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CORRELATION OF QUADRUPOLE SPLITTING AND ISOMERIC SHIFT BY MÖSSBAUER SPECTROSCOPY IN SOME TRIALKYLTIN HALIDES*

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SUMMARY

A systematic study of the Mössbauer spectra of trialkyltin halides (methyl, ethyl, propyl, butyl, isobutyl) has been made with the object of correlating the quadrupole splitting and the isomeric shift with the molecular structure. Assuming four-coordination (except for methyl), a simple model is presented which takes into account *s, p, d* hybridization of the tin as well as the ionic characters of the tin–halogen and the tin–alkyl bonds. The possibility of back donation by a p_π–d_π or p_π–p_π bond is taken into account. The importance of the *s* electron shielding is stressed. The correlation with experimental data is good and yields satisfactory values for the parameters. The analysis suggests that there is substantial back donation.

INTRODUCTION

Experimental and theoretical aspects of the Mössbauer effect in organotin compounds has been reviewed by Herber[1], Cordey–Hayes[2], and Gibb and Greenwood[3]. As far as R_3SnX compounds are concerned, the quadrupole splitting is not satisfactorily explained by the different ionic characters of the bond on the basis of a simple Townes–Dailey analysis. On the one hand some compounds have no quadrupole splitting although the difference between electronegativities should lead to one; R_3SnX compounds show a much larger quadrupole splitting (QS) than allowed by the difference of the electronegativities of carbon and the halogens. The mixing of *d* character is not likely to increase notably the QS. On the other hand, back donation of electrons from the halogen into the vacant *5d* and/or *6p* orbitals of the tin[3–5] would enhance the QS. There is no definite evidence yet for such an effect. No definite information is available on the structure of the triethyl-, tripropyl- or tributyltin halides. The trimethyltin derivatives, in solution or in the solid state, are known to contain a pentacoordinated metal atom[18], but an observation made by Van der Kerk and his colleagues[21] suggests strongly that the higher trialkyltin

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molecules could be unassociated and thus tetracoordinated: trimethyltin acetate has been found to be a polymeric solid, while triisopropyltin acetate is monomeric even in the solid state, and thus the behaviour of methyltin derivatives cannot be extrapolated to the higher alkyltin compounds. It is thus reasonable to make the provisional assumption that except for the trimethyl compounds the trialkyltin halides are four-coordinated in the solid state, and we have thus made a simple theoretical analysis of 4-coordinate R_3SnX compounds and have run the Mössbauer spectra of these derivatives in order to compare experimental and theoretical results. If our assumption is justified, the Mössbauer data for the trimethyltin halides should be different from those of the other trialkyl compounds.

EXPERIMENTAL

Mössbauer spectrometry

The parabolic movement which has been used is made by coupling a loudspeaker and a Sanborn velocity pick-up. The velocity is regulated by a function generator producing a triangular waveform at 30 Hz. The differential linearity of the velocity signal is better than 1% during 95% of the cycle. The calibration is periodically repeated with a ^{57}Co source diffused in Fe-α and a 310 stainless steel absorber. With this calibration, we obtain (2.60 ± 0.05) mm/sec for the isomeric shift between β-Sn and SnO_2. Each experimental run is composed of two reference spectra (β-Sn and SnO_2) and the spectrum of interest. The two sources used are Mg_2Sn ($\Gamma_s = 0.077 \pm 0.003$) and SnO_2 ($\Gamma_s = 0.29 \pm 0.02$). The spectrum is recorded on an Intertechnique 400 channel analyser working in time of flight (1 channel = 0.156 mm/sec). In each run, at least $2 \cdot 10^5$ counts per channel were accumulated. All measurements were made with the source at room temperature and the absorber cooled at liquid nitrogen temperature. The sample is placed in an aluminium cell of about 0.2 mm thickness. The temperature is controlled with a Cu-constantan thermocouple. The analysis of the experimental data is made by an iterative least squares fitting to a sum of Lorentzian peaks, corrected to take into account interference and the solid angle effect.

