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Partial Quadrupole Splittings in Four Coordinate Sn^{IV} Compounds and Six Coordinate Fe^{II} Compounds. The Effect of Distortions

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Using recently derived partial quadrupole splittings (pqs), we have tabulated previously calculated and observed quadrupole splittings for a large number of four coordinate Sn^{IV} compounds and six coordinate Fe^{II} compounds. A plot of calculated versus observed quadrupole splittings for 92 Sn compounds gives a slope of 1.01, an intercept of +0.03 mm s^{-1}, and a correlation coefficient r = 0.992. A similar plot for 81 Fe^{II} compounds gives a slope of 1.03, an intercept of –0.04 mm s^{-1} and r = 0.979. Except for very distorted Sn^{IV} compounds such as X_3SnM [X = Cl, Br; M = $Mn(CO)_5$, $Fe(CO)_2cp$], and Fe^{II} compounds containing CO, the agreement between predicted and observed Q.S. is within the proposed 0.4 mm s^{-1} (Sn) and 0.2 mm s^{-1} (Fe) for 90% of the compounds. In addition, the above slopes and intercepts are very close to those expected (1.00 and 0.00 mm s^{-1} respectively).

Consideration of the crystallographic distortions in four coordinate Sn^{IV} compounds enables us to calculate "absolute" pqs values. However, we do not obtain an improvement in agreement between predicted and observed Q.S. using these pqs values.

Introduction

Additive treatments of quadrupole splittings[1,2,3] using partial quadrupole splittings[1] have now been widely used to rationalize and predict quadrupole splittings in compounds of Fe^{II} low spin[1,4,5,6], Sn^{IV} [1,2,7–13], Co^{III} [14] and Sb^{V} [15]. The treatment has also been used to distinguish structural isomers in five and six coordinate compounds of the above species[1,2,4,16], and to predict bonding properties of ligands[1,4,7]. Generally, the agreement between predicted and observed quadrupole splittings has been surprisingly good considering the gross simplifying assumptions of the treatment[17]. From a detailed treatment of Sn^{IV} results, Clark *et al.*[7] concluded that acceptable agreement between predicted and observed quadrupole splittings was 0.4 mm s^{-1}, while for Fe^{II} low spin compounds Bancroft and Libbey[4] concluded that 0.2 mm s^{-1} was acceptable agreement. Reasons for discrepancies outside these values have been discussed. They include: distortions from regular symmetry[1,2,3,18,19], association[1,2] and changes in bonding properties of a ligand from one compound to another due to changes in *s* character or changes in π bonding[1,4,7].

Enough data for four coordinate Sn^{IV} compounds and six coordinate Fe^{II} compounds is now available to examine the predictive uses of the pqs treatment in more detail, along with the affect of distortions on quadrupole splittings. We correlate the known Fe^{II} and Sn^{IV} data, and then examine the effect of distortions on the quadrupole splittings using recent structural data.

Results and Discussion

Partial quadrupole splittings for a large number of ligands in four coordinate Sn^{IV} compounds have been previously calculated, and are listed in Table I. Nearly all of these were initially defined by Clark *et al.*[7], but Bancroft and Butler[8,9] redefined several values using new quadrupole splittings for compounds known not to be seriously distorted from tetrahedral geometry. Thus, all pqs values were calculated from compounds in which the Sn *s* characters in the four bonds are reasonably similar. Using these partial quadrupole splittings, we have calculated quadrupole splittings for 99 Sn compounds in Table II which are likely to be four coordinate. For ten compounds (27, 28, 36, 37, 81, 82, 83, 90, 91, 92), no quadrupole splitting was detected, but it is possible that a Q.S. up to at least 0.6 mm s^{-1} would not be detected. Except for the three $Me_{3-x}SnPh_x$ compounds, we do not include the above compounds in the following discussion.

For 92 compounds, the agreement between predicted and observed quadrupole splittings is generally very good*. For eleven compounds, the predicted Q.S. differs

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* When the sign of the Q.S. is not known, we assume that the observed Q.S. has the same sign as the predicted Q.S. No discrepancy in sign (when $\eta \neq 1$) is yet known for four coordinate Sn^{IV} compounds or for the Fe^{II} low spin compounds discussed here.

TABLE I. Partial Quadrupole Splittings for Four Coordinate Sn^{IV} (mm s^{-1}).

Ligand	Compound[a]	Value	Ligand	Compound[a]	Value
NCS	46	+0.04	$Mo(CO)_3cp$	79	−0.75
			C_6F_5	107–111, 113	−0.76
F, Cl, Br	assigned	0.00	$Re(CO)_5$	84	−0.80
$MeCO_2$	100	−0.15	C_6Cl_5	117	−0.83
I	99	−0.17	$Mn(CO)_5$	1	−0.97
HCOO	48	−0.36	Fe(dppe)cp	52	−1.02
CF_3	121	−0.63	$Fe(CO)_2cp$	26	−1.08
			Ph	101, 102	−1.26
$Co(CO)_4$	69	−0.71	Me	93, 94, 97	−1.37

[a] See Table II.

TABLE II. 119-Tin Quadrupole Splittings ($^1/_2\, e^2qQ$): Observed, and Predicted from Partial Quadrupole Splittings for Four Co-ordinate Tin Compounds.

