

A reference compound for $^{199\text{m}}\text{Hg}$ Perturbed angular correlation of γ -rays spectroscopy

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Abstract

$^{199\text{m}}\text{Hg}$ is a very useful probe for perturbed angular correlation of γ -rays (PAC) spectroscopy. Here we present $^{199\text{m}}\text{Hg}$ PAC data for a Hg^{2+} containing compound, $\text{Hg}(\text{Cys})_2(\text{s})$, giving one unique nuclear quadrupole interaction (NQI). Four separate sample preparations were carried out, and measured on analogue and digital PAC setups, leading to the following reference data: $\nu_Q = 1.458(7)$ GHz and $\eta = 0.10(6)$. The compound may be applied as an easy-to-synthesize reference sample, providing fast control of the effective anisotropy and time calibration of PAC instruments to be used for $^{199\text{m}}\text{Hg}$ PAC experiments.

Introduction

It is common practice in many spectroscopic techniques to use reference compounds to calibrate or test the performance of instruments. In time differential perturbed angular correlation (TDPAC / PAC) spectroscopy [1,2], it is not strictly necessary to use such reference compounds, but it may be very useful as validation and quality control of recorded PAC data, in particular when different instruments are used during experimental campaigns with short lived probe isotopes. Two central parameters may be quantified using such reference compounds: 1) the time calibration of the PAC

instrument, which must be known accurately in order to achieve accurate determination of the recorded frequencies, most commonly reported in the literature as the quadrupole coupling constant $\nu_Q = eQV_{zz}/h$, where Q is the nuclear quadrupole moment and V_{zz} is the numerically largest diagonal element of the electric field gradient tensor in the principal axis coordinate system; 2) the effective anisotropy, A_{22}^{eff} , which is the maximal amplitude of the PAC signal for a given PAC probe, a given sample-detector geometry, and a given PAC instrument. If more than one NQI is observed, the individual amplitudes must add up to A_{22}^{eff} , and therefore missing fractions may be identified if A_{22}^{eff} is known. With this work we present ^{199m}Hg PAC data on a Hg^{2+} containing compound, $\text{Hg}(\text{Cys})_2(\text{s})$ which is very easy and fast to synthesize using commercially available chemicals, and gives a simple PAC spectrum with one well defined high frequency NQI. Therefore, this compound is well suited to be a reference compound for ^{199m}Hg PAC experiments.

Methods

Isotope production

^{199m}Hg PAC measurements were performed at the ISOLDE laboratories at CERN. Radioactive mercury was obtained by irradiating a liquid Pb target with protons (1.4 GeV). During this process the produced Hg isotopes are vaporized, selectively ionized and accelerated at 30 keV to be extracted as an ion beam that is further mass separated into the desired ^{199m}Hg isotope. At the end of a specific vacuum beam line a picoamp current of ^{199m}Hg ions is collected in ca. 150 μL frozen solution of milliQ water. The frozen solution is placed in a small Teflon cup sitting on copper base, cooled by a liquid nitrogen cold finger during the collection of up to $2 \cdot 10^{11}$ radioactive ^{199m}Hg atoms per sample.

Preparation of the reference compound

Mercury(II) acetate (47.80 mg) was dissolved in a solution of perchloric acid (350 μL , 0.10 M) and mixed with 150 μL milliQ water irradiated with a beam of ^{199m}Hg , as described above. Two equivalents of L-cysteine (36.35 mg dissolved in 500 μL milliQ water), relative to the quantity of mercury(II), was added dropwise into this solution with continuous stirring. This was accompanied by the intense formation of a white precipitate that nearly disappeared around the addition of the final drops of L-cysteine but re-appeared again in a form of a loose but settling, cotton-like solid. The

stirring of the solution was continued for a short time (ca. 1 minute) followed by a centrifugation step, using for example a Labdoctor 8 MiniFuge at 6000 rpm for 2 minutes. The upper clean supernatant layer was sucked off from the precipitate by using a 1.0 mL automatic pipette and pressing the pipette tip down to the bottom of the tube, thereby minimizing the loss of the precipitate. The precipitate was then washed with 500 μ L milliQ water: the tube containing the precipitate and the added water was shaken for a few seconds by a Vortex and re-centrifuged by applying the same speed and time duration as noted above. The clean liquid was taken off from the precipitate as described above and the tube with the hot precipitate was immediately placed at the geometrical centre of the 6-Detector PAC setups. The PAC data were recorded at room temperature.