The programme which has been written covers different shapes of line with and without interference and also the numerical integration of the transmitted spectrum as given by Margulies and Ehrman. The spectrum of Et_3SnF with 1.300.000 counts per channel gives differences of 10% on the quadrupole splitting between a sum of Lorentzian shape and the exact integration. The display of both fitted spectra is the same. All results are corrected to give the real quadrupole splitting.

Trialkyltin halides

The trialkyltin halides were synthesized by Mr. Y. Goscinny and Mr. G. Mayence, in Prof. R. H. Martin's laboratory, using a method[19] which yields very pure derivatives. The preparations have been described elsewhere[20].

A SIMPLE THEORETICAL MODEL

Quadrupole splitting

In order to get a semiquantitative understanding, we use the simplified model of Townes and Dailey[6]. The accurate evaluation of the electric field gradient is sensitive to details of the molecular structure and more elaborate models (for a

review, see Scrocco[7]) are not useful at the present stage.

We describe the neighborhood of the tin atom in the following way: the angle of the tin–halogen bond axis z(Sn–X) with each tin–carbon bond axis (Sn–R) is θ and we assume a C_{3v} symmetry. Accordingly we have the four hybrids:

$$\begin{aligned}
\psi_1 &= s_X \cdot \psi_s + (1-s_X^2-d_X^2)^{\frac{1}{2}} \cdot \psi_{p(z)} + d_X \cdot \psi_{d(z)} \\
\psi_2 &= s_R \cdot \psi_s + (1-s_R^2)^{\frac{1}{2}} \cdot (\psi_{p(z)} \cdot \cos\theta - \psi_{p(x)} \cdot \sin\theta) \\
\psi_3 &= s_R \cdot \psi_s + (1-s_R^2)^{\frac{1}{2}} \cdot (\psi_{p(z)} \cdot \cos\theta + \tfrac{1}{2}\psi_{p(x)} \cdot \sin\theta - \tfrac{1}{2}\sqrt{3}\psi_{p(y)} \cdot \sin\theta) \\
\psi_4 &= s_R \cdot \psi_s + (1-s_R^2)^{\frac{1}{2}} \cdot (\psi_{p(z)} \cdot \cos\theta + \tfrac{1}{2}\psi_{p(x)} \cdot \sin\theta + \tfrac{1}{2}\sqrt{3}\psi_{p(y)} \cdot \sin\theta)
\end{aligned} \tag{1}$$

We assume that d hybridization is present in the halogen–tin bond. If ψ_X and ψ_R are respectively the bonding atomic orbitals for the halogen and the carbon atom in the radical, we have the molecular orbitals

$$\begin{aligned}
\phi_1 &= \frac{\psi_1 + i_X \cdot \psi_X}{(1+i_X^2)^{\frac{1}{2}}} \\
\phi_j &= \frac{\psi_j + i_R \cdot \psi_R}{(1+i_R^2)^{\frac{1}{2}}}
\end{aligned} \tag{2}$$

neglecting overlap.

Let

$$I_X = \frac{1-i_X^2}{1+i_X^2}, \qquad I_R = \frac{1-i_R^2}{1+i_R^2} \tag{3}$$

be the ionic characters for the Sn–X and Sn–R bonds. (This means that the inductive effect of the radical may affect the equivalent electronegativity of the carbon atom and therefore I_R.)

Orthogonality of ψ_1 with one ψ_j (for instance $j=2$) yields

$$\cos^2\theta = \frac{s_R^2 \cdot s_X^2}{(1-s_R^2)\cdot(1-s_X^2-d_X^2)} \tag{4}$$

and from orthogonality of ψ_j and ψ_k (for instance $j=3$, $k=4$) we obtain:

$$s_R^2 = \frac{1-3\cos^2\theta}{3\sin^2\theta} \tag{5}$$

$$s_X^2 = 2\cot^2\theta \cdot (1-d_X^2) \tag{6}$$

$$s_R^2 = \frac{1-s_X^2-d_X^2}{3(1-d_X^2)} \tag{7}$$

With two electrons in each molecular orbital, the component of the electric field gradient is, for the orbital j:

$$(q_{zz})_j = 2\int |\phi_j|^2 \cdot \frac{3\cos^2\theta - 1}{r^3}\, dV \tag{8}$$

where r is the electron distance to Sn and θ the polar angle with the Sn–X bond axis.

