^{57}Fe Isomer Shifts and the Problem of Calibration

A. X. Trautwein and H. Winkler

Institut für Physik, Medizinische Universität Lübeck,
D-2400 Lübeck

Z. Naturforsch. **42a,** 211–212 (1987);
received November 24, 1986

The ^{57}Fe isomer shift calibration problem is discussed, and critical comments concerning the paper "^{57}Fe Isomer Shift Calibration Experiment" by Daniel et al. (1985) are given. We consider $-\langle \Delta r^2 \rangle = (20 \pm 3) \cdot 10^{-3}\,\mathrm{fm}^2$ at the moment as the most reliable estimate for the change of nuclear radius during gamma absorption; this value has been derived by measuring changes in isomer shift δ and calculating corresponding changes in electron contact density $\varrho(0)$ according to $\Delta\delta = C \langle \Delta r^2 \rangle \Delta\varrho(0)$.

A reliable calibration of the isomer shift δ is the prerequisite for deriving contact densities $\varrho(0)$ from Mössbauer spectra. It is therefore important to design experiments with the aim to measure directly the change of nuclear radius $\langle \Delta r^2 \rangle$ during gamma resonance absorption. Such experiments have been performed for ^{57}Fe on the basis of life time variations in the electron capture decay of ^{52}Fe [1] or on the basis of conversion electron spectroscopy with ^{57}Co(^{57}Fe) sources [2]. However, the results, which have been obtained with these two methods, $-\langle \Delta r^2 \rangle = (33 \pm 3) \cdot 10^{-3}\,\mathrm{fm}^2$ [1] and $-\langle \Delta r^2 \rangle < 9 \cdot 10^{-3}\,\mathrm{fm}^2$ [2], respectively, do not agree at all. Other authors, including ourselves, strived for this goal by measuring changes in δ and calculating corresponding changes in $\varrho(0)$ [3, 4]:

$$\Delta\delta = C \langle \Delta r^2 \rangle \Delta\varrho(0) . \tag{1}$$

If δ is given in mm s^{-1}, $\langle \Delta r^2 \rangle$ in $10^{-3}\,\mathrm{fm}^2$, and $\varrho(0)$ in a_0^{-3}, the constant C takes the value 0.011 for ^{57}Fe. From the combined experimental ($\Delta\delta$) and calculational ($\Delta\varrho(0)$) procedure we have derived $\langle \Delta r^2 \rangle$ for a large variety of iron-containing compounds, i.e. $-\langle \Delta r^2 \rangle = (20 \pm 3) \cdot 10^{-3}\,\mathrm{fm}^2$ [4–6].

Due to its importance it is desirable to have a widely accepted isomer shift calibration. In our view there are serious drawbacks which cause us to question the value $-\langle \Delta r^2 \rangle < 9 \cdot 10^{-3}\,\mathrm{fm}^2$ (at 80% confidence) [2], due to the following reasons:

(i) The absolute value of the Fe 4s contact density $\varrho_{4s}(0)$ was obtained in [2] from the experimental ratio α_{4s}/α_{3s} and the calculated relativistic Fe 3s value ($\varrho_{3s}(0) \sim 180\, a_0^{-3}$), i.e.

$$\begin{aligned} &\text{from } \alpha_{4s}/\alpha_{3s} = 0.061 \pm 0.005 \text{ the value} \\ &\qquad \varrho_{4s}(0) = (10.98 \pm 0.90)\, a_0^{-3} \text{ for } {}^{57}\text{Fe/Au}, \end{aligned} \tag{2a}$$

and

$$\begin{aligned} &\text{from } \alpha_{4s}/\alpha_{3s} = 0.17 \pm 0.10 \text{ the value} \\ &\qquad \varrho_{4s}(0) = (30.6 \pm 18.0)\, a_0^{-3} \text{ for } {}^{57}\text{Fe/graphite}. \end{aligned} \tag{2b}$$