Compound	Quadrupole Splitting (mm s^{-1})		Reference	η
	Observed	Calculated		Calculated
1. $Me_3SnMn(CO)_5$	0.82	(−ve)[a]	1	0.00
2. $Et_3SnMn(CO)_5$	0.88	−0.82	2	0.00
3. $Me_2Sn[Mn(CO)_5]_2$	0.92	0.92	3	1.00
4. $MeSn[Mn(CO)_5]_3$	0.95	+0.82	3	0.00
5. $Me_2ClSnMn(CO)_5$	−2.60	−2.59	1	0.41 (0.35 observed)
6. $Me_2BrSnMn(CO)_5$	2.54	−2.59	4	0.41
7. $MeCl_2SnMn(CO)_5$	+2.62	+2.79	1	0.89 (0.46 observed)
8. $MeBr_2SnMn(CO)_5$	2.51	+2.79	4	0.89
9. $Cl_3SnMn(CO)_5$	+1.60	+1.94	1	0.00 (~0 observed)
10. $Br_3SnMn(CO)_5$	1.53	+1.94[b]	1	0.00
11. $I_3SnMn(CO)_5$	1.32	+1.60	5	0.00
12. $Cl_2Sn[Mn(CO)_5]_2$	2.10	2.24	6	1.00
13. $Br_2Sn[Mn(CO)_5]_2$	2.12	2.24	6	1.00
14. $Cl\,Sn[Mn(CO)_5]_3$	1.55	−1.94	7	0.00
15. $Ph_3SnMn(CO)_5$	0.41	−0.58	1	0.00
16. $Ph_2ClSnMn(CO)_5$	2.50	−2.39	1	0.32
17. $Ph_2BrSnMn(CO)_5$	2.31	−2.39	1	0.32
18. $PhCl_2SnMn(CO)_5$	2.52	+2.62	1	0.94
19. $PhBr_2SnMn(CO)_5$	2.65	+2.62	1	0.94
20. $PhI_2SnMn(CO)_5$	2.19	2.23	5	0.91
21. $Ph_2(C_6F_5)SnMn(CO)_5$	0.95	−0.97	1	0.78
22. $Ph(C_6F_5)_2SnMn(CO)_5$	1.06	+0.95	1	0.58
23. $(C_6F_5)_3SnMn(CO)_5$	+0.99	+0.42[b]	1	0.00 ~0 observed)
24. $Sn[Fe(CO)_2cp]_4$	0.00	0.00	6	0.00
25. $Me_3SnFe(CO)_2cp$	0.46	−0.58	8	0.00 (~0 observed)
26. $Bu_3SnFe(CO)_2cp$	−0.59	(−ve)[a]	9	0.00
27. $Me_2Sn[Fe(CO)_2cp]_2$	0[b]	0.67[c]	2	1.00
28. $Et_2Sn[Fe(CO)_2cp]_2$	0[b]	0.67[c]	2	1.00
29. $Cl_3SnFe(CO)_2cp$	+1.83	+2.16[b]	1	0.00 (~0 observed)
30. $Br_3SnFe(CO)_2cp$	1.63	+2.16[b]	1	0.00
31. $I_3SnFe(CO)_2cp$	1.50	+1.82	10	0.00
32. $Cl_2Sn[Fe(CO)_2cp]_2$	+2.39	2.50	9, 10	1.00 (0.65 observed)
33. $Br_2Sn[Fe(CO)_2cp]_2$	2.42	2.50	6	1.00
34. $I_2Sn[Fe(CO)_2cp]_2$	2.25	2.09	10	1.00
35. $Ph_3SnFe(CO)_2cp$	0.32	−0.36	1	0.00
36. $Ph_2Sn[Fe(CO)_2cp]_2$	0[b]	0.42[c]	11	1.00
37. $PhSn[Fe(CO)_2cp]_3$	0[b]	+0.36[c]	11	0.00
38. $Ph_2ClSnFe(CO)_2cp$	2.54	−2.42	1	0.20
39. $Ph_2BrSnFe(CO)_2cp$	2.52	−2.42	1	0.20
40. $PhCl_2SnFe(CO)_2cp$	2.84	+2.72	1	0.98

TABLE II. (Cont.)

Compound	Quadrupole Splitting (mm s^{-1})		Reference	η
	Observed	Calculated		Calculated
41. $PhBr_2SnFe(CO)_2cp$	2.65	+2.72	1	0.98
42. $Ph_2(C_6F_5)SnFe(CO)_2cp$	0.93	−0.94	1	0.50
43. $Ph(C_6F_5)_2SnFe(CO)_2cp$	1.37	+0.99	1	0.84
44. $(C_6F_5)_3SnFe(CO)_2cp$	1.21	+0.64^b	1	0.00
45. $ClSn[Mn(CO)_5][Fe(CO)_2cp]_2$	2.02	−2.10	11	0.14
46. $(NCS)_3SnFe(CO)_2cp$	2.24	(+ve)^a	10	0.00
47. $(NCS)_2Sn[Fe(CO)_2cp]_2$	+2.56	2.58	9, 10	1.00 (<0.5 observed)
48. $(HCOO)_3SnFe(CO)_2cp$	1.45	(+ve)^a	10	0.00
49. $(HCOO)_2Sn[Fe(CO)_2cp[_2$	2.19	1.67^b	10	1.00
50. $(CH_3COO)_3SnFe(CO)_2cp$	1.87	+1.86	10	0.00
51. $(CH_3COO)_2Sn[Fe(CO)_2cp]_2$	2.60	2.14^b	10	1.00
52. $Me_3SnFe(dppe)cp$	0.70	(−ve)^a	12	0.00
53. $Cl_3SnFe(dppe)cp$	1.76	+2.04	12	0.00
54. $Br_3SnFe(dppe)cp$	1.60	+2.04^b	12	0.00
55. $I_3SnFe(dppe)cp$	1.53	+1.70	12	0.00
56. $Sn[Co(CO)_4]_4$	0	0.00	1	0.00
57. $Me_3SnCo(CO)_4$	1.73	−1.32^b	1	0.00
58. $Me_2Sn[Co(CO)_4]_2$	1.53	1.52	1	1.00
59. $MeSn[Co(CO)_4]_3$	1.29	+1.32	1	0.00
60. $Me_2ClSnCo(CO)_4$	2.73	−2.62	1	0.66
61. $MeClSn[Co(CO)_4]_2$	2.38	−2.27	1	0.99
62. $Cl_3SnCo(CO)_4$	1.20	+1.42	1	0.00
63. $Br_3SnCo(CO)_4$	1.29	+1.42	6, 13	0.00
64. $I_3SnCo(CO)_4$	0.71	+1.08	13	0.00
65. $Cl_2Sn[Co(CO)_4]_2$	1.44	1.64	1	1.00
66. $Br_2Sn[Co(CO)_4]_2$	1.46	1.64	1	1.00
67. $I_2Sn[Co(CO)_4]_2$	1.07	1.25	1	1.00
68. $FSn[Co(CO)_4]_3$	0.97	−1.42^b	1	0.00
69. $ClSn[Co(CO)_4]_3$	1.42	(−ve)^a	1	0.00
70. $BrSn[Co(CO)_4]_3$	1.06	−1.42	13	0.00
71. $ISn[Co(CO)_4]_3$	0.95	−1.08	13	0.00
72. $Ph_3SnCo(CO)_4$	1.20	−1.10	1	0.00
73. $Ph_2Sn[Co(CO)_4]_2$	1.27	1.27	1	1.00
74. $PhSn[Co(CO)_4]_3$	1.28	+1.10	14	0.00
75. $Ph_2ClSnCo(CO)_4$	2.18	−2.39	1	0.60
76. $PhClSn[Co(CO)_4]_2$	1.88	−2.07	1	0.83
77. $Me_2Sn[Mn(CO)_5][Co(CO)_4]$	1.46	−1.30	1	0.80
78. $Ph_2Sn[Mn(CO)_5][Co(CO)_4]$	1.15	−1.06	7	0.72
79. $Me_3SnMo(CO)_3cp$	1.25	(−ve)^a	15	0.00
80. $Cl_2Sn[Mn(CO)_5][Mo(CO)_3cp]$	2.0	+1.90	7	0.66
81. $Ph_3SnRe(CO)_5$	0^b	−0.92^c	7	0.00
82. $Ph_2Sn[Re(CO)_5]_2$	0^b	1.06^c	7	1.00
83. $PhSn[Re(CO)_5]_3$	0^b	+0.92^c	7	0.00
84. $ClSn[Re(CO)_5]_3$	1.60	(+ve)^a	11	0.00
85. $BrSn[Re(CO)_5]_3$	1.60	+1.60	7	0.00
86. $Cl_2Sn[Mn(CO)_5][Re(CO)_5]$	2.48	2.06^b	7	0.96
87. R_4Sn (R = Me, Et, Pr, Bu, Neo, cy)	0	0.00	16, 17	0.00
88. Ph_4Sn	0	0.00	16	0.00
89. $(C_6X_5)_4Sn$ (X = F, Cl)	0	0.00	16	0.00
90. Me_3SnPh	0^b	−0.22	16	0.00
91. Me_2SnPh_2	0^b	0.25	16	1.00
92. $MeSnPh_3$	0^b	+0.22	16	0.00
93. Neo_3SnF	2.79	(−2.74)^a	17	0.00
94. Neo_3SnCl	2.65	(−2.74)^a	17	0.00
95. $(PhCH_2)_3SnCl$	2.80	−2.74	18	0.00
96. $(PhCH_2)_2SnCl_2$	2.84	3.15	18	1.00
97. Neo_3SnBr	2.65	(−2.74)^a	17	0.00
98. Bu_3SnI	2.65	−2.40	16	0.00