pH-potentiometric analysis of the composition of the reference compound

In order to determine the composition of the reference compound, it was prepared according to the above detailed protocol (without the $^{199\text{m}}\text{Hg}$ radioisotope) in a separate laboratory, dedicated to solution equilibrium studies. The only modification introduced in the synthesis procedure concerns the washing of the precipitate, which could be executed more thoroughly in the absence of the decaying $^{199\text{m}}\text{Hg}$ isotopes. The washing step was repeated four times using (4 \times) 500 μ L of milliQ water. The obtained solid was dried in vacuum for 48 h to ensure the removal of traces of remaining solvent, allowing for the determination of the composition of the compound by pH-potentiometric titration, based on the mass of the titrated amount.

pH-potentiometric titrations were executed in aqueous solutions ($T = 298.0 \pm 0.1$ K, $I = 0.1$ M KCl) under Argon atmosphere using a KOH standard solution ($c \sim 0.1$ M). The titrations were carried out by an automatic titration instrument setup consisting of a PC-controlled Metrohm Dosimat 765 autoburette, an Orion 710A digital pH-meter and a Metrohm Slim Combined Micro Electrode (125 \times 6 mm). The calibration procedure and conversion of the pH-meter readings to hydrogen ion concentrations was done according to the method described by Irving [3]. We carried out two separate potentiometric titrations: 1) To 9.20 mg of the dried reference compound (which is a white powder) 10.0 mL of KCl solution ($c = 0.1$ M) and 0,7 mL of hydrochloric acid ($c = 0.1$ M) was added, however, the particles did not dissolve. After 10 minutes of stirring, the titration process was started. Along with the addition of the titrant (KOH), a complete dissolution was observed between ca. pH 7 and 9.5. 2) In a second titration 9.22 mg of the solid, mixed only with 10.0 mL of KCl solution ($c = 0.1$

M), was titrated by the same KOH solution and similarly to the first experiment, the particles completely dissolved in the slightly alkaline pH-regime.

PAC instruments and data analysis

For the PAC setups, digital DIGIPAC [4] using #6 1.5”x1.5” LaBr₃(Ce) detectors and analogue PERM [5] upgraded with #6 1”x1” CeBr₃ detectors, time resolutions of 0.7 ns and 0.5 ns, respectively were obtained by averaging the values obtained during determination of t_0 channels for every single spectrum obtained (there are #30 spectra, #6 at 180° and #24 at 90° γ_1 - γ_2 detector pair combinations). Time-per-channel calibrations of 0.04883 ns and 0.05019 ns were used with the digital and analogue PAC setups, respectively.

Data analysis was carried out with the Winfit program (provided by prof. T. Butz) using 400 data points (excluding the first 7 points due to t_0 determination uncertainties near time zero where the prompt resolution dependency is more notorious). A Lorentzian line shape was used to account for a small line broadening, given by the parameter δ , due to a static distribution of EFGs. Fourier transformation of the data and fits were carried out using 800 points after mirroring 400 data points multiplied by a Keiser-Bessel window function with set parameter equal to 4.

The intermediate ($E = 158.3$ keV) excited state of the ¹⁹⁹Hg nucleus, in which the NQI is measured in ^{199m}Hg PAC spectroscopy, has spin 5/2. For nuclear spin 5/2 and randomly oriented identical Hg²⁺ sites, considering only static electric fields, the observable NQI is described by [1,2]:

$$A_{22}^{eff} G_{22}(t) = A_{22}^{eff} (a_0 + a_1 \cos(\omega_1 t) + a_2 \cos(\omega_2 t) + a_3 \cos(\omega_3 t))$$

where A_{22}^{eff} is the effective anisotropy, and a_i and ω_i depend on the quadrupole coupling constant ν_Q and the asymmetry parameter η [6,7].

