

Calibration of the Mössbauer isomer shift in ^{119}Sn

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The calibration constants for the Mössbauer isomer shift in ^{119}Sn are determined. This is based on an essentially model-independent technique, using the chemical changes in electron density on tin nuclei, determined from the measured changes in the probability of electron capture by the ^{113}Sn nuclei. The following values of the calibration constants are obtained: $C = \delta/\Delta\rho(0) = 0.045 \pm 0.004 \text{ mm}\cdot\text{s}^{-1}/\text{a.u.}$, $\Delta\langle r^2 \rangle = (3.5 \pm 0.3) \times 10^{-3} \text{ fm}^2$, $\Delta R/R = (0.83 \pm 0.07) \times 10^{-4}$.

The calibration of the Mössbauer isomer shift in ^{119}Sn has had a considerable history (see the reviews and references in Ref. 1) but, so far, the problem has remained unsolved. Moreover, recently published results²⁻⁷ are very contradictory, with reported calibration constants differing by factors of up to four.^{6,7}

The problem is to determine the coefficient of proportionality in the relation between the isomer shift δ and the change $\Delta\rho(0)$ in the electron density on the nucleus, which is equivalent to determining the change $\Delta\langle r^2 \rangle$ in the mean square charge radius of the nucleus, or the relative change $\Delta R/R$ in the radius of the equivalent uniformly-charged sphere, when the nucleus undergoes a transition to an excited state. These changes are related to δ by⁸

$$\delta = \frac{2\pi Ze^2 c}{3E} \Delta\langle r^2 \rangle \Delta\rho(0) = \frac{4\pi Ze^2 c R^2}{5E} \frac{\Delta R}{R} \Delta\rho(0), \quad (1)$$

where δ is in velocity units, Z is the atomic number, e is the elementary charge, c is the velocity of light in vacuum, and E is the γ -transition energy. Before we can find $\Delta\langle r^2 \rangle$, or $\Delta R/R$, we must determine $\Delta\rho(0)$ for two compounds for which δ is known.

The reasons for the contradictory results of different determinations of the calibration constants can be traced to the fact that practically all the methods used to determine $\Delta\rho(0)$ are based on different physical models of the atom in chemical compounds and rely on approximations, the validity of which is not always obvious or sufficiently justified. It is therefore important to determine $\Delta\rho(0)$ by methods that have a minimal dependence on the approximations introduced by the physical model employed. It was pointed out some years ago that a method based on the determination of the chemical change in electron capture probability can satisfy this condition.⁹

In our previous papers,^{10,11} we reported measurements of chemical changes in the probability of electron capture by

^{113}Sn nuclei ($T_{1/2} = 115.2 \text{ d}$) and found a correlation between the relative change $\Delta\lambda/\lambda$ in the capture probability and the isomer shift of the Mössbauer transition in ^{119}Sn nuclei. The inadequate understanding of the contribution of different factors to $\Delta\lambda/\lambda$ (other than the change in the electron density in the nucleus, the change in the neutrino energy, exchange effects, and overlap effects) that prevailed at the time^{12,13} prevented us, however, from obtaining accurate values $\Delta\rho(0)$ and the calibration constants. All we could do was to obtain some very approximate estimates ($\Delta R/R \approx 10^{-4}$). However, this difficulty has now been obviated.¹⁴⁻¹⁷ The effect of changes in neutrino energy on $\Delta\lambda/\lambda$ is negligible in the case of ^{113}Sn as compared with the experimental uncertainties in $\Delta\lambda/\lambda$ (Ref. 15). A considerable increase in the probability of capture of valence electrons due to exchange has little effect on the total capture probability because it is due to a reduction in the probability of capture of electrons from inner shells. This also applies to changes in the probability accompanying changes in the electron configuration. Exchange and overlap effects largely cancel out.¹⁷ These factors can therefore be neglected when one evaluates the change in the total capture probability. In the case of ^{113}Sn , the following formula¹⁷ is valid to within about 1%.

$$\Delta\lambda/\lambda \approx \sum_x q_x^2 \Delta\rho_x(0) / \sum_x q_x^2 \rho_x(0) \approx K \Delta\rho(0)/\rho(0), \quad (2)$$

where x represents the electron subshell, q_x is the neutrino energy, and $\rho_x(0)$ and $\Delta\rho_x(0)$ are, respectively, the density of x -electrons in the nucleus and the change in this density [although changes in the individual terms in the sum in the numerator of (2), with the exception of the exchange and overlap effects mentioned above, do not reflect changes in $\Delta\lambda_x$ for the subshells x]. The proportionality coefficient is given by

TABLE I. Total electron density $\rho(0)$ and the contribution of K -, N -, and O -electrons to it, calculated using the $\text{DFS}_{c=1}$, $\text{DFS}_{c=1/2}$, and DF wave functions,¹⁸ and the values of the coefficients $\rho(0)/K$ (in atomic units for the tin atom with $5s^2 5p_{1/2}^2$ valence electrons).