TABLE II. (Cont.)

Compound	Quadrupole Splitting (mm s^{-1})		Reference	η
	Observed	Calculated		Calculated
99. Neo_3SnI	2.40	(–ve)[a]	17	0.00
100. $Neo_3Sn(O_2CMe)$	2.45	(–ve)[a]	17	0.00
101. Ph_3SnCl	−2.54	(−2.52)[a]	18	0.00
102. Ph_3SnBr	2.50	(−2.52)[a]	18	0.00
103. Ph_3SnI	2.15	−2.02	18	0.00
104. Ph_2SnCl_2	2.82	2.90	18	1.00
105. Ph_2SnBr_2	2.54	2.90	18	1.00
106. Ph_2SnI_2	2.38	2.47	18	1.00
107. $Me_3Sn(C_6F_5)$	−1.35	(−1.34)[a]	18	0.00
108. $Me_2Sn(C_6F_5)_2$	1.51	(1.54)[a]	18	1.00
109. $MeSn(C_6F_5)_3$	1.14	(+1.34)[a]	19	0.00
110. $Ph_3Sn(C_6F_5)$	−0.95	(−1.12)[a]	18	0.00
111. $Ph_2Sn(C_6F_5)_2$	1.11	(1.29)[a]	18	1.00
112. $(4\text{-}MeC_6H_4)_2Sn(C_6F_5)_2$	1.18	1.29	19	1.00
113. $PhSn(C_6F_5)_3$	0.92	(+1.12)[a]	19	0.00
114. $(4\text{-}MeC_6H_4)Sn(C_6F_5)_3$	1.02	+1.12	19	0.00
115. $ClSn(C_6F_5)_3$	1.55	−1.40	19	0.00
116. $BrSn(C_6F_5)_3$	1.60	−1.40	19	0.00
117. $Me_3Sn(C_6Cl_5)$	1.09	(–ve)[a]	20	0.00
118. $Ph_3Sn(C_6Cl_5)$	0.84	−0.86	20	0.00
119. $Ph_2Sn(C_6Cl_5)_2$	1.14	0.99	20, 21	1.00
120. $PhSn(C_6Cl_5)_3$	0.80	+0.86	21	0.00
121. Me_3SnCF_3	1.48	(–ve)[a]	20, 22	0.00
122. $Me_3SnCF_2CF_3$	1.63	−1.48	22	0.00

Abbreviations: Me, methyl (CH_3); Et, ethyl (CH_3CH_2); Pr, n-propyl ($CH_3CH_2CH_2$); Bu, n-butyl ($CH_3CH_2CH_2CH_2$); Neo, neophyl ($C(CH_2)_2(CH_2C_6H_5)$); cy, cyclohexyl (C_6H_{11}); Ph, phenyl (C_6H_5); cp, *h*-cyclopentadienyl (C_5H_5); dppe, 1,2-bis(diphenylphosphino)ethane.

[a] Compound used to derive a ligand p.q.s. value. The sign assumed is shown; and the predicted value is also shown if the ligand p.q.s. value was averaged from more than one compound. [b] Calculated value differs from observed value by more than 0.4 mm s^{-1}.

[c] Not included in the correlation in Figure 1, because there is most likely a small Q.S. present which has not been detected.

References

1 (a) G.M. Bancroft, K.O. Butler and A.T. Rake, *J. Organometal. Chem., 34,* 137 (1972); (b) G.M. Bancroft, K.D. Butler, A.T. Rake and B.W. Dale, *J.C.S. Dalton,* 2025 (1972); (c) G.M. Bancroft and K.D. Butler, *J.C.S. Dalton,* 1694 (1973).