With the experimental isomer shifts 0.65 mm s^{-1} for ^{57}Fe/Au and 0.25 mm s^{-1} for ^{57}Fe/graphite and the values (2a, b) we derive from (1)

$$-\langle \Delta r^2 \rangle = 1.85 \cdot 10^{-3}\,\mathrm{fm}^2 .$$

Comparison with the upper limit of $9 \cdot 10^{-3}\,\mathrm{fm}^2$ given in [2] shows that the error margin is about $7 \cdot 10^{-3}\,\mathrm{fm}^2$, which means that the confidence grows only slowly when one raises the upper limit. By exhausting the full uncertainty of (2a, b) on arrives at

$$-\Delta \langle r^2 \rangle \lesssim 50 \cdot 10^{-3}\,\mathrm{fm}^2 ,$$

without even having considered any uncertainties of isomer shifts, because they were not reported in [2]!

(ii) The values for $\varrho_{4s}(0)$ in (2a) and (2b) are larger than the corresponding value $\varrho_{4s}(0) = 8.36\, a_0^{-3}$ for Fe^0 ($3d^6 4s^2$) as derived from Dirac-Fock calculations [4], the same calculations which yield $\varrho_{3s}(0) \sim 180\, a_0^{-3}$ from above. This implies that the isomer shifts of ^{57}Fe/Au and ^{57}Fe/graphite should be even more negative than that of Fe^0 in solid noble gas ($\delta_{\alpha\text{-Fe}} \sim -0.75$ mm s^{-1} [7]), which is by far not the case.

(iii) The value for $\langle \Delta r^2 \rangle$ was estimated by Daniel et al. [2] on the basis of (1) by assuming $\Delta\varrho(0) = \Delta\varrho_{4s}(0)$. But this assumption is not necessarily satisfied, as shown in a conversion electron study of $\varrho_{4s}(0)$ of Fe-impurity atoms in transition and noble metals [8]. In fact, we have found from electronic structure calculations [4, 5] that core contributions to $\Delta\varrho(0)$ can be significantly larger than $1\, a_0^{-3}$.

In conclusion, we consider $-\langle \Delta r^2 \rangle = (20 \pm 3) \cdot 10^{-3}\,\mathrm{fm}^2$ at the moment as the most reliable estimate, because we do not regard the result

---

Reprint requests to Prof. A. X. Trautwein, Institut für Physik, Medizinische Universität, D-2400 Lübeck.

0340-4811 / 87 / 0200-0211 $ 01.30/0. – Please order a reprint rather than making your own copy.

reported in [2] as conclusive, and because the value $-\langle \Delta r^2 \rangle = (33 \pm 3) \cdot 10^{-3}\,\mathrm{fm}^2$ given by Meykens et al. [1] seems to be overestimated by about 30 per cent due to reasons described in [2].

[1] A. Meykens, R. Coussement, J. Ladrière, M. Cogneau, M. Bogè, P. Auric, R. Bouchez, D. Benabed, and J. Godard, Phys. Rev. **B 21,** 3816 (1980).

[2] H. Daniel, F. Hartmann, and B. Pitesa, Z. Naturforsch. **40 a,** 539 (1985).

[3] In: Mössbauer Isomer Shifts (G. K. Shenoy and F. E. Wagner, eds.), North Holland, Amsterdam 1978.

[4] R. Reschke, A. X. Trautwein, and J. P. Desclaux, J. Phys. Chem. Solids **38,** 837 (1977).

[5] V. R. Marathe and A. X. Trautwein, in: Advances in Mössbauer Spectroscopy (B. V. Thosar, J. K. Srivastava, P. K. Iyengar, and S. C. Bhargava, eds.), Elsevier Scientific Publ. Comp., Amsterdam 1983, p. 419.

[6] A. X. Trautwein, E. Bill, R. Bläs, S. Lauer, H. Winkler, and A. Kostikas, J. Chem. Phys. **82,** 3584 (1985).

[7] T. K. McNab, H. Micklitz, and P. H. Barrett, Phys. Rev. **B 4,** 3787 (1971).

[8] T. Shinohara, M. Fujioka, H. Onodera, K. Hisatake, H. Yamamoto, and H. Watanabe, Hyperf. Interaction **1,** 345 (1976).

Verantwortlich für den Inhalt: A. KLEMM
Satz und Druck: Konrad Triltsch, Würzburg