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Goldanskii-Karyagin Effect on Hyperalkaline Tin(II)-Hydroxide

Attila Lengyel[1], Zoltán Klencsár[2], Zoltán Homonnay[1], Pál Sipos[3#], Éva G. Bajnóczi[3#], István Pálinkó[4#] and Ernő Kuzmann[1*]

[1] *Laboratory of Nuclear Chemistry, Institute of Chemistry, Eötvös Loránd University, H-1117 Budapest, Hungary*

[2] *Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, H-1117 Budapest, Hungary*

[3] *Department of Inorganic and Analytical Chemistry, University of Szeged, Dóm tér 7, Szeged, H-6720 Hungary*

[4] *Department of Organic Chemistry, University of Szeged, Dóm tér 8, Szeged, H-6720 Hungary*

[#] *Materials and Solution Structure Research Group, University of Szeged*

Abstract. Frozen aqueous solution of hyperalkaline tin(II)-hydroxide was analysed by ^{119}Sn Mössbauer spectroscopy at low temperature in order to determinate the structure of the hydroxo complex formed under hyperalkaline (pH > 13) conditions. Interestingly, the quadrupole doublet characteristic of this complex in the ^{119}Sn Mössbauer spectrum exhibited asymmetry in the line intensities. Analysis of the temperature dependence of the Mössbauer spectra demonstrated that this phenomenon can be rationalised by the Goldanskii-Karyagin effect. The effect emerges due to the vibrational anisotropy of bonds in the tin complex formed in hyperalkaline solution, similarly to what has been found earlier for SnF_2 with analogous Sn bond structure.

Keywords: Stannous ion, aqueous solution, Goldanskii-Karyagin effect, Mössbauer spectroscopy

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[*] Corresponding author. *E-mail address:* kuzmann@caesar.elte.hu (E. Kuzmann)

1. Introduction

Very basic (often called hyper-alkaline, pH > 13) conditions may give rise to the formation of complex compounds with unusual structure and composition [1,2]. Under such conditions metal ions may form hydroxo complexes that are not possible to observe otherwise. In the present study our main goal was to prepare and characterize tin(II) compounds forming in hyperalkaline environment. Characterization of the hydroxo complexes in question by means of X-ray absorption- and FT-Raman spectroscopy has been previously described [3]. Results of attempts to detect the Mössbauer signal of the complexes forming in solution by using capillary-Mössbauer measurement were also communicated [4]. Here we focus our attention on ^{119}Sn Mössbauer-spectroscopy measurements carried out as a function of temperature on samples of frozen solutions.

Investigation of structural and bonding properties of tin compounds via Mössbauer spectroscopy can be based on chemical information obtained by analyzing ^{119}Sn Mössbauer parameters such as the isomer shift and quadrupole splitting [5,6]. In the case of samples that display an isotropic random orientation of a non-zero electric field gradient (EFG, as measured at the ^{119}Sn nuclei), tin microenvironments are represented by a symmetric quadrupole doublet in the ^{119}Sn Mössbauer spectra. Such spectra can be typically observed for random powders and frozen solutions. In certain cases, however, the intensities (areas) of the individual peaks contributing to the quadrupole doublet can be different. Asymmetry of this kind may occur due to several reasons. In the presence of multiple tin microenvironments in the sample, an asymmetric doublet may be formed as the superposition of two or more overlapping subspectra. At the same time, asymmetry may also be observed for a single type of microenvironment provided that the sample is subject to texture (see, e.g., [7]), i.e. the spherical distribution of the alignment of the principal axes of the EFG tensor deviates from being completely isotropic. Asymmetry of this type depends solely on the sample geometry with respect to the γ-ray direction, and thus it can be expected to be independent of sample temperature. Assuming an axially symmetric EFG tensor (i.e. the EFG asymmetry parameter η being zero), for tin it can be described with the formula

$$\frac{I_2}{I_1} = \frac{\int_0^{\pi} 3(1+\cos^2\theta)\, h(\theta) \sin\theta \, d\theta}{\int_0^{\pi} (5-3\cos^2\theta)\, h(\theta) \sin\theta \, d\theta}, \tag{1}$$

where I_2 and I_1 stands for the intensity of the peak belonging to the $|I,|I_z|\rangle = |3/2,3/2\rangle \rightarrow |1/2,1/2\rangle$ and $|3/2,1/2\rangle \rightarrow |1/2,1/2\rangle$ nuclear transitions, respectively, θ denotes the polar angle of the γ ray as measured in the eigensystem of the EFG tensor, and $h(\theta)$ gives the probability that this polar angle takes on the value of θ. For an isotropic powder $h(\theta)$ is constant and $I_2/I_1 = 1$ resulting in a symmetric quadrupole doublet.