2 R.H. Herber and A. Hoffmann, *Progr. Inorg. Chem., 8,* 35 (1967).

3 C. Wynter and L. Chandler, *Bull. Chem. Soc. Japan, 43,* 2115 (1970).

4 S. Onaka, Y. Sasaki and H. Sano, *Bull. Chem. Soc. Japan, 44,* 126 (1971).

5 S.R.A. Bird, J.D. Donaldson, A.F. Le C. Holding, B. Ratcliff and S. Cenini, *Inorg. Chim. Acta, 6,* 379 (1972).

6 R.V. Parish, *Progr. Inorg. Chem., 15,* 59 (1972).

7 A.N. Karasev, N.E. Kolobova, L.S. Polak, V.S. Shpinel and K.N. Anisimov, *Teor. i Eksp. Khim., Akad. Nauk. Ukr., 2,* 126 (1966).

8 W.R. Cullen, J.R. Sams and J.A.J. Thompson, *Inorg. Chem., 10,* 843 (1971).

9 B.A. Goodman, R. Greatrex and N.N. Greenwood, *J. Chem. Soc. (A),* 1868 (1971).

10 S.R.A. Bird, J.D. Donaldson, A.F. Le C. Holding, B.J. Senior and M.J. Tricker, *J. Chem. Soc. (A),* 1616 (1971).

11 V.I. Gol'danskii, B.V. Borshagovskii, E.F. Makarov, R.A. Stukan, K.N. Anisimov, N.E. Kolobova and V.V. Skripkin, *Teor. i Eksp. Khim., Akad. Nauk. Ukr., 3,* 478 (1967).

12 M.J. Mays and P.L. Sears, *J.C.S. Dalton,* 1873 (1973).

13 S. Ichiba, M. Katada and H. Negita, *Bull. Chem. Soc. Japan, 45,* 1679 (1972).

14 D.E. Fenton and J.J. Zuckermann, *J. Am. Chem. Soc., 90,* 6226 (1968).

15 S.R.A. Bird, J.D. Donaldson, S.A. Keppie and M.F. Lappert, *J. Chem. Soc. (A),* 1311 (1971).

16 Average value from several sources, or private communication, listed in P.J. Smith, *Organometal. Chem. Rev. (A), 5,* 373 (1970).

17 R.H. Herber, H.A. Stöckler and W.T. Reichle, *J. Chem. Phys., 42,* 2447 (1965).

18 Average value from several sources, or private communication, listed in G.M. Bancroft and R.H. Platt, *Adv. Inorg. Radiochem., 15,* 59 (1972).

19 H.A. Stöckler and H. Sano, *Trans. Faraday Soc., 64,* 577 (1968).

20 R.V. Parish and R.H. Platt, *J. Chem. Soc. (A),* 2145 (1969).

21 M. Cordey Hayes, R.D.W. Kemmitt, R.D. Peacock and G. Rimmer, *J. Inorg. Nucl. Chem., 31,* 1515 (1969).

22 W.R. Cullen, J.R. Sams and M.C. Waldman, *Inorg. Chem., 9,* 1682 (1970).

from the observed by over 0.4 mm s^{-1}, and in only four cases (23, 30, 44, 49) is the discrepancy larger than 0.5 mm s^{-1}. A number of these discrepancies can be rationalized by considering either distortions or a large change in *s* character of the Sn–M [M = Fe(CO)$_2$cp, Mn(CO)$_5$] bond. Thus for compounds 10, 29, 30 and 54, the discrepancy is readily rationalized by considering the large increase of *s* character in the Sn–M bond from the R$_3$SnM compounds (from which the pqs values were derived) to the X$_3$SnM compounds. As the *s* character of the Sn–M bond increases, the "effective" pqs of the M group becomes less negative. For compound 68, it is quite possible that there is some intermolecular association through the F atom, which would lead to this low Q.S.[9]

The generally very good agreement between predicted and observed values is emphasized by the excellent correlation between predicted and observed Q.S. given in Figure 1. For the 92 compounds, we obtain a straight line of slope 1.01, intercept +0.03, and a correlation coefficient r = 0.992. Both slope and intercept are very close to the theoretical values of 1.00 and 0.00.

In a similar way, we have collected all the known quadrupole splittings for Fe^{II} low spin compounds containing ligands for which pqs values have been derived. These pqs values are listed in recent publications[1,4], and were derived from *trans* compounds of the type *trans*-FeL$_2$L'$_4$ wherever possible. Using these pqs values, we calculate quadrupole splittings for eighty-one Fe^{II} low spin compounds (Table III).

Agreement between predicted and observed quadrupole splittings is generally reasonable, but 21 compounds have predicted Q.S. which differs from that observed by over 0.2 mm s^{-1}. Only six lie outside 0.3 mm s^{-1}. Of the twenty-one compounds, fourteen contain CO whose bonding properties are known to vary substantially. In addition, Clark *et al.*[7] have suggested that localized orbitals are a necessary condition for additivity. Since it is not possible to write down localized π orbitals between CO and Fe, Clark suggested that additivity would not be expected for strong π acceptor ligands such as CO.

The plot of calculated versus observed Q.S. gives a straight line of slope 1.03, an intercept of −0.04 mm s^{-1} with an r of 0.979, for 81 compounds. If we exclude the carbonyl compounds (71, 73, 74) which contain Co *trans* to a strong σ donor and weak π acceptor, then for 78 compounds we obtain a straight line of slope 1.02, intercept −0.06 and r = 0.987. Once again, we have very good correlations considering the gross assumptions.

The Effect of Distortions

In the above calculations, regular tetrahedral (Sn^{IV}) or octahedral (Fe^{II}) geometry was assumed for all molecules. However, a number of four coordinate tin structures have been determined by diffraction methods,

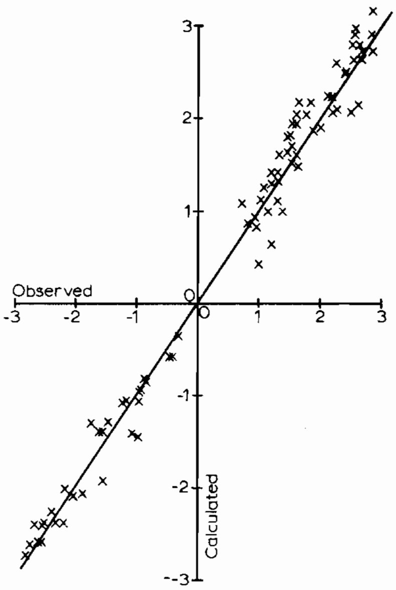


Figure 1. Calculated *vs.* observed ^{119}Sn quadrupole splittings (mm s^{-1}) for four coordinated Sn^{IV} compounds (see Table II and text).