Let

$$(q_{zz})_1 = 2\left[\frac{1-s_X^2-d_X^2}{1+i_X^2}\cdot q_{p(z)} + \frac{i_X^2}{1+i_X^2}\cdot q_x + \frac{2i_X\cdot(1-s_X^2-d_X^2)^{\frac{1}{2}}}{(1+i_X^2)^{\frac{1}{2}}}\cdot q_{p(z,x)}\right] \tag{9}$$

Similarly the contribution from p_z orbitals in molecular orbitals 2, 3, 4, is

$$\sum_{j=2}^{4}(q_{zz})_j = 6\,\frac{1-s_R^2}{1+i_R^2}\cdot q_{p(z)}\cdot\cos^2\theta$$

The contribution from p_x and p_y orbitals are

$$\sum_{j=2}^{4}(q_{xx})_j = 3\,\frac{1-s_R^2}{1+i_R^2}\cdot q_{p(x)}\cdot\sin^2\theta$$

$$\sum_{j=2}^{4}(q_{yy})_j = 3\,\frac{1-s_R^2}{1+i_R^2}\cdot q_{p(y)}\cdot\sin^2\theta$$

Since $q_{p(x)}=q_{p(y)}=-\frac{1}{2}q_{p(z)}$ the total contribution from p electrons is

$$q_{zz} = 2q_{p(z)}\cdot\left[\frac{1-s_X^2-d_X^2}{1+i_X^2} + 3\,\frac{1-s_R^2}{1+i_R^2}\cdot\left(\frac{3\cos^2\theta-1}{2}\right)\right] \tag{10}$$

Introducing (3) and (4) into (10)

$$q_{zz} = q_{p(z)}\cdot\left[(1-s_X^2-d_X^2)\cdot(1+I_X) - \frac{(1-s_X^2-d_X^2)}{1-d_X^2}\cdot(1+I_R)\right] \tag{11}$$

Therefore the tetrahedral structure has no relevance to the existence of a gradient of the electric field due to the p electrons, (considering that $d_X^2 \ll 1$) but the unbalance of the ionic characters has. To this contribution must be added the contributions of q_X, q_R, $q_{p(z),X}$, $q_{p(z),R}$ which are usually taken of a lower order of magnitude than $q_{p(z)}$.

The quadrupole splitting is (for spin $I=\frac{3}{2}$) $\Delta E_Q = e^2\cdot Q\cdot V_{zz}$ and for a p electron

$$V_{zz} = q_{p(z)} = -\frac{4}{5}\left\langle\frac{1}{r^3}\right\rangle$$

Introducing n'_p the effective number of p electrons, *i.e.* the number of electrons giving rise to the quadrupole splitting, we have

$$\Delta E_Q = e^2\cdot Q\cdot q_{p(z)}\cdot|n'_p| \tag{12}$$

with

$$|n'_p| = (1-s_X^2-d_X^2)\cdot\left(\frac{|I_R|-d_X^2}{1-d_X^2} - |I_X|\right) \tag{13}$$

since I_X and I_R are both negative in our experiments.

If we make the assumption of dative p_π–p_π or p_π–d_π bonding which transfers non bonding electron pairs of the halogen into the vacant $6p$ orbital of tin, we would add to n'_p a contribution

$$n_\pi\cdot\left(\frac{q_{p(x)}+q_{p(y)}}{2}\right)\cdot\beta$$

where n_π is the number of equivalent electrons transfered to the $6p$ orbitals and β the ratio of $q_{p(z)}$ for a $6p$ electron to $q_{p(z)}$ for a $5p$ electron. Therefore eqn. (13) becomes

$$|n'_p| = \left|\frac{\beta \cdot n_\pi}{2} + (1-s_X^2-d_X^2)\cdot\left(|I_X| - \frac{|I_R|-d_X^2}{1-d_X^2}\right)\right| \tag{14}$$