At the same time, even for an isotropic powder with a single type of tin microenvironment an asymmetry may be observed in the corresponding ^{119}Sn quadrupole doublet when the mean amplitude of atomic vibrations of tin atoms depends on the direction of vibration with respect to the eigensystem of the EFG, resulting in an anisotropic Lamb-Mössbauer factor and associated Goldanskii-Karyagin effect [8-11]. For an axially symmetric EFG whose eigensystem coincides with that of the local atomic vibrations, the asymmetry due to the Goldanskii-Karyagin effect can be expressed as [11,12]

$$\frac{I_2}{I_1} = \frac{\int_0^{\pi} 3(1+\cos^2\theta)\, \mathrm{e}^{-k^2(\langle r_\parallel^2\rangle - \langle r_\perp^2\rangle)\cos^2\theta} \sin\theta\, d\theta}{\int_0^{\pi} (5-3\cos^2\theta)\, \mathrm{e}^{-k^2(\langle r_\parallel^2\rangle - \langle r_\perp^2\rangle)\cos^2\theta} \sin\theta\, d\theta}, \tag{2}$$

where k is the absolute value of the wave vector of the Mössbauer radiation ($k = 2\pi/\lambda \approx 12.1$ Å^{-1} for the Mössbauer transition of ^{119}Sn), and $\langle r_\parallel^2\rangle - \langle r_\perp^2\rangle$ is the difference between the mean squared displacement of tin nuclei parallel and perpendicular to the z axis of the eigensystem of the EFG tensor. A typical trait of the asymmetry caused by the Goldanskii-Karyagin effect is that it tends to diminish with decreasing temperature, as already found for example for $(CH_3)_3SnF$ [13] and α-SnF_2 [14].

Here we report a ^{119}Sn Mössbauer spectroscopy study of tin(II)-hydroxide formed in hyperalkaline solution, and demonstrate the presence and elucidate the origin of an asymmetry found concerning the quadrupole doublet representing the tin microenvironment in the tin(II) complex under study.

2. Experimental

2.1 Materials and the preparation of the samples

Sample synthesis was done in two steps. The first one was the preparation of the hyperalkaline, while the second step was that of the tin(II) containing acidic (with HCl or $HClO_4$) stock. To produce the hyperalkaline solution, analytical grade NaOH (ANALR NORMAPUR) was dissolved in distilled water with intense stirring and cooling. The solution was stored in tightly closed highly base resistant Pyrex bottles. The maximum achievable

NaOH concentration was ~ 19 mol dm^{-3}. The concentration was determined by a picnometer, and then, by calculating from the density of solution, following the literature [14]. The carbonate content was minimized as described elsewhere [15].

To prepare the tin(II) containing stock solution, two methods were used. In one case, the tin concentration was $C_{\mathrm{Sn(II)}} \approx 0.05 - 0.6$ mol dm^{-3} while the acid concentrations were varied in the $C_{\mathrm{acid}} \approx 0.1 - 1.5$ mol dm^{-3} range.

$Sn(ClO_4)_2$ in $HClO_4$ solution was prepared from cleaned metallic Sn and Cu(II)-perchlorate with known concentration under argon atmosphere, according to the procedure described in the literature [16,17]. 0.05 – 0.10 mol dm^{-3} Sn(II) concentrations were achieved in 0.1 – 0.5 mol dm^{-3} $HClO_4$ with this method.

The other way was to dissolve metallic tin in diluted analytical grade hydrochloric acid under anaerobic conditions (in nitrogen atmosphere). This process took about four days under reflux at 50°C; however, this method resulted in almost Sn(IV)-free solutions, because the evolving hydrogen gas prevented the oxidation. Then calculated amount of tin(II) stock solution was added to the hyperalkaline solution with continuous and intense argon bubbling through the sample.