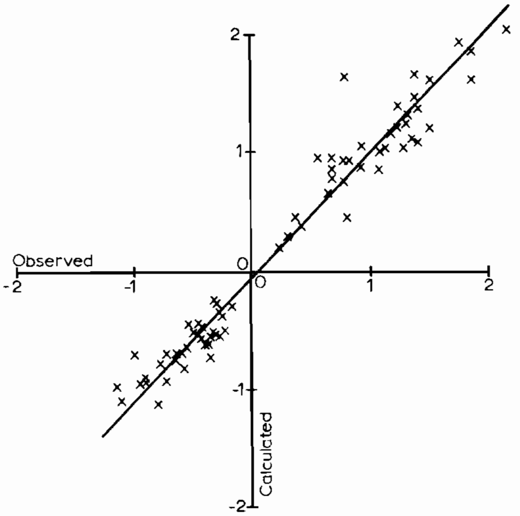


Figure 2. Calculated *vs.* observed ^{57}Fe quadrupole splittings (mm s^{-1}) for six coordinate Fe^{II} low spin compounds (see Table III and text).

and the bond angles deviate significantly from the tetrahedral value of 109° 47′ by up to 20°. In particular, the largest deviations are found in X$_3$SnM (X = Cl, Br) compounds. Such large distortions, with the accompanying variations in Sn–M *s* character, are most probably a major cause of discrepancies between predicted and observed Q.S. Clark *et al.*[7] tried to account for these distortions in their molecular orbital model, but concluded that at least for small distortions it was

TABLE III. 57-Iron Quadrupole Splittings: Observed and Predicted from Partial Quadrupole Splittings for Octahedral Iron(II) Low-Spin Compounds.

	Compound	Quadrupole Splitting (mm s^{-1})		Reference
		Observed	Calculated	
1.	*cis*-$\mathrm{Fe(SnCl_3)Cl(P(OMe)_3)_4}$	0.44	−0.58	1
2.	$\mathrm{[FeSnCl_3(P(OMe)_3)_5]BPh_4}$	+0.36	+0.44	1
3.	$\mathrm{[Fe(P(OMe)_3)_6][BPh_4]_2}$	<0.10	0.0	1
4.	*fac*-$\mathrm{Fe(CO)_3I_2P(OMe)_3}$	0.36	−0.72[a]	1
5.	$\mathrm{Fe(CO)_2I_2(P(OMe)_3)_2}$	0.73	−0.92	1
6.	*trans*-$\mathrm{[Fe(CO)I(P(OMe)_3)_4]I}$	0.83	+0.92	1
7.	*trans*-$\mathrm{[Fe(CO)I(P(OMe)_3)_4]BPh_4}$	0.77	+0.92	1
8.	*mer*-$\mathrm{[Fe(CO)_2I(P(OMe)_3)_3]BPh_4}$	0.67	+0.84	1
9.	*trans*-$\mathrm{[Fe(CO)Br(P(OMe)_3)_4]BPh_4}$	0.68	+0.94[a]	1
10.	$\mathrm{Fe(CO)_2Br_2(P(OMe)_3)_2}$	0.93	−0.94	1
11.	$\mathrm{Fe(CO)_2Cl_2(P(OMe)_3)_2}$	0.89	−0.90	1
12.	*cis*-$\mathrm{Fe(NCS)_2(P(OMe)_3)_4}$	0.30	−0.28	1
13.	*cis*-$\mathrm{Fe(NCS)_2(ArNC)_4}$	0.42	+0.38	2
14.	$\mathrm{Fe(CO)_2I_2(PMe_3)_2}$	0.90	−0.96	2
15.	$\mathrm{Fe(CO)_2I_2(PMe_3)_2}$	+1.32	+1.31	2
16.	$\mathrm{Fe(CO)_3I_2(ArNC)}$	0.58	−0.82[a]	2
17.	$\mathrm{Fe(CO)_2I_2(ArNC)_2}$	0.79	−1.12[a]	2
18.	$\mathrm{Fe(CO)_2Cl_2(dppe)}$	0.61	−0.67	2
19.	$\mathrm{Fe(CO)_2Cl_2(dppe)}$	0.33	−0.24	2
20.	$\mathrm{Fe(CO)_2Br_2(dppe)}$	0.63	−0.71	2
21.	$\mathrm{Fe(CO)_2I_2(dppe)}$	0.60	−0.69	2
22.	*cis*-$\mathrm{Fe(CO)_4(SnCl_3)_2}$	0.20	+0.24	3
23.	$\mathrm{Fe(CO)_3I_2PPh_2Et}$	0.46	−0.52	2
24.	$\mathrm{Fe(CO)_2Br_2(PPh_2Et)_2}$	0.55	−0.66	2
25.	$\mathrm{Fe(CO)_2I_2(PPh_2Et)_2}$	0.37	−0.64[a]	2
26.	$\mathrm{Fe(CO)_2Br_2(PPh_2Me)_2}$	0.56	−0.66	2
27.	$\mathrm{Fe(CO)_2I_2(PPh_2Me)_2}$	0.39	−0.64[a]	2
28.	$\mathrm{Fe(CO)_3I_2PPh_3}$	0.43	−0.48	2
29.	$\mathrm{Fe(CO)_2Br_2(PPh_3)_2}$	0.34	−0.56[a]	2
30.	$\mathrm{Fe(CO)_3Br_2P(OPh)_3}$	0.27	−0.54[a]	2
31.	$\mathrm{Fe(CO)_3I_2(P(OPh)_3)}$	0.33	−0.52	2
32.	$\mathrm{Fe(CO)_2Br_2(P(OPh)_3)_2}$	0.45	−0.54	2
33.	$\mathrm{Fe(CO)_2I_2(P(OPh)_3)_2}$	0.32	−0.52	2
34.	*cis*-$\mathrm{Fe(CO)_4Cl_2}$	0.24	−0.50[a]	2
35.	*cis*-$\mathrm{Fe(CO)_4Br_2}$	0.30	−0.54[a]	2
36.	*cis*-$\mathrm{Fe(CO)_4I_2}$	0.30	−0.52[a]	2
37.	$\mathrm{Fe(CO)_3I_2AsPh_3}$	0.54	−0.44	2
38.	$\mathrm{Fe(CO)_2Br_2(AsPh_3)_2}$	0.26	−0.38	2
39.	$\mathrm{Fe(CO)_2Br_2(SbPh_3)_2}$	0.27	−0.34	2
40.	$\mathrm{Fe([14]ane\ N_4)(CN)_2}$	−1.10	−1.10	4
41.	$\mathrm{[Fe(Me_2[14]ane\ N_4)(CH_3CN)_2][ClO_4]_2}$	0.65	+0.64	4
42.	$\mathrm{Fe([14]4,11\text{-}diene\ N_4)(SCN)_2}$	0.77	+0.74	4
43.	$\mathrm{[Fe([14]4,11\text{-}diene\ N_4)(Im_2)][BPh_4]_2}$	1.07	+0.84	4
44.	$\mathrm{[Fe([14]4,11\text{-}diene\ N_4)(CH_3CN)_2][ClO_4]_2}$	1.07	+1.00	4
45.	$\mathrm{Fe([14]4,11\text{-}diene\ N_4)(CN)_2}$	−0.70	−0.74	4
46.	$\mathrm{[Fe([14]1,4,11\text{-}triene\ N_4)(CH_3CN)_2][ClO_4]_2}$	1.28	+1.23	4
47.	$\mathrm{[Fe([14]1,4,8,11\text{-}tetraene\ N_4)(CH_3CN)_2][ClO_4]_2}$	1.36	+1.46	4
48.	$\mathrm{[Fe([14]1,3,8\text{-}triene\ N_4)(SCN)_2}$	1.35	+1.11[a]	4
49.	$\mathrm{[Fe([14]1,3,8\text{-}triene\ N_4)(Im)_2][BF_4]_2}$	1.50	+1.21[a]	4
50.	$\mathrm{[Fe([14]1,3,8\text{-}triene\ N_4)(CH_3CN)_2][PF_6]_2}$	1.23	+1.37	4
51.	$\mathrm{[Fe([14]1,3,7,10\text{-}tetraene\ N_4)(CH_3CN)_2][PF_6]_2}$	1.51	+1.60	4
52.	$\mathrm{[Fe([14]1,3,7,11\text{-}tetraene\ N_4)(CH_3CN)_2][BPh_4]_2}$	1.86	+1.60[a]	4
53.	$\mathrm{[Fe([14]1,3,8,10\text{-}tetraene\ N_4)(CH_3CN)_2][PF_6]_2}$	1.41	+1.08[a]	4
54.	$\mathrm{Fe([14]1,3,8,10\text{-}tetraene\ N_4)(NO_2)_2}$	1.39	+1.36	4
55.	*cis*-$\mathrm{FeCl_2(ArNC)_4}$	−0.78	−0.78	5
56.	$\mathrm{[FeCl(ArNC)_5]ClO_4}$	0.73	+0.78	5
57.	*cis*-$\mathrm{Fe(SnCl_3)_2(ArNC)_4}$	0.50	−0.52	5