Method of calc.	$\rho(0)$	$\rho_K(0)$	$\rho_N(0)$	$\rho_O(0)$	$\rho(0)/K$
$\text{DFS}_{c=1}$	2.033(+5)	1.667(+5)	8.06(+2)	8.921(+1)	1.880(+5)
$\text{DFS}_{c=1/2}$	2.019(+5)	1.657(+5)	7.883(+2)	7.732(+1)	1.868(+5)
DF	2.023(+5)	1.660(+5)	7.368(+2)	6.579(+1)	1.871(+5)

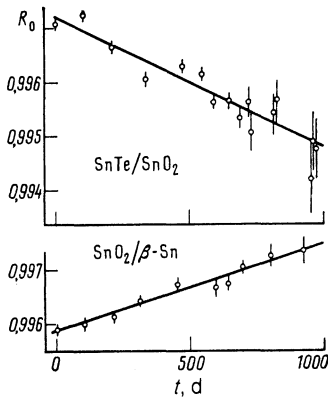


FIG. 1. ^{113}Sn activity ratio $R_0(t)$ as a function of t for two pairs of sources. The slope of the straight lines gives the following values of $\Delta\lambda/\lambda$: SnTe relative to SnO_2 , $(4.0 \pm 0.9) \times 10^{-4}$, SnO_2 relative to $\beta\text{-Sn}$, $(2.7 \pm 0.45) \times 10^{-4}$.

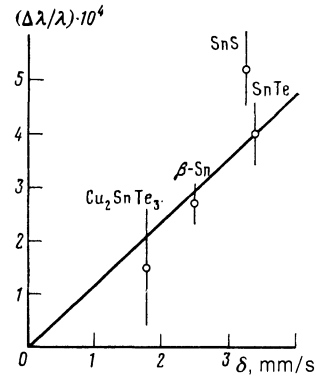


FIG. 2. Dependence of $\Delta\lambda/\lambda(^{113}\text{Sn})$ on $\delta(^{119}\text{Sn})$ relative to SnO_2 . The slope of the straight line obtained by the method of least squares corresponds to $(\Delta\lambda/\lambda)/\delta = (1.19 \pm 0.09) \times 10^{-4} \text{ mm}^{-1}\text{s}$ and $\Delta\rho(0)/\delta = (22 \pm 2) \text{ a.u./mm} \cdot \text{s}^{-1}$.

$$K = \{1 - [\rho_{1s}(0)/\rho(0)](1 - q_{1s}^2/Q^2)\}^{-1},$$

where Q is the total energy released in capture. Using the values of $\rho_{1s}(0)$ and $\rho(0)$ given in Ref. 18 together with $Q = 632 \text{ keV}$ (Refs. 11 and 19) and the electron binding energies given in Ref. 20, we find that $K = 1.081$. Before we can determine $\Delta\rho(0)$ from the measured $\Delta\lambda/\lambda$, we must know $\rho(0)/K$. The main contribution to $\rho(0)$ is provided by deep internal shells of the atom for which the densities $\rho_x(0)$ calculated in Ref. 18 are relatively insensitive to the particular physical model employed. Table I lists the values of $\rho(0)$ (in atomic units) and the contributions of certain shells to the total electron density in the case of neutral atoms of tin with $5s^2 5p_{1/2}^2$ valence electrons in the Dirac-Fock-Slater (DFS) model (with C in front of the exchange term equal to 1 and $2/3$) and the Dirac-Fock model (DF). The Table also lists the resulting values of the proportionality coefficient between $\Delta\rho(0)$ and $\Delta\lambda/\lambda$. These values agree to within 1%, so that, independently of the relativistic model of the atom employed,

$$\Delta\rho(0) = [\rho(0)/K] \Delta\lambda/\lambda = (18.8 \pm 0.1) \cdot 10^4 \Delta\lambda/\lambda. \quad (3)$$

Since the contribution of the valence electrons to $\rho(0)$ is small, the same value is obtained for the coefficient $\rho(0)/K$ to within the indicated uncertainty when $\rho(0)$ is calculated for any tin ion with any configuration of valence electrons. Moreover, the result is practically independent of the change in the density of valence electrons in the nucleus due to solid-state effects.

We have continued our experiments with ^{113}Sn , concentrating our attention on compounds which have typically

large isomer shifts in ^{119}Sn . We have extended the experimental time scale to $8T_{1/2}$ in our measurements of the time dependence of the source activity ratios, which enabled us to introduce more accurate methodological corrections, especially those for long-lived impurity radionuclides (the sources produced by neutron activation in a reactor, in which a 72.9% enrichment with ^{112}Sn was achieved, were found to contain the ^{125}Sb impurity with $T_{1/2} = 2.77 \text{ y}$, formed after the β -decay of ^{125}Sn). The experimental details are similar to those described in Ref. 11.