2.2. Mössbauer spectroscopic measurements

^{119}Sn Mössbauer spectra of frozen solution with Sn surface density of 15.7 mg/cm^2 were recorded with a conventional Mössbauer spectrometer (WISSEL) working in constant acceleration mode. A 16 mCi activity $Ca^{119m}SnO_3$ source supplied the γ rays for the ^{119}Sn Mössbauer measurements that were performed in transmission geometry. An APD type close circuit refrigerator cryostat was used to set sample temperatures in the range of 20 to 180 K. The velocity scale calibration was performed by a ^{57}Fe Mössbauer spectroscopy measurement of α-Fe foil. The quoted isomer shifts are given relative to that of the source material at room temperature. The evaluation of the Mössbauer spectra was carried out by the least square fitting with Lorentzian lines using version 4.0 of the MOSSWINN software [18]. In the calculations of the quadrupole split ^{119}Sn Mössbauer spectra a value of −0.132 b was assumed for the quadrupole moment of the excited ($I_e = 3/2$) state of the ^{119}Sn nucleus.

3. Results and discussion

Figure 1 shows ^{119}Sn Mössbauer spectra of the frozen hyperalkaline tin(II)-hydroxide solution recorded at different temperatures between 20 K and 180 K. All spectra exhibit an asymmetric doublet envelope with no sign of any tin(IV) impurity that could form due to aerial oxidation.

In order to elucidate the roots of the asymmetry, the spectra were first analysed by fitting them with two independent Lorentzians. The temperature dependence of the relative intensity (I_1/I_2) and the individual FWHM line widths of the two Lorentzians observed in this way are depicted in Figure 2. One clearly observes that the asymmetry, as characterized by I_1/I_2, depends on temperature in a way that makes it diminish with decreasing temperature to rather low levels at the lowest temperatures applied. This excludes texture as being the main source of the observed asymmetry, and can be regarded as a typical sign for the Goldanskii-Karyagin effect [12,13]. At the same time, the line widths of the doublet peaks turn out to be the same inside the statistical error down to the lowest experimental temperatures applied (Figure 2), which makes it unlikely that different tin microenvironments would exist in the sample (cf., e.g., [19]). The observed line widths are also quite close to their natural value of ~ 0.646 mm/s. The slightly larger widths observed can be caused by a broadening of the source line width as well as by a moderate thickness effect. Since the Lamb-Mössbauer factor increases with decreasing temperature, which results in a simultaneous increase of the effective thickness, the tendency of the line width to increase with decreasing temperature also suggests that sample thickness may have an influence on it.

As neither texture nor a superposition of multiple components can account for the observed asymmetry, the Goldanskii-Karyagin effect needs to be taken into account to fit and interpret the spectra. Assuming isotropic random powder geometry and equal line widths for the peaks making up the doublet, the spectra were fitted with a model essentially identical to that expressed by Eq. (2), by treating the quantity $k^2(\langle r_\parallel^2\rangle - \langle r_\perp^2\rangle)$ as a fit parameter. The corresponding fit results are summarized in Table 1, whereas the fit envelopes resulting from the fit are shown in Figure 1. At the applied temperatures the ^{119}Sn isomer shift of the complex remains in the range of 2.4 – 2.5 mm/s, clearly exceeding the range of isomer shift values (below ~ 2 mm/s) characteristic to Sn(IV) compounds [20,21], at the same time residing around the lower limit of typical ^{119}Sn isomer shift values of Sn(II) compounds [21,22]. On the basis of the obtained range of isomer shift values the complex under study can be identified as being a complex of Sn(II) with considerable covalence where the lone electron pair has a reduced ‘s’ character due to the formation of sp^3 hybrid orbitals. This is also reflected in the rather large quadrupole splitting of 1.8 – 1.9 mm/s observed (Table 1). Despite the quite wide range of temperatures applied, only a minor change is observed in the isomer shift value, which can be recognized as a usual trait of ^{119}Sn isomer shifts [23]. Nevertheless, on the basis of data listed in Table 1, overall (though not without outlying points) the isomer shift appears to show a tendency of increase with decreasing temperature, which can be ascribed to the temperature dependence of the second order Doppler shift. In contrast, the Δ quadrupole splitting clearly displays a monotonic decrease with increasing temperature (Table 1, Figure 3). The magnitude and direction of change detected in Δ for the present complex is close to corresponding values found for $(CH_3)_3SnF$ [13] and $(CH_3)_3SnCN$ [12], and can be ascribed to the increase of the mean interatomic distances as a result of thermal expansion. Among known tin(II) complexes, on the basis of the observed isomer shift and quadrupole splitting values (Table 1), the bonding structure of tin in the present complex must lie closest to that in hydrous trihydroxostannate(II) [24], confirming previous assignment to the trihydroxostannate(II) complex $[Sn(OH)_3]^-$ concerning an analogous sample [3].