TABLE III. (Cont.)

	Compound	Quadrupole Splitting (mm s^{-1})		Reference
		Observed	Calculated	
58.	*cis*-$Fe(SnCl_3)Cl(ArNC)_4$	0.61	−0.69	5
59.	$[Fe(SnCl_3)(ArNC)_5]ClO_4$	0.32	+0.52	5
60.	*trans*-$FeHCl(depe)_2$	<0.12	−0.20	5
61.	*trans*-$FeHI(depe)_2$	<0.19	−0.18	5
62.	*trans*-$FeClSnCl_3(depe)_2$	1.28	+1.02[a]	5
63.	*trans*-$FeBr_2(depe)_2$	1.22	+1.20	5
64.	*cis*-$Fe(CN)_2(EtNC)_4$	0.29	+0.30	5
65.	$[Fe(CN)(EtNC)_5]ClO_4$	0.17	−0.30	5
66.	$Fe(niox)_2(Im)_2$	1.38	+1.64[a]	5
67.	$Fe(niox)_2(Py)_2$	1.75	+1.92	5
68.	$Fe(niox)_2(but)_2$	1.83	+1.84	5
69.	$K_2Fe(niox)_2(CN)_2$	0.80	+0.44[a]	5
70.	$KFe(niox)_2Im(CN)$	0.93	+1.04	5
71.	$Fe(niox)_2Im(CO)$	0.77	+1.62[a]	5
72.	$[FeH(ArNC)(depe)_2]BPh_4$	−1.14	−0.98	5
73.	$[FeH(CO)(depe)_2]BPh_4$	1.00	−0.70[a]	5
74.	*cis*-$FeH_2(CO)_4$	0.55	+0.98[a]	6
75.	*trans*-$[FeH[P(OMe)_3](depe)_2]BPh_4$	0.90	−0.90	6
76.	*trans*-$[FeH[P(OPh)_3](depe)_2]BPh_4$	0.72	−0.70	6
77.	*trans*-$[FeH(MeCN)(depe)_2]BPh_4$	0.46	−0.44	6
78.	*trans*-$\{[FeCl(depe)_2]_2(succ)\}(BPh_4)_2$	1.17	+1.14	7
79.	*trans*-$[FeCl(NCPh)(depe)_2]BPh_4$	1.12	+1.02	7
80.	*trans*-$[Fe(NCMe)_2(depe)_2](BPh_4)_2$	0.93	+0.88	7
81.	*trans*-$[FeCl(NO)(depe)_2](BPh_4)_2$	2.15	+2.04	7

Abbreviations: ArNC, *p*-methoxyphenylisocyanide; EtNC, ethylisocyanide; but, N-butylamine; dmpe, 1,2-bis(dimethylphosphino)ethane; depe, 1,2-bis(diethylphosphino)ethane; dppe, 1,2-bis(diphenylphosphino)ethane; depb, *o*-phenylenebisdiethylphosphine; py, pyridine; Im, imidazole; Ph, phenyl; Me, methyl; Et, ethyl; niox, 1,2-cyclohexanedione dioxime.

[a] Calculated value differs from observed value by over 0.2 mm s^{-1}.