The experimental equivalent of $A_{22}^{eff} G_{22}(t)$, and therefore the experimental data to which the theoretical perturbation function is fitted, called $R(t)$, is constructed as [2]:

$$R(t) = 2 \frac{W(180^\circ, t) - W(90^\circ, t)}{W(180^\circ, t) + 2W(90^\circ, t)}$$

where $W(180^\circ, t)$ and $W(90^\circ, t)$ are the geometrical mean of coincidence spectra recorded with 180° and 90° between detectors, after removal of chance coincidences and time zero shift synchronisation, respectively.

Results and Discussion

In this section we first address the identification of the reference compound, and next account for experimental data recorded by PAC-spectroscopy for the reference compound.

The composition of the reference compound was determined by two independent pH-potentiometric titrations. Calculation of the molecular mass of the reference compound, based on the titrated masses and the quantity of the consumed KOH in the two titrations, leads to an average value of $M_{\text{experimental}} = 445.0$ g/mol (432.5 and 457.4 g/mol from the first and second titrations, respectively). This is very close to the theoretical molecular mass of the bis-L-cysteinato complex of Hg^{2+} containing deprotonated carboxyl and thiol but protonated amino groups and no other molecules or counter ions ($M_{\text{theoretical}} = 440.8$ g/mol). Accordingly, if the fully protonated cysteine is noted as $[\text{CysH}_3]^+$, the precise composition of the reference compound is $\text{Hg}(\text{CysH})_2(\text{s})$, where two ligands are coordinated to the metal ion via their thiolate groups. Figure 1 shows base consumptions (moles KOH) normalized to the quantity of Hg^{2+} (moles) in the samples by assuming that half equivalent of Hg^{2+} per ligand is present in the prepared complex. Consumption of KOH for the added extra acid (HCl) in the first titration was subtracted from the calculated base equivalents, allowing the direct comparison of the two curves. This comparison suggests that the obtained solid is reasonably homogenous since the shape of the two curves are rather similar and the difference between the two equivalence points (in moles of consumed base) differ only by ca. 5 %. An important finding is that the first equivalence point, observed for the titration with extra acid added, represents a base quantity that perfectly matches the quantity of the added hydrochloric acid. In other words, there are no protonated groups or possible counter ions in the compound dissociating below neutral pH. This excludes the presence of acetate ions, that could originate from the starting material mercury(II) acetate, but also indicates that the carboxylate groups in the Hg^{2+} -bound cysteine molecules are all deprotonated in the complex. Since the cysteine ligands are undoubtedly coordinated to Hg^{2+} via the deprotonated thiol moieties, the observed deprotonation step(s) with an estimated average $\text{p}K_a$ around 8.5 (see Figure 1), must be

attributed to proton releases from the amino groups of two bound cysteine ligands. Thus, the reference compound is $\text{Hg}(\text{Cys})_2(\text{s})$, in which the carboxyl groups and thiols are deprotonated, and the amino groups are protonated, see Scheme 1.