The isomeric shift

In the simple molecular orbital description eqn. (1) the contribution of the s electron density at the nucleus from the $5s$ shell is

$$\delta|\psi_s(0)|^2 = 2\left[\frac{s_X^2}{1+i_X^2} + \frac{3s_R^2}{1+i_R^2}\right]\cdot|\psi_s(0)|^2 \tag{15}$$

We neglect the presence of electrons from atoms X and R and we neglect also the small contribution from relativistic $p_{\frac{1}{2}}$ electrons. Therefore if we let n_s be the effective number of s electrons

$$\frac{\delta|\psi_s(0)|^2}{|\psi_s(0)|^2} = n_s = s_X^2\cdot(1+I_X)+(1+I_R)\cdot\frac{1-s_X^2-d_X^2}{1-d_X^2} \tag{16}$$

The isomeric shift is[8]

$$\Delta E_s = \tfrac{2}{5}\cdot\pi\cdot Z_e^2\cdot[R_e^2-R_f^2]\cdot S'(Z)\cdot\delta|\psi_s(0)|^2 \tag{17}$$

where $Z_e = 50\ e$ is the charge of tin, R_e, R_f respectively the radius in the excited and fundamental levels, $S'(Z)$ a relativistic correction taken as 2.3 for tin[8].

Choice of the parameters

The effect of shielding of the electric field gradient. The value of $\langle(a_0/r)^3\rangle$ where a_0 is the Bohr radius is dependent upon the shielding from other electrons. A Hartree–Fock calculation[9] yields the following correlation for tin

$$\left\langle\left(\frac{a_0}{r}\right)^3\right\rangle_{5p} = 14.15-2n_s-\tfrac{7}{4}n_p \tag{18}$$

for a configuration $5s^{n_s}5p^{n_p}$. We see that an exchange between a p and an s electron leaves $\langle(a_0/r)^3\rangle_{5p}$ almost unaltered. The number of p electrons is easily evaluated from (1) and (2)

$$n'_p = 2\,\frac{1-s_X^2-d_X^2}{1+i_X^2} + 2\,\frac{3(1-s_R^2)}{1+i_R^2} = (1-s_X^2-d_X^2)\cdot(I_X+1)+(1+I_R)\cdot\left[\frac{s_X^2+2(1-d_X^2)}{1-d_X^2}\right] \tag{19}$$

Neglecting s_X^2 and d_X^2 we have

$$\left\langle\left(\frac{a_0}{r}\right)^3\right\rangle = 6.9-5.5I_R-1.75I_X \tag{20}$$

within the range corresponding to $1 \leqslant n_s \leqslant 2$, $0 \leqslant n_p \leqslant 3$.

The effect of shielding on $|\psi_s(0)|^2$. The main problem is the correct evaluation of $|\psi_s(0)|^2$, *i.e.* of the influence of the shielding of the $5p$ electrons. A self-consistent Hartree–Fock calculation[9] yields a set of values for $|\psi_{5s}(0)|^2$ for n_s ranging from 0 to 2 and n_p from 0 to 3. If we make the assumption[14] of an sp^3 structure for grey tin and of an increasing isomeric shift from Sn^{4+} ($4d^{10}$) to Sn^{2+} ($4d^{10}5s^2$) going through sp^3,

we interpolate linearly between $|\psi_{5s}(0)|^2$ pertaining to Sn^{4+} and $|\psi_{5s}(0)|^2$ pertaining to sp^3 because all the data of R_3SnX correspond to that range. The results of Ruby *et al.*[9] can be represented by

$$a_0^3 \cdot |\psi_{5s}(0)|^2 = 19 n_s \cdot (1 - 0.11 n_p + 0.0075 n_p^2) \tag{21}$$

the last factor taking into account the shielding. We define the effective number of s electrons as $n_s' = n_s \cdot (1 - \alpha \cdot n_p - \beta \cdot n_p^2)$ with $\alpha = 0.11$, $\beta = -0.0075$

$$\left.\frac{\delta n_s'}{\delta n_p}\right|_{n_p=3} = n_s \cdot (1 - \alpha - 6\beta) = n_s \cdot (1 - 0.065)$$

Therefore in the neighbourhood of $n_p = 3$

$$n_s' = n_s(0.933 - 0.065 n_p)$$

The problem of finding $|\psi_{5s}(0)|^2$ is closely related to the ionic character. The ionic character is only dependent on the nature of the bond within a first order approximation; if we admit a negligible influence of neighboring bonds, the compounds SnX_4 are well suited for the investigation of I_X. The usual scale of ionic character is the one derived by Schawlow[10] from nuclear quadrupole effects in tetrahalides. A more recent discussion has been given by Whitehead and Jaffé[11]. Both scales are given in Table 1. There is a notable difference for Cl.