References

1 E.T. Libbey and G.M. Bancroft, *J. Chem. Soc. (Dalton)*, 87 (1974) at 80° K.

2 G.M. Bancroft and E.T. Libbey, *J. Chem. Soc. (Dalton)*, 2103 (1973) at 80° K.

3 N. Dominelli, E. Wood, P. Vasudev and C.H.W. Jones, *Inorg. Nucl. Chem. Lett.*, *8*, 1077 (1972).

4 J.C. Dabrowiak, P.H. Merrell, J.A. Stone and D.H. Busch, *J. Am. Chem. Soc.*, *95*, 6613 (1973) (at 295°).

5 G.M. Bancroft and R.H. Platt, *Adv. Inorg. Radiochem.*, *15*, 59 (1972): Table 44, with correction for $(pqs)_{CO} = -0.55$ mm s^{-1}.

6 This work, $(pqs)_{RCN}$ taken from reference 4.

7 J. Bellerby and M.J. Mays, *J. Chem. Soc. (Dalton)*, to be published.

best to use the regular tetrahedral model. Since La Rossa and Brown[14] usefully applied the "distorted" version of the point charge model for Co^{III} compounds, we felt it would be instructive to use the numerous Sn^{IV} crystal structures to apply the literal point charge model including distortions.

The chief difficulty in the distortion calculations arises because it is no longer sufficient to use *relative* pqs values, and "absolute" pqs values must be derived. One possible way of deriving these "absolute" values is to apply the equations defining Q.S. and η (from V_{XX}, V_{YY} and V_{ZZ}) to a molecule where the Q.S. (and its sign) and η have been measured (and $\eta \neq 0$). The only appropriate compound so far reported[20] is $Cl_2Sn[Fe(CO)_2cp]_2$, which has the parameters Q.S. $= +2.35$ mm s^{-1}, and $\eta = 0.65$. Considering the axis system shown below Table IV, V_{ii}, V_{jj} and V_{kk} are the principal efg axes V_{XX}, V_{YY} and V_{ZZ} – but not necessarily in that order. From the reported crystallographic study[21] of this compound, $\alpha = 128.6$ and $\beta = 94.1$; so that the efg components are given by

$$-eQV_{ii} = -0.8716\{Fe\} + 0.7855\{Cl\} \quad (1a)$$

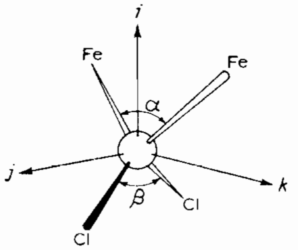
$$-eQV_{jj} = -2.0000\{Fe\} + 1.2154\{Cl\} \quad (1b)$$

$$-eQV_{kk} = +2.8716\{Fe\} - 2.0000\{Cl\} \quad (1c)$$

where $\{Fe(CO)_2cp\}$ is abbreviated as $\{Fe\}$.

TABLE IV. Calculated Absolute pqs Values for Cl and Fe (CO)$_2$cp (method 1).

Assignment	{Cl} (mm s^{-1})	{Fe(CO)$_2$cp} (mm s^{-1})	QS (Cl$_3$SnFe (CO)$_2$cp) (calculated) (mm s^{-1})
1. i = x j = y k = z	+6.70	+3.90	−2.05
2. i = y j = x k = z	−1.86	−2.06	+2.53
3. i = x j = z k = y	+11.0	+7.79	−6.14
4. i = y j = z k = x	+5.05	+4.17	−4.01
5. i = z j = x k = y	−11.8	−8.07	+6.02
6. i = z j = y k = x	−9.16	−5.73	+3.60



Clearly, there are six ways in which axes i, j, k can be assigned to X, Y, Z; but there seems to be no simple way in which they can be identified. Thus, the above equations (1a–c) were solved against $\eta = (V_{XX} - V_{YY})/V_{ZZ}$ for {Fe} and {Cl} for each possible assignment, and the results are shown in Table IV. The most straightforward test of these derived absolute pqs values is to use them, together with the measured[22] crystallographic angles, to calculate the Q.S. for Cl$_3$SnFe(CO)$_2$cp. V_{ZZ} is unambiguously defined for this molecule and η is known to be zero[20, 23].

The |Q.S.| of Cl$_3$SnFe(CO)$_2$cp is 1.83 (Table II) and its sign is positive[20, 23]. Thus solutions 1, 3 and 4 in Table IV do not predict the correct sign, and can be neglected. Of the other solutions, solution 2 shows the best agreement; but this is not as good as the +2.16 mm s^{-1} predicted using regular tetrahedral angles.

A possible problem with the above analysis is the fact that the uncertainty in the η value measured for Cl$_2$Sn[Fe(CO)$_2$cp]$_2$ is relatively large (0.05)[20]. Consequently, an alternative (and possibly more accurate) approach is to solve for {Cl} and {Fe(CO)$_2$cp} using the V_{ZZ} expressions for Cl$_2$Sn[Fe(CO)$_2$cp]$_2$ and Cl$_3$SnFe(CO)$_2$cp. For the latter compound,

$$-eQV_{ZZ} = 0.8589\{Cl\} - 2.0000\{Fe\} \qquad (2)$$

and V_{ZZ} for the former compound is defined by one of equations 1a–c. Consequently, there are three possible solutions as, once again, it is possible that V_{ii}, V_{jj} or V_{kk} for Cl$_2$Sn[Fe(CO)$_2$cp]$_2$ could be assigned to V_{ZZ}. However, of the three possible solutions, only the one for $V_{kk} = V_{ZZ}$ correctly reproduces the correct Q.S. and η for Cl$_2$Sn[Fe(CO)$_2$cp]$_2$.

The {Cl} and {Fe(CO)$_2$cp} thus derived were used to also derive {Ph}, {Mn(CO)$_5$} and {Co(CO)$_4$} from the compounds listed in Table V, once again applying crystallographically determined bond angles[24, 25, 26]. It can be seen that these pqs values are not greatly different from those calculated using regular tetrahedral angles (Table I), and the order of the ligand pqs values is similar (except for Mn(CO)$_5$ and Co(CO)$_4$ whose pqs values are now nearly equal).