The probability of the Mössbauer effect is given by the Lamb-Mössbauer factor f whose temperature dependence is reflected in that of the normalized spectral area A_n, which latter is obtained by dividing the total spectral area (in the present case the sum of the area of two Lorentzians) divided by the baseline counts. Expressing A_n in units of its value at 20K ($A_{n,20K}$), we observe the temperature dependence of $A_n/A_{n,20K}$ as depicted in Figure 3. Clearly, the probability of the Mössbauer effect, i.e. the recoilless fraction is strongly reduced with increasing temperature in the present sample: at 180K f takes on only ~ 28% of its value characteristic to 20K. Taking into account the similar (~1 day) measuring time of the individual spectra, this is also reflected in the signal-to-noise (S/N) ratio of the measured spectra (Figure 1) that diminishes with increasing temperature. Strongly reduced recoilless fraction values refer to an enhanced mean square displacement of the tin atom in its complex, showing that the amplitude of vibration of tin atoms increases considerably with temperature in the applied temperature range. Such characteristic can be quantified by the so called Mössbauer temperature, θ_M, a quantity analogous to the Debye temperature in the frame of the corresponding model [13]. According to [13], in the thin-absorber approximation the Mössbauer temperature can be estimated on the basis of the high temperature limit of $d\ln(A_n)/dT$ as follows:

$$\theta_M = \sqrt{\frac{3E_\gamma^2}{k_B mc^2} \cdot \frac{-1}{\frac{d\ln A_n}{dT}}}\,, \tag{3}$$

where $E_\gamma \approx 23.871$ keV is the energy of the Mössbauer γ photon, m stands for the mass of a corresponding free tin atom, k_B is the Boltzmann constant, whereas c is the speed of light in vacuum. By using normalized areas observed for the measurements carried out at 140 K and 180 K (Table 1) on the basis of Eq. (3) a value of $\theta_M \approx 118.7$ K is observed that is similar but slightly higher than corresponding values found for $(CH_3)_3SnF$ [13] having a near three-fold rotational symmetry similarly to the compound being subject of the present study, suggesting that from the point of view of its vibrational atomic displacements in the present complex tin is approximately as strongly (and perhaps slightly stronger) bound as in trimethyltin fluoride.

By taking into account the anisotropy of the Lamb-Mössbauer factor in accordance with Eq. (2), the temperature dependence of V_{zz}, the main component of the EFG tensor, and that of the quantity $\rho = \langle r_{\|}^2 \rangle - \langle r_{\perp}^2 \rangle$ characterizing the vibrational anisotropy of tin atoms can be obtained as depicted in Table 1 and Figure 3. It should be noted that the set of parameter values given here for V_{zz} and ρ is not a unique solution of the fitting problem: there is another solution with identical fitness value, where both V_{zz} and ρ take on positive values. There are, however, reasons to accept the solution given here as the physically reasonable one. On the one hand, considering the structure put forward for the present complex [3], it is to be expected that the major contribution to the EFG is provided by the lone electron pair with considerable p character, and consequently V_{zz} is to be measured along the tin - lone pair axis (z axis). A point charge model predicts negative V_{zz} at the tin nucleus for an electron charge along the z axis, and this is what we expect to dominate for the lone pair, too. This situation is similar to what was found for α-SnF_2 [14]. On the other hand, and in further agreement with [14], the mean square displacement of tin atoms along the z axis ($\langle r_{\|}^2 \rangle$, stretching the bonds) is expected to be lower than that ($\langle r_{\perp}^2 \rangle$, bending the bonds) in the corresponding perpendicular (xy) plane, and consequently we expect ρ to be negative. Thus, both considerations favor the validity of the results given in Table 1 against the alternative (V_{zz} and ρ both positive) solution. We note that for negative V_{zz} the lower-velocity peak of the doublet can be attributed to the $|I,|I_z|\rangle = |3/2,1/2\rangle \rightarrow |1/2,1/2\rangle$ nuclear transition, so that our notation on Figure 2 concerning I_1 and I_2 is consistent with that of Eqs. (1-2).