TABLE 1

IONIC CHARACTERS

X	Schawlow[10]	Whitehead–Jaffé[11]	Cordey–Hayes[14]
Cl	0.38	0.338	0.50
Br	0.28	0.275	0.38
I	0.17	0.177	0.12
F			(0.95)

If we plot isomeric shifts against the ionic character as derived by various workers, two main conclusions are unescapable:

1. The dispersion of results is much greater than the accuracy claimed by most experimenters (usually 0.1 mm/sec).
2. Although a linear trend is clearly perceptible, no single value can be selected. If we adopt a mean value, there is a disagreement with the simple formula $n_s = (1 + I_X)$ [*i.e.* eqn. (16) with $d = 0$, $I_X = I_R$].

Indeed going from a covalent structure ($I_X = 0$) to a completely ionic structure ($I_X = 1$) would involve according to Fig. 1 an isomeric shift of 4 mm/sec, which is about twice as much as presently agreed for, *i.e.* 2 mm/sec for Ruby *et al.*, 2.6 mm/sec for Cordey–Hayes[2] and Shirley[8].

Cordey–Hayes used his data to redefine an ionic character scale (Table 1) chosen to yield 2.6 mm/sec at full scale. It is thus clearly necessary to introduce the shielding effect. If we neglect d character, the number of p electrons is $n_p = 3(1 + I_X)$ and therefore $a_0^3 \cdot |\psi_{5s}(0)|^2 = 19[1 - 3\alpha(1 + I_X)]$.

If the halogen is more electronegative than the tin $I_X < 0$ and therefore an increase of $|I_X|$ means an increase of the effective value of $|\psi_{5s}(0)|^2$ although there are