The number of compounds to which these pqs values can be applied is limited by the number whose structural parameters have been measured. These compounds, together with the predicted and observed Q.S. and η values, are listed in Table VI. It can be seen that in every case the regular geometry calculations give better agreement between predicted and observed Q.S., than the calculations using crystallographic bond angles. Thus, the use of these "absolute" pqs values rather than the previously defined relative values do not seem justified for a number of reasons. First, agreement between predicted and observed Q.S. is not improved by using the "absolute" values. Second, the use of the treatment is severely limited to the small number of compounds whose structural parameters have been determined by diffraction studies. Third, the calculations are much less straightforward; and fourth, the use of the point charge treatment in such calculations probably has less chemical significance. We conclude that the semiquantitative agreement (in the Mössbauer sense) provided by the regular geometry pqs values may well be as good as is possible for these Sn^{IV} and Fe^{II} compounds using such an oversimplified

TABLE V. Calculated Absolute Ligand pqs Values for Four Co-ordinate Tin (method 2).

L	pqs (mm s^{-1})	Derived from (QS; mm s^{-1})
Fe(CO)$_2$cp	−1.15	Cl$_n$Sn[Fe(CO)$_2$cp]$_{4-n}$(n = 2,3)
Cl	−0.556	
Ph	−1.66	Ph$_3$SnFe(CO)$_2$cp
Mn(CO)$_5$	−0.996	ClSn[Mn(CO)$_5$]$_3$
Co(CO)$_4$	−1.02	ClSn[Co(CO)$_4$]$_3$

TABLE VI. Calculated and Observed QS Values for some Four Co-ordinate Tin Compounds Using Crystallographically Measured Bond Angles.

Compound	QS (mm s^{-1})		
	Observed	Calculated from crystallographic data	Calculated assuming regular tetrahedral geometry
Ph_3SnCl	−2.54 ($\eta \sim 0.0$)	−2.68 ($\eta = 0.00$)	−2.52 ($\eta = 0.00$)
$Ph_3SnMn(CO)_5$	0.41	−0.76 ($\eta = 0.00$)	−0.58 ($\eta = 0.00$)
$PhCl_2SnFe(CO)_2cp$	2.84	−3.10 ($\eta = 0.30$)	+2.72 ($\eta = 0.98$)
$Ph_2Sn[Mn(CO)_5][Co(CO)_4]$	1.15	+1.30 ($\eta = 0.95$)	−1.06 ($\eta = 0.72$)

treatment. Such agreement is, and will be, still extremely useful for distinguishing isomers, comparing bonding properties of ligands, and predicting Q.S. for isoelectronic isostructural species[17].

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References

1 G.M. Bancroft and R.H. Platt, *Adv. Inorg. Chem. Radiochem., 15,* 59 (1972).

2 R.V. Parish, *Prog. Inorg. Chem., 15,* 101 (1972).

3 M.G. Clark, in *"Molecular Structure and Properties"*, ed. A.D. Buckingham, MTP International Review of Science, Physical Chemistry Series 2, Vol. 2, Butterworths, London, in press.

4 G.M. Bancroft and E.T. Libbey, *J. Chem. Soc. (Dalton),* 2103 (1973) and references.

5 J.C. Dabrowiak, P.H. Merrell, J.A. Stone and D.H. Busch, *J. Am. Chem. Soc., 95,* 6613 (1973).

6 N. Dominelli, E. Wood, P. Vasudev and C.H.W. Jones, *Inorg. Nucl. Chem. Lett., 8,* 1077 (1972).

7 M.G. Clark, A.G. Maddock and R.H. Platt, *J. Chem. Soc. (Dalton),* 281 (1972).

8 G.M. Bancroft, K.D. Butler, A.T. Rake and B.W. Dale, *J. Chem. Soc. (Dalton),* 2025 (1972).

9 G.M. Bancroft and K.D. Butler, *J. Chem. Soc. (Dalton),* 1694 (1973).

10 R. Barbieri, L. Pellerito, N. Bertazzi and G.C. Stocco, *Inorg. Chim. Acta, 11,* 173 (1974) and references.

11 J.N.R. Ruddick and J.R. Sams, *J. Chem. Soc. (Dalton),* 470 (1974).

12 G.M. Bancroft, V.G. Kumar Das, T.K. Sham and M.G. Clark, *J. Chem. Soc. Chem. Comm.,* 236 (1974); *J. Chem. Soc. (Dalton),* in press.

13 G.M. Bancroft, V.G. Kumar Das and K.D. Butler, *J. Chem. Soc. (Dalton),* 2355 (1974).

14 R.A. La Rossa and T.L. Brown, *J. Am. Chem. Soc., 96,* 2072 (1974).

15 J.N.R. Ruddick, J.R. Sams and J.C. Scott, *Inorg. Chem., 13,* 1503 (1974).

16 G.M. Bancroft, R.E.B. Garrod, A.G. Maddock, M.J. Mays and B.E. Prater, *J. Am. Chem. Soc., 94,* 648 (1972).

17 G.M. Bancroft, *Coord. Chem. Rev., 11,* 247 (1973).

18 G.M. Bancroft and A.T. Rake, *Inorg. Chim. Acta, 13* 175 (1975).

19 R.J. Dickinson and R.V. Parish, Paper presented at Mössbauer Discussion Group (Chemical Society), September, 1973.

20 B.A. Goodman, R. Greatrex and N.N. Greenwood, *J. Chem. Soc. (A),* 1868 (1971); T.C. Gibb, R. Greatrex and N.N. Greenwood, *J. Chem. Soc. (Dalton),* 238 (1972).

21 J.E. O'Connor and E.R. Corey, *Inorg. Chem., 6,* 968 (1967).

22 P.J. Greene and R.F. Bryan, *J. Chem. Soc.,* 1696 (1970).

23 S.R.A. Bird, J.D. Donaldson, A.F. Le C. Holding, B.J. Senior and M.J. Tricker, *J. Chem. Soc. (A),* 1616 (1971).

24 B.P. Bir'yukov, E.A. Kukhtenkova, Yu.Y. Struckov, K.N. Anisimov, N.E. Kolobova and V.I. Khandozhko, *J. Organomet. Chem., 27,* 337 (1971).

25 R.F. Bryan, *J. Chem. Soc. (A),* 192 (1967).

26 J.H. Isai, J.J. Flynn and J.P. Boer, *Chem. Comm.,* 702 (1967).