The vibrational anisotropy expressed by ρ tends to diminish with decreasing temperature (Figure 3), which confirms that the asymmetry in peak intensities (Figure 1) is indeed due to the Goldanskii-Karyagin effect. Similarly to the case of α-SnF_2 where the Goldanskii-Karyagin effect has been found both by Mössbauer spectroscopy and by neutron diffraction measurements [14,25], the origin of the Goldanskii-Karyagin effect is connected to the electronic structure of the tin atom through the effect of the non-bonding electron pair on the lattice vibration [15,16]. The resulting anisotropic vibration leads to an anisotropic Lamb-Mössbauer factor and in turn to asymmetric line intensities in the quadrupole split Mössbauer spectra, in accordance with Eq. (2). The phenomenon that tin atom can vibrate differently in direction parallel and perpendicular to its inert electron pair's direction can also be rationalized on the basis of theoretical consideration of bonding in Sn-O and related systems [26]. Our results indicate that the bonds of tin-hydroxide in hyperalkaline environment can have similarities with the bonds of tin-fluoride, which may be related to the similarities of the hydroxide and fluoride ligands as stated by Grimm's rule [27].

4. Conclusions

^{119}Sn Mössbauer measurements performed on stannous hydroxide in frozen hyperalkaline solutions as a function of temperature revealed Mössbauer parameters ($\delta = 2.4 - 2.5$ mm/s, $\Delta = 1.8 - 1.9$ mm/s) indicative of the trihydroxostannate(II) complex, along with an asymmetry in the relative line intensities of the Mössbauer spectrum, which latter could be identified as being the result of the Goldanskii-Karyagin effect. The results are in accordance with a negative value of the main component (V_{zz}) of the electric field gradient, and simultaneously with a vibrational anisotropy of the tin atom that makes the mean square amplitude of tin atoms to be smaller along the z axis, given by the tin - lone pair axis, than perpendicular to it. This phenomenon can be seen as an effect of tin's inert electron pair on the atomic vibrations, by resulting in tin atoms that are less tightly bound in the direction perpendicular to the axis of the inert electron pair than in the parallel direction, similarly to the case of α-SnF_2.

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References

[1] A. Pallagi É. G. Bajnóczi, S. E. Canton, T. Bolin, G. Peintler, B. Kutus, Z. Kele , I. Pálinkó, and P. Sipos, 2014: *Env. Sci. Technol.* **48**: 6604-6611.

[2] A. Pallagi, Á. Gy. Tasi, G. Peintler, P. Forgo, I. Pálinkó and P. Sipos, 2013: *Dalton Trans.* **42**: 13470-13476.

[3] É. Bajnóczi, E. Czeglédi, E. Kuzmann, Z. Homonnay, Sz. Bálint, Gy. Dombi, P. Forgo, O. Berkesi,I. Pálinkó, G. Peintler, P. Sipos and I. Persson, 2014: *Dalton Trans.*, **43**: 17971-17979.

[4] É.G. Bajnóczi, B. Bohner, E. Czeglédi, E. Kuzmann, Z. Homonnay, A. Lengyel, I. Pálinkó, P. Sipos, 2014: *J. Radioanal. Nucl. Chem.* **302:** 695-700.

[5] E. Kuzmann, Z. Homonnay, S. Nagy, K. Nomura, 2010: Mössbauer Spectroscopy, – in: Vértes A., Nagy S., Klencsár Z. (editor): *Handbook of Nuclear Chemistry. – Springer* B.V.: 3-65.

[6] J. D. Donaldson, A. Jelen, 1968**:** *J. Chem. Soc. A*: 1448-1450.

[7] E. Kuzmann, A. Lengyel, Z. Homonnay, Cs. Várhelyi Jr, Z. Klencsár, S. Kubuki, R. Szalay, 2014: *Hyperfine Interactions* **226:** 181-185.

[8] V.I. Goldanskii, E.F. Makarov, 1968*:* Academic*,* New York, *Chemical Applications of Mössbauer Spectroscopy,* p. 102.