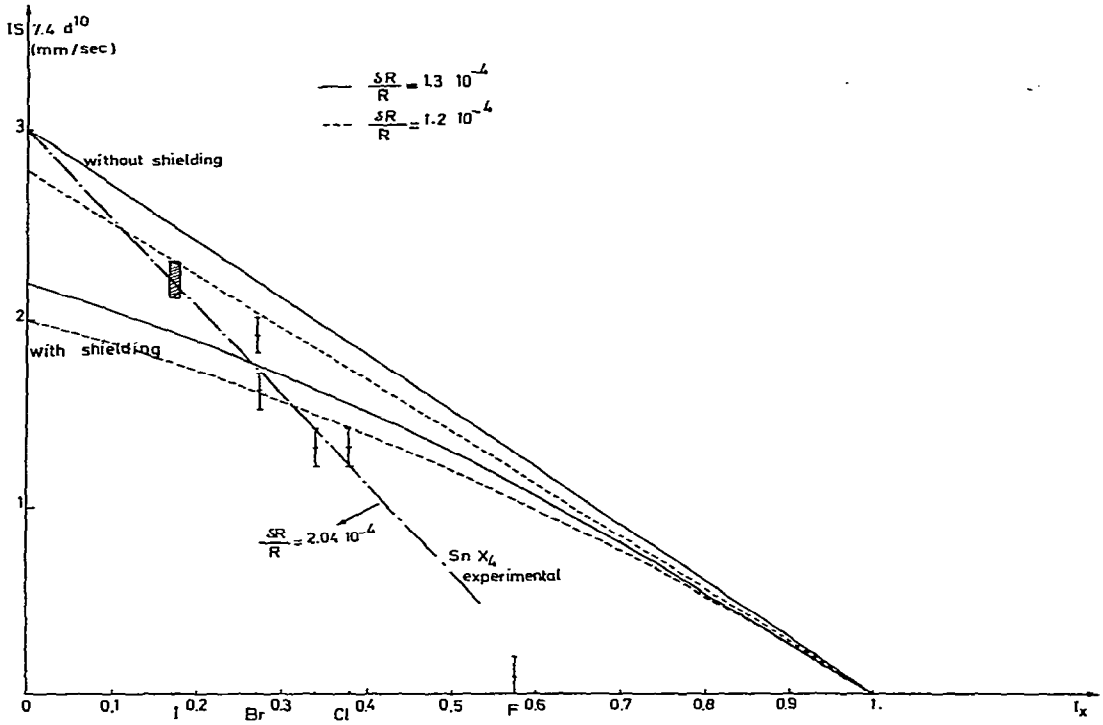

Fig. 1. Isomeric shift versus halogen electronegativity for various assumptions.

less s electrons. We have

$$\delta|\psi_{5s}(0)|^2 = |\psi_{5s}(0)|^2 \cdot (1+I_X) \cdot (1-3\alpha-3\cdot\alpha\cdot I_X)$$
$$= |\psi_{5s}(0)|^2 \cdot [1-3\alpha-|I_X|\cdot(1-6\alpha+3\alpha\cdot|I_X|)]$$

and

$$\frac{\partial}{\partial|I_X|}\cdot\left(\frac{\partial|\psi_{5s}(0)|^2}{|\psi_{5s}(0)|^2}\right) = -(1-6\cdot\alpha+6\cdot\alpha\cdot|I_X|)$$

If $\alpha < \frac{1}{6}$, the observed slope leads to $\delta R/R > 0$ as is usually assumed. The discrepancy obtained by Goldanskii *et al.*[15] is due to a larger value of α which leads to $\delta R/R < 0$. It is surprising to see that such a fundamental matter as the sign of $\delta R/R$ is dependent upon the balance of opposite shielding effects. The linear dependance of the isomeric shift on the ionic character is a normal and well understood phenonemon. It cannot be expected, however, for tin tetrahalides unless we take shielding into account. Indeed we see that a covalent structure would have a shift of 0.6 mm/sec which is well outside experimental error, if we extrapolate the curve of Fig. 1.

Using

$$v = 15.6\cdot 10^{-26}\,\frac{Z\cdot A^{\frac{2}{3}}}{E_j}\,(\mathrm{cm}^4\cdot\mathrm{sec}^{-1})\cdot S'(Z)\cdot\delta|\psi|^2\cdot\frac{\delta R}{R}$$

we obtain, with $\delta R/R = 1.3\cdot 10^{-4}$ (see experimental) and with $S'(Z) = 2.3$ (ref. 8), the

curves of Fig. 1 (with and without shielding). The experimental values are taken from various authors[13]. The ionic characters are those of Whitehead and Jaffé because the evidence is more in favor of 0.3 than 0.4 for the ionic character of chlorine. The SnF_4 value fits a straight line for an assumed I_X of 0.58 (see Goldanskii[16]), a reasonable value obtained for R_3SnX compounds (see experimental). On the other hand, the experimental value is far below the theoretical curve and would fit only if a value of nearly $I_X = 0.95$ were assumed, which brings us back to the electronegativity scale of Cordey–Hayes. However, the greater values for ionic character obtained by Cordey–Hayes for SnX_4 compounds should not be used for R_3SnX, since SnF_4 for example is definitely not tetrahedral[1-3]. On the whole, the present experimental evidence is consistent with the values of Ruby *et al.* for $a_0^3 \cdot |\psi_{5s}(0)|^2$.

