	+30	-0.2	$0.0 < \alpha \leq 0.2$

<sup>a</sup>  $\Delta\chi_{HF} = \chi_{HF} - \sum_i C_i \chi_{bf}^i$ . <sup>b</sup> 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<sup>16</sup> in calculating the diamagnetism of organic molecules. Finally equation (3) makes it possible to compute the mixing parameter  $\alpha$ , and the values so obtained are presented in Table 6.

It must be realized that in calculating  $\alpha$  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  $\alpha$  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  $\alpha$  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 TII 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 TII. 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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