[9] S.V. Karyagin, 1963: *Dokl. Akad. Nauk. SSSR* **148:** 1102-1105.

[10] V. I. Goldanskii, E.F. Makarov, V.V. Khrapov, 1963: *Theor. Fizz.* **44** 752.; *Phys. Lett.* **3** 344-346.

[11] G. K. Shenoy, J. M. Friedt, 1976: *Nuclear Instruments and Methods* **136:** 569-574.

[12] R.H. Herber, S. Chandra, Y. Hazony, 1970: *The Journal of Chemical Physics* **53:** 3330-3335.

[13] R.H. Herber, S. Chandra, 1971: *The Journal of Chemical Physics* **54:** 1847-1851.

[14] T. Birchall, G. Dénès, K. Ruebenbauer, J. Pannetier, 1986: *Hyperfine Interactions* **29:** 1327-1330.

[15] P. Sipos, G.T. Hefter and P.M. May, 2000: *J. Chem. Eng. Data* **45**(4): 613-617.

[16] P. Sipos, P.M. May and G.T. Hefter, 2000: *Analyst* **125**(5): 955-958.

[17] R. S. Tobias, Studies on the Hydrolysis of Metal Ions, 1958: *Acta Chem Scand* **12**(2): 198-223.

[18] Z. Klencsár, E. Kuzmann, A. Vértes, 1996: *J. Radioanal. Nucl. Chem.* **210:** 105-118.

[19] A.J. Rein, J.L.K.F. De Vries, R.H. Herber, 1974: *J. lnorg. Nucl. Chem.* **36**: 825-831.

[20] R.H. Herber, H.A. Stöckler, W.T. Reichle, 1965: *The Journal of Chemical Physics* **42:** 2447-2452.

[21] N.N. Greenwood, T.C. Gibb, 1971: *Mössbauer Spectroscopy* (Chapman and Hall Ltd., London): 386-392.

[22] J.J. Zuckerman, 1967: *J. lnorg. Nucl. Chem.* **29**: 2191-2202.

[23] B. King, H. Eckert, D.Z. Denney, R.H. Herber, 1986: *Inorganica Chimica Acta* **122**: 45-53.

[24] C.G. Davies, J.D. Donaldson, 1968: *J. Chem. Soc. A* 946-948.

[25] T. Birchall, G. Dénès, K. Ruebenbauer, J. Pannetier, 1986: *Hyperfine Interactions* **30:** 167-183.

[26] G.B. Watson, 2001: *Journal of Chemical Physics* **114**, 2: 758-763.

[27] I. Langmuir, 1919: *J. Am. Chem. Soc.*, ***41***: 1543-1559.

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Tables

Table 1. ^{119}Sn Mössbauer parameters of the studied complex at various temperatures, as derived on the basis of the model accounting for the Goldanskii-Karyagin effect. Numbers in parentheses denote the standard error (1σ) in the last digits. See text for notations.

T / K	20	40	70	100	140	180
A_n	0.0802(4)	0.0789(5)	0.0673(5)	0.0533(6)	0.0376(6)	0.0226(5)
δ / mm s^{-1}	2.486(3)	2.496(3)	2.472(4)	2.446(5)	2.467(6)	2.461(10)
V_{zz} / 10^{21} V/m^2	−22.80(6)	−22.77(7)	−22.58(8)	−22.46(11)	−22.40(14)	−22.29(23)
Δ / mm s^{-1}	1.890(5)	1.888(6)	1.872(7)	1.862(9)	1.857(12)	1.848(19)
$k^2(\langle r_\parallel^2\rangle - \langle r_\perp^2\rangle)$	−0.43(6)	−0.33(8)	−0.57(9)	−0.73(11)	−0.69(16)	−1.08(25)
$\langle r_\parallel^2\rangle - \langle r_\perp^2\rangle$ / pm^2	−29(4)	−22(5)	−39(6)	−50(8)	−47(11)	−74(17)
Γ / mm s^{-1}	0.882(7)	0.843(8)	0.837(9)	0.832(13)	0.778(17)	0.783(27)

