A New Method for Determining Signs of Mössbauer Quadrupole Splittings: Relative Signs of ^{119}Sn and ^{57}Fe Quadrupole Splittings in $\{Fe(SnCl_3)[P(OMe)_3]_5\}^+BPh_4^-$

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Summary The observed intensity asymmetries in the ^{57}Fe and ^{119}Sn spectra of $\{Fe(SnCl_3)[P(OMe)_3]_5\}^+BPh_4^-$ show that the signs of the ^{119}Sn and ^{57}Fe quadrupole splittings are the same; since the sign of $(\frac{1}{2}e^2qQ)^{119}$Sn is certainly positive, $(\frac{1}{2}e^2qQ)^{57}$Fe is also positive; the application of this method for determining signs of quadrupole splittings for such nuclei as ^{197}Au, ^{99}Ru, and ^{193}Ir is discussed.

Although the simple Mössbauer spectra of random samples lead readily to a determination of the centre shift and quadrupole splitting, the sign of the latter quantity cannot be obtained from the random sample, pure quadrupole spectrum of a $\frac{3}{2} \leftrightarrow \frac{1}{2}$ nuclear spin transition. Without this knowledge, detailed interpretation of Mössbauer parameters in terms of varying bond electron density (*via* hybridisation of σ and π bonding interactions) is incomplete. Of the two methods used to obtain the sign of the electric field gradient in a $\frac{3}{2} \leftrightarrow \frac{1}{2}$ transition,[1,2] (i) oriented single crystals, (ii) perturbation of the quadrupole splitting by a large applied external magnetic field at *ca.* 4K, the latter has been more widely and successfully used since it requires only powdered samples and no additional crystallographic data. However it is not without its difficulties and limitations since the quadrupole splitting should be significantly larger than the natural line width ($\Delta > 2\,\Gamma$), and computer synthesis of the spectra is sometimes necessary.

Twin Mössbauer resonances have been used to discuss bonding in, for example, Sn–Fe, Fe–I, and Fe–Sb bonds.[3–7] However in no reported case has any attempt been made to investigate the effect of oriented or partially oriented samples. We report here the use of a simple "twin resonance" technique to determine the relative signs of the quadrupole splittings of two inequivalent Mössbauer nuclei.

Mössbauer parameters for $\{Fe(SnCl_3)[P(OMe)_3]_5\}^+BPh_4^-$ *at* 80K

	$\frac{1}{2}e^2qQ$	C.S.	Γ (linewidth)
^{57}Fe	+0·36 ± 0·01	0·34 ± 0·01	0·25 ± 0·01
^{119}Sn	+2·05 ± 0·02	1·98 ± 0·02	1·17 ± 0·04

C.S.(^{57}Fe) given with respect to sodium nitroprusside, at room temperature. C.S.(^{119}Sn) given with respect to barium stannate, at room temperature.

Intensity ratios[a]

Sample	Sn ratio	Fe ratio
Oriented (1)	1·38 ± 0·03	1·11 ± 0·02
Oriented (2)	1·33 ± 0·02	1·14 ± 0·02
Oriented (3)	1·34 ± 0·04	
Oriented (4)		1·23 ± 0·02
Random (average of three spectra)	1·17 ± 0·02	1·01 ± 0·01

[a] $\text{Intensity ratio} = \frac{I\ (\text{high velocity})}{I\ (\text{low velocity})}$

If, for a $\frac{3}{2} \leftrightarrow \frac{1}{2}$ nuclear spin *M*1 Mössbauer transition, the angle between the incident gamma beam and the *Z* electric field gradient axis in a crystallite is θ, then the transitions show intensity ratios due to orientation that vary from $3{:}1(\theta = 0°)$ to $3{:}5(\theta = 90°)$.[1] For a polycrystalline sample, with partial orientation of crystallites, the observed intensity asymmetry will vary between unity and the totally oriented ratios. However, for such a sample containing two different Mössbauer nuclei, M–M′, *e.g.* M = Fe, Au, Ru; M′ = Sn, I, *etc.*, the *degree* of orientation for both nuclei must be the same. Therefore, if in such a compound the Z electric field gradient axes in *both nuclei are colinear* (or nearly so) then, in the absence of Goldanskii-Karyagin effects, the asymmetry in both Mössbauer spectra should be of equal magnitude. These asymmetries will be in the same sense if the quadrupole splittings are of the same *sign, and vice versa*. For a spin system other than the $\frac{3}{2} \leftrightarrow \frac{1}{2}$ discussed above, comparable arguments, involving different expected intensity ratios, will be equally valid.

Mössbauer spectra of $\{Fe(SnCl_3)[P(OMe)_3]_5\}^+BPh_4^-$,[8] obtained for both ^{119}Sn and ^{57}Fe resonances on the same unground sample, showed considerable intensity asymmetry in both spectra (Table), in the same sense, whereas powdered samples gave substantially reduced asymmetry, the iron spectrum being within experimental error of unity. Hence, the sign of the quadrupole splittings ($\frac{1}{2}e^2qQ$) for both tin and iron are the same. Since $(\frac{1}{2}e^2qQ)_{Sn}$ is always positive in a bonded $-SnCl_3$ unit,[2] and the recently reported Mössbauer parameters for a wide series of metal–$SnCl_3$ derivatives show a very small change over a wide range of metals and metal substituents,[5,7,9] the sign of $(\frac{1}{2}e^2qQ)_{Fe}$ must also be positive, thus confirming the sign calculated from partial quadrupole splitting values.[8,10] Residual asymmetry in the ^{119}Sn random spectra is almost certainly due to the Goldanskii-Karyagin effect.

The value of this method of determining the signs of quadrupole splittings lies in its applicability to systems that are not amenable to other methods. For example, the iron quadrupole splitting for $\{Fe(SnCl_3)[P(OMe)_3]_5\}^+$-$BPh_4^-$ is too small to allow the sign to be measured easily using the magnetic field method. However, this new method should be of much greater value for determining signs of quadrupole splittings for isotopes other than ^{57}Fe and ^{119}Sn, such as ^{197}Au, ^{99}Ru, and ^{193}Ir. No signs of quadrupole splittings have been measured for any of these isotopes,[2] either because of small magnetic moments, poor resolution, or the high order of the Mössbauer transitions (other than $M1$). These signs could be readily determined in M–$SnCl_3$ or M–I compounds (M = Au, Ru, Ir) in which the Z electric field gradient axes for both Mössbauer nuclei are colinear.

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