Therefore, collecting various results, we obtain:

$$(1).\quad \Delta E_s = 15.6 \cdot 10^{-26} \frac{Z \cdot A^{\frac{1}{3}}}{E_j} \cdot S'(Z) \cdot \left(\frac{\delta R}{R}\right) \cdot [19 n_s \cdot (1 - 0.11 n_p + 0.0075 n_p^2)] \tag{22}$$

If the isomeric shift is measured with respect to the covalent structure:

$$IS = \Delta E_s(n_s, n_p) - \Delta E_s(1, 3) \tag{23}$$

and with respect to the ionic structure, finally

$$IS = \Delta E_s(n_s, n_p) - \Delta E_s(0, 0) \tag{24}$$

$$(2).\quad \Delta E_Q = e^2 \cdot Q \cdot |q_{zz}| \cdot |n'_p| = \tfrac{4}{5} \frac{e^2 \cdot Q}{a_0^3} \cdot [14.15 - 2n_s - 1.75 n_p] \cdot |n'_p| \tag{25}$$

EXPERIMENTAL

The experimental results given in Table 2 have been analyzed by least-squares. The following aspects of the analyses should be noted:

(1). Methyl compounds show greater errors; the analysis was carried out with inclusion and exclusion of these compounds, which are probably all pentacoordinated[2,18].

(2). We have assumed that different alkyl radicals had different I_R but we have also carried out the analysis with the assumption of a common I_R.

(3). There is considerable uncertainty as to the value of the ionic character of fluorine. Different values have been assumed ranging from 0.50 to 0.60.

On the whole, the least squares fit are rather insensitive to these changes, except possibly for the ionic character of fluorine, and the changes do not much affect the values of $\delta R/R$, Q, s^2, d^2, I_R and $\beta \cdot n_\pi$ which increases our confidence in the results.

For all samples, we have measured the isomeric shift relative to Cs_2SnF_6, which is identical to K_2SnF_6. For these compounds, we assume $4d^{10}$ configuration[14]. If this is not exact, we should have to modify the conclusion about the isomeric shift, but the quadrupole splitting would not be affected. The results show the following features:

(*a*). The value of $\delta R/R$ is $+0.133 \cdot 10^{-3}$, in good agreement with some previous results.

(*b*). The value of $Q = -0.122 \cdot 10^{-24}$ cm^2 is little affected by the fact that a common

TABLE 2

QUADRUPOLE SPLITTINGS (mm/sec) AND ISOMERIC SHIFTS (mm/sec)[a] IN R_3SnX

X	$(CH_3)_3SnX$		$(CH_3CH_2)_3SnX$		$(CH_3CH_2CH_2)_3SnX$		$(CH_3CH_2CH_2CH_2)_3SnX$		$[(CH_3)_2CHCH_2]_3SnX$	
	QS	IS	QS	IS	QS	IS	QS	IS	QS	IS
F	3.97	1.35	3.99	1.47	4.05	1.47	3.70	1.31	3.82	1.47
Cl	4.24	1.43	3.72	1.62	3.70	1.62	3.56	1.38	3.36	1.61
Br	3.95	1.30	3.31	1.62	3.57	1.67	3.32	1.33	3.20	1.60
I			3.07	1.55			2.54	1.39	2.73	1.63

[a] IS with respect to SnO_2. The variation between different runs rise to 0.08 mm/sec for IS; for QS the variation between different runs rise to 0.3 mm/sec with increase or decrease for the full width at half maximum. The analysis on the basis of Lorentzian shape with overlapping gives variations of 0.05 mm/sec for QS between different runs. This overlapping has no theoretical fundations except in the cases of single crystals[12].

I_R is adopted. This is a reflection of the fact that the values of I_R are very close. This value of Q is substantially larger than the usual value, *viz.* $Q = (-0.08 \pm 0.04) \cdot 10^{-24}$ cm^2.

(*c*). The hybridization parameters have also a constant value, whatever hypothesis is adopted:

$$s^2 = 0.19 \pm 0.02$$
$$d^2 = 0.08 \pm 0.01$$

The errors are indicative of the dispersion of the results for the different assumptions but are not related to statistical intervals of confidence. We observe that these values are compatible with an almost tetrahedral structure and are close to expectation. However there is considerable fluctuation in d^2 if we assume a common I_R. On the contrary, if we allow different I_R, d^2 settles to the common value 0.08. As confirmed by Greenwood, Perkins and Wall the effect of the inclusion of 5*d* orbitals is slight[22].

(*d*). The least-square fit is notably improved if we allow a different value of I_R for each alkyl radical, *viz.*:

methyl(0.08) < propyl(0.11) < ethyl(0.13) < isobutyl(0.17) < butyl(0.18)

A typical least square fit is shown in Fig. 2 for Et_3SnX.