Figures

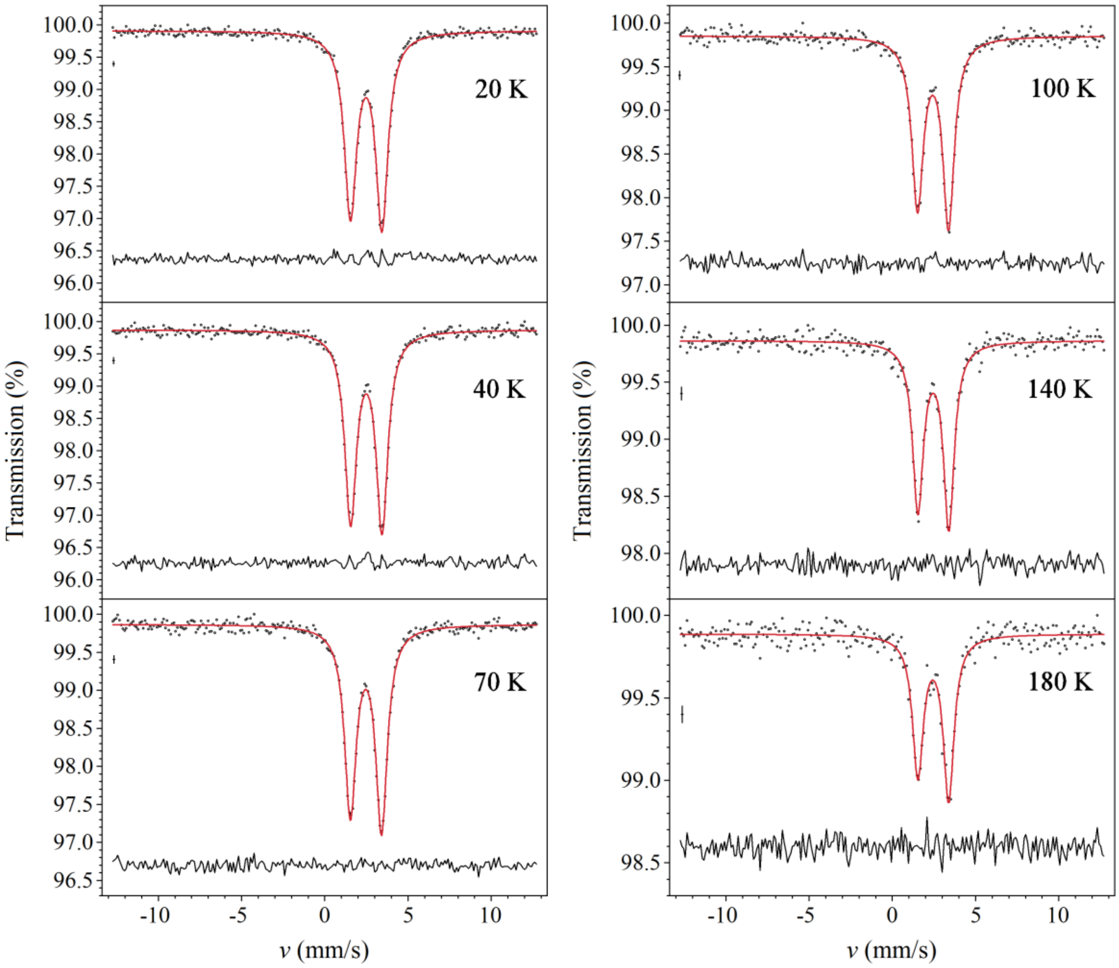

Figure 1. ^{119}Sn Mössbauer spectra of frozen hyperalkaline tin(II)-hydroxide solution, recorded at the indicated temperatures, with corresponding fit envelopes calculated by taking into account the Goldanskii-Karyagin effect as described in the text. Below the spectra the corresponding fit residuals are displayed. Small vertical bars on the left side of the graphs denote ±σ where σ is the statistical uncertainty of the baseline counts.

