Metal atom dynamics in organometallics: Resolving the dichotomy between Mössbauer and X-ray derived values

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Abstract. Temperature-dependent 57Fe and 119Sn Mössbauer spectroscopy (ME) has been employed to study the metal atom dynamics in a number of organometallic compounds. Such experiments can yield information concerning the vibrational amplitudes of the metal atom as well as the anisotropy (if any) of this motion as a function of temperature. The difference between the vibrational amplitudes derived from ME data and that derived from single crystal X-ray data is considered in the light of the structural details of these compounds.

1. Background
The determination of the temperature dependence of both the hyperfine parameters (I.S. and Q.S.) and the recoil-free fraction observed in ME examination of organometallics has proven to provide significant information concerning the effective vibrating mass (M_{eff}), a phenomenological lattice temperature (\Theta_M), the anisotropy of the metal atom vibration (\chi_{para} and \chi_{perp}) with respect to the molecular symmetry axis, and the mean-square-amplitude-of-vibration (m_{sav}) of the metal atom motion [1]. This latter parameter is sensitive to the metal atom-ligand binding mode as well as the detailed molecular structures involved. The focus of the present study is on the m_{sav} of related organo-iron and organo-tin complexes.

From the temperature dependence of the area under the resonance curve [A(T)] for an optically thin absorber it is possible to extract the parameter $F = k^2\langle x^2 \rangle$, where k is the wave vector of the appropriate ME gamma ray, and $\langle x^2 \rangle$ is the m_{sav} of the metal atom. It is moreover also possible to derive $F$ from the $U_{ij}$ values reported for single crystal X-ray diffraction data of the pertinent compounds. As will be shown below, there are interesting differences between $F_{X,T}$ derived from X-ray data at temperature T, and $F_{M,T}$ extracted from ME data at temperature T. In order to effect this comparison it is necessary to normalize the ME data and this is done by making the assumption the recoil-free fraction approaches unity as T→0 K. This assumption, which has previously been invoked in studies of biopolymers [2], neglects the zero-point motion at low temperatures, but extrapolation of the high-temperature ME data suggest that this is (at best) a small correction.

2. Experimental
The details of the ME measurements, using 57Co and 119mSn sources, has been described previously [3]. The various organometallic compounds were used as received, and - in the case of the air/moisture sensitive organotin complexes - transferred to O-ring provided plastic sample holders in an inert...
atmosphere glove-box and immediately cooled to liquid nitrogen temperature. All Fe isomer shifts are referred to the centroid of an α-Fe room temperature absorber spectrum (also used to effect spectrometer calibration), while the Sn isomer shifts are referred to the center of a room temperature BaSnO₃ absorber spectrum.

3. Results and discussion

(a) Organo-iron Compounds: to test the applicability of determining $F_M$ or $X$ for a typical compound, the ME spectra of cyano-ferrocene (C₅H₅FeC₅H₄CN) have been determined over the temperature interval 96<T<296 K. In addition, single crystal X-ray data were acquired at 5 different temperatures. The temperature dependence of the recoil-free fraction in the interval 96<T<193 K, is found to be: $-(4.75 \pm 0.58) \times 10^{-3}$ K⁻¹ (corr. coeff. = 0.985 for 6 data points). A comparison of $k^2<\chi_\text{ave}^2>$ for the ME data and that derived from the X-ray data is summarized graphically in Fig. 1.

![Figure 1. Comparison of $F_M$ (open circles) and $F_X$ (full circles) for Cyano Ferrocene](image)

It is noted that the $F_{M,T}$ data are consistently lower than the $F_{X,T}$ data and both data sets deviate increasingly from the low temperature linear temperature dependence as T increases. At 296 K the two F values are nearly identical. The difference between the two data sets is ascribed to the presence of low-frequency librational or torsional modes to which the X-ray data are sensitive but the ME data are not. Moreover, this assumption is also consistent with the increasing deviation from linearity at the higher temperatures. It is assumed that the low frequency modes are increasingly populated as the temperature increases and become significant with respect to the ME atom vibrational amplitudes. The close similarity between the X-ray derived data (full circles) and the ME derived data (open circles) shown at the highest temperature in Fig 1 reflects this interpretation. These results are completely consistent with comparable $^{57}$Fe ME data for other ferrocenoids [4] in which the $F_X$ values are always observed to be somewhat larger than the $F_M$ values at the same temperature.

(b) Organo-tin Compounds: Motivated by the fact that the metal atom-ligand binding modes are very different for ferrocenoids (involving primarily 3d-π electron interactions) and for tin complexes (involving primarily 5s5p-np σ bonding) the F factors for a number of organo-tin complexes have been determined. A comparison of F factors is summarized in Fig. 2 in which the ME values (ordinate) are plotted against the X-ray values (abscissa). The straight line corresponds to $F_M = F_X$. The five data points, starting from the lower left, correspond to Adams Re₂(CO)₈-(μ-SnPh₂)₂ [5], Power's [SnN(Dipp)]₄ [6], Wesemann's Cd(SnB₁₁H₁₁)₄ and [NH(C₂H₅)₃]₂SnB₁₁H₁₁ [7], and finally Saito's spiro stanna bifluorene compounds [8]. In each of these, the tin atom is "anchored" in the three-dimensional
molecular structure by multiple metal-ligand bonding. Any torsional or librational modes are of sufficiently high frequency that they are not reflected sensitively in the X-ray U_{ij} values. The differences between the two values is on the order of a few percent.

![Graph](image)

**Figure 2.** Comparison of $F_M$ (ordinate) and $F_X$ (abscissa) for some organo-tin compounds

In contrast, a number of organotin complexes in which the metal-ligand bonding involves one or two sigma bonds show very marked differences between the $F_M$ and $F_X$ values. A typical case in point is reflected in the data for Power’s recently reported [9] (4-t-Bu Ar’Sn)₂ where Ar’ is the dipp ligand C₆H₃-2,6(C₆H₃-i-Pr₂)₂. The structure of this compound is shown in Fig. 3.

![Molecular Structure](image)

**Figure 3.** A representative tin compound with an Sn-Sn sigma bond.
The two corresponding dynamical parameters are $F_{M,90} = 2.004 \pm 0.041$ and $F_{X,90} = 2.750 \pm 0.044$. This $38\%$ difference is tentatively associated with low frequency rotational motion around the Sn-Sn $\sigma$ bond (2.646 Å at 90 K) which is reflected in the X-ray $U_{ij}$ value but not in the corresponding ME data at 90 K. Major differences in $F_X$ and $F_M$ have been observed for other organo-tin compounds which have structures that permit low frequency torsional or librational modes to influence the rmsav of the metal atom, as determined by the two techniques discussed above. Reaction behavior which depends on metal atom interactions with other chemical constituents (e.g. catalysis and reaction rates) present in reacting systems should be reflected in these dynamical properties.

4. Summary and conclusions
It has been shown that temperature-dependent ME data can elucidate a number of details associated with the dynamics of the Mössbauer atom in organometallic compounds. In particular, the msav of the metal atom in a number of organo-iron and organo-tin complexes has been studied over an extended temperature range. The differences in the $F$ parameter derived from ME and single crystal $U_{ij}$ values have been studied in detail, in particular for a number of organotin complexes.

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