(*e*). The value $y_X = \beta \cdot n_\pi/2$ *i.e.* of the effective number of electrons *equivalent to 5p electrons* donated by the halogen in the 6*p* orbitals of tin are given below for an assumed ionic character of fluorine $0.55 < I_F < 0.60$ (see *f*):

I: 0.22; Br: 0.19; Cl: 0.14; F: 0.10 to 0.05.

If we assume that the electric gradient varies as $1/n^3$ where n is the principal quantum number, we find that the halogens (except fluorine) donate about 0.8 electrons *i.e.* 0.4 for each π orbital. The regular decrease of n_π with increasing electronegativity is also noteworthy and adds some confidence to the order of magnitude. However detailed LCAO calculations are needed to substantiate these numbers. Anyway, whatever the mechanism of backdonation may be (for which this analysis cannot shed any light) the necessity of a positive value of $\beta \cdot n_\pi$ cannot be denied.

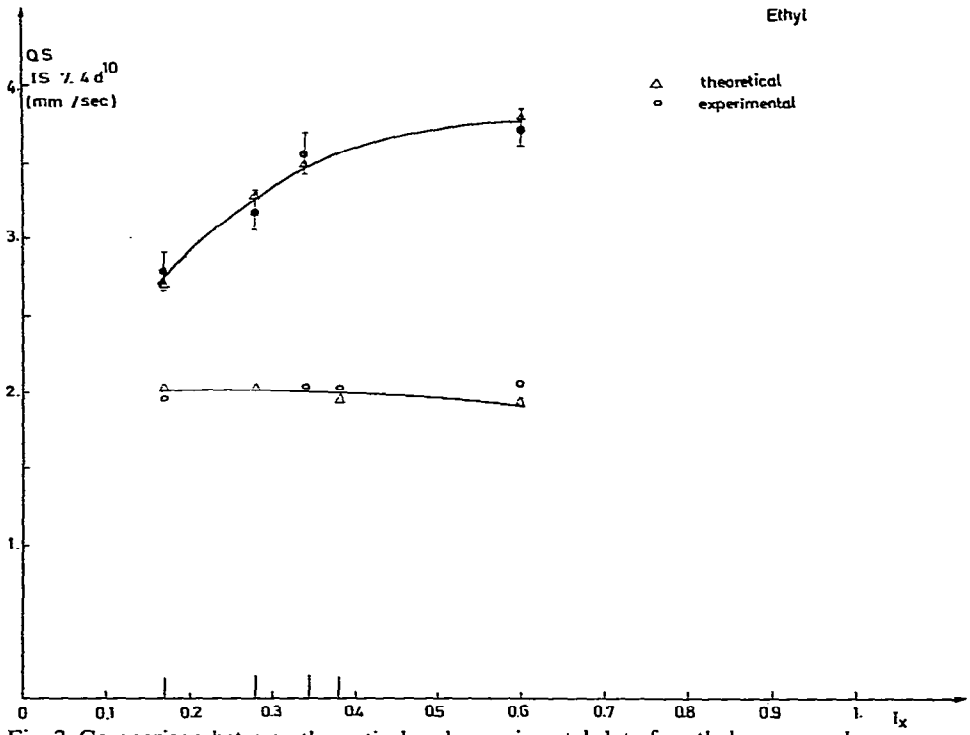

Fig. 2. Comparison between theoretical and experimental data for ethyl compounds.

(*f*). Values of the ionic character of fluorine greater than 0.65 would result in a negative value of n_π; moreover, the fit is definitely poorer. Within the range $0.50 < I_F < 0.60$, there is very little variation of all other parameters. We have adopted a value of $0.55 < I_F < 0.60$ for the values of the parameters quoted above and which is in good agreement with the value adopted by Goldanskii[16], though the significance of the agreement is not clear because compounds like SnF_4 which are assumed to be almost completely ionic are definitely not tetrahedral[1-3]. It seems safer, however, to conclude that the ionic character of fluorine in R_3SnF compounds lies around 0.57.

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