Figure 1 shows the experimental results obtained for two paired sources of ^{113}Sn ($^{113}\text{SnTe}$ and $^{113}\text{SnI}_2$, $^{113}\text{SnO}_2$ and $\beta\text{-}^{113}\text{Sn}$). We now reproduce the ^{113}Sn activity ratio $R_0(t)$ (corrected for the dead time and the presence of ^{125}Sb ; these corrections were introduced by the method described in Refs. 11 and 21, using a computer to perform the least-squares calculations). The ratios $\Delta\lambda/\lambda$ were determined from the slope of the straight lines $R_0(t) = R_0(0)[1 - (\Delta\lambda/\lambda)\lambda t]$.

Table II lists the values of $\Delta\lambda/\lambda$ relative to SnO_2 , measured in different experiments, together with their average values. The indicated uncertainties are the root mean square errors. We list the values of $\Delta\rho(0)$, determined from (3), and the isomer shifts of ^{119}Sn relative to SnO_2 (Refs. 22–24). For SnTe and $\beta\text{-Sn}$, we list the values of δ recommended in Ref. 22 as standards (at $T = 300^\circ\text{K}$), whereas in other cases the isomer shifts were calculated using the results published in Refs. 23 and 24. Figure 2 plots $\Delta\lambda/\lambda(^{113}\text{Sn})$ as a function of $\delta(^{119}\text{Sn})$ for SnO_2 . The slopes of the straight lines obtained by the method of least squares were found to yield the following values of the calibration constants: $C = \delta/\Delta\rho(0)$

TABLE II. Values of $\Delta\lambda/\lambda(^{113}\text{Sn})$ determined in different experiments and their averages, together with the values of $\Delta\rho(0)$ and δ for SnO_2 from Refs. 22–24.

Experiment	Compound	$(\Delta\lambda/\lambda) \cdot 10^4$	$\overline{(\Delta\lambda/\lambda)} \cdot 10^4$	$\Delta\rho(0)$ a.u.	δ , mm/s
I	SnTe	3.9 ± 0.8	4.0 ± 0.6	75 ± 11	3.38
II	SnTe	4.1 ± 0.8	—	—	—
I	SnS	5.7 ± 0.9	5.2 ± 0.7	98 ± 13	3.24
II	SnS	4.7 ± 0.9	—	—	—
I	$\beta\text{-Sn}$	2.7 ± 0.8	2.7 ± 0.4	51 ± 8	2.51
II	$\beta\text{-Sn}$	2.7 ± 0.45	—	—	—
	Cu_2SnTe_3	1.5 ± 1.1	—	28 ± 21	1.77

$= 0.045 \pm 0.004 \text{ mm} \cdot \text{s}^{-1} / \text{a.u.}$, $\Delta \langle r^2 \rangle = (3.50.3) \times 10^{-3} \text{ fm}^2$, $\Delta R / R = (0.83 \pm 0.07) \times 10^{-4}$ (for $R = 5.919 \text{ fm}$). A comparable determination of $\Delta R / R$ from the measured $\Delta \lambda / \lambda$ (^{113}Sn), published in Ref. 11, gave $(0.7 \pm 0.1) \times 10^{-4}$.

Muramatsu *et al.*⁵ have recently used values of $\Delta \rho(0)$ determined from chemical changes in the intensity of the O line in the internal conversion spectrum, and the values of $\rho_{4s}(0)$ calculated by the DF method, to show that $\Delta \langle r^2 \rangle = (3.6 \pm 1.0) \times 10^{-3} \text{ fm}^2$, which is in good agreement with these nearly model-independent calibration constants. However, this method is more sensitive to the model of the atom [the values of $\rho_{4s}(0)$, calculated with the DF and $\text{DFS}_{C=1}$ wave functions, differ by about 10% (Ref. 18); see also the values of $\rho_N(0)$ in Table I; comparison of the measured and calculated intensity ratios for internal conversion electrons shows that the $\text{DFS}_{C=1}$ model provides a better description of the N -electron wave functions near the nucleus than does the DF model³⁵]. The method is also sensitive to the different assumptions about the contribution of inner shells and $5p$ valence electrons to the change in the internal conversion probability, which may significantly restrict its possibilities as the experimental uncertainties are reduced. This also applies to the method used to determine $\Delta \rho(0)$ from the measured change in the total internal conversion probability.²⁶ Different relative changes in the total internal conversion probability correspond to the same changes in density of s and $p_{1/2}$ electrons at the nucleus. For atoms in crystals, this difference may be even greater because of the rigid-body effect. All this must be taken into account since, otherwise, considerable errors will be introduced into the values of $\Delta \rho(0)$ determined from the measured $\Delta \lambda / \lambda$ for particular conversion transitions.²⁷

The uncertainties in the calibration constants determined in this paper are largely due to uncertainties in the measured $\Delta \lambda / \lambda$ and are largely associated with the presence of the ^{125}Sb activity in our sources. The uncertainty can be substantially reduced by using radiochemically pure ^{113}Sn . The use of such sources is, at present, a very realistic prospect.²⁸ There is therefore real hope that it will be possible to obtain calibration constants with precision approaching that of (2) and (3).

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