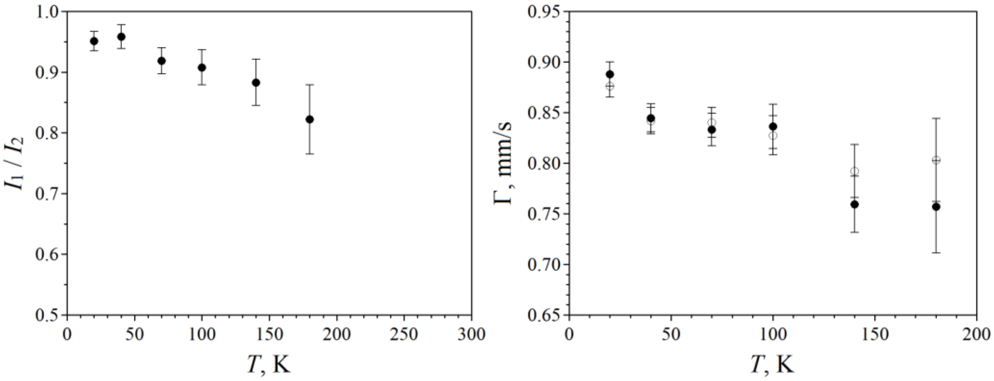

Figure 2. Results obtained by fitting the spectra on Figure 1 to two Lorentzians with independent position, intensity (I) and line width (Γ) parameters. On the left, I_1 and I_2 refer to the intensity (spectral area) of the lower- and higher velocity peak, respectively. On the right, full and hollow symbols refer to the line width (FWHM) of the lower- and higher velocity peak, respectively. Error bars correspond to ±1σ, where σ denotes the standard statistical error of fit parameters.

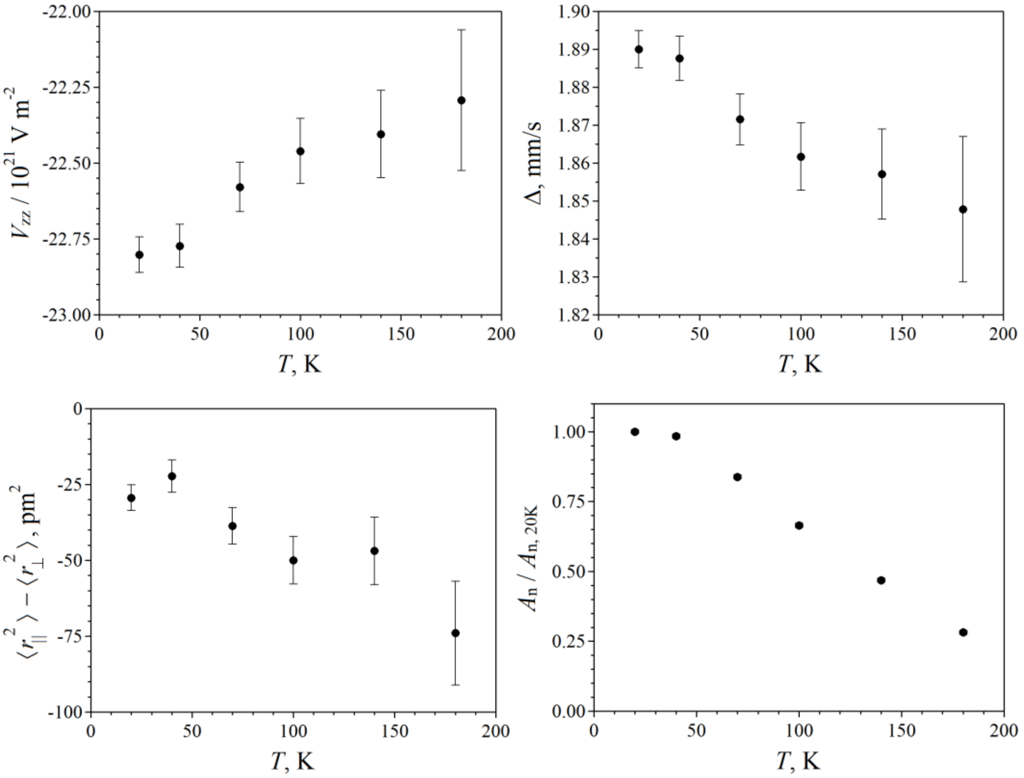

Figure 3. Results obtained by fitting the spectra on Figure 1 to a quadrupole doublet (two Lorentzians with common line width) and accounting for the intensity asymmetry by taking into account the Goldanskii-Karyagin effect. Error bars correspond to ±1σ, where σ denotes the standard statistical error of fit parameters. For the relative A_n values σ is in the order of the size of the points. See also Table 1 and the text for notations.