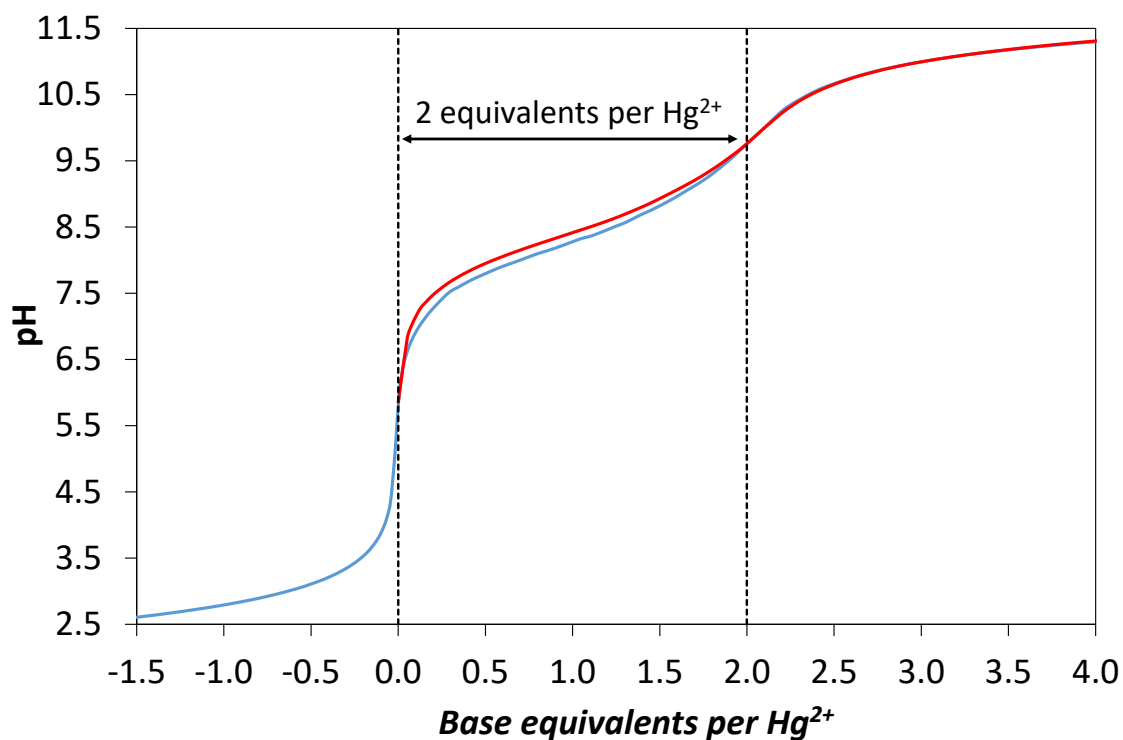
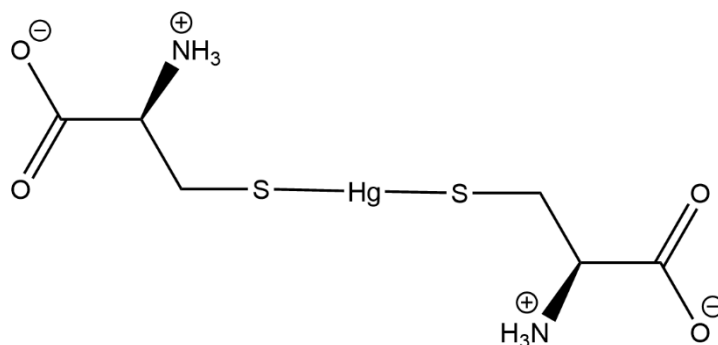


Figure 1 Normalized titration curves, presented as consumed base equivalents per Hg^{2+} , of the complex mixed with 10.0 mL of a 0.1 M KCl solution in the absence (red curve) and presence of added HCl acid (6.4×10^{-3} M) (blue curve). The quantity of the added HCl acid was subtracted from the consumed base quantity before calculating the consumed base equivalents per Hg^{2+} ions. Calculation was based on the assumption that half equivalent of Hg^{2+} per ligand is present in the complex.



Scheme 1 Composition of the bis(cysteinato)mercury(II) reference compound.

The $^{199\text{m}}\text{Hg}$ PAC data were recorded for four different sample preparations of the reference compound, $\text{Hg}(\text{Cys})_2(\text{s})$, and on two different instruments, see Table 1 and Figure 2. Most importantly, the data recorded for the different experiments are highly similar, and the average NQI parameters are $\nu_Q = 1.458(7)$ GHz and $\eta = 0.10(6)$. These parameters may be used as reference values for the testing of the proper function and of the time calibration of PAC instruments when conducting $^{199\text{m}}\text{Hg}$ PAC experiments. The difference between ν_Q determined on the analogue and the digital PAC instrument is almost within the statistical error, and the difference presumably originates from slight inaccuracies of the time calibration of the analogue PAC instrument. The indicated standard deviations on ν_Q and η include only the statistical error determined from the PAC data for each experiment, but not variations due to minor differences in sample preparation from one sample to the next. However, sample to sample variation may be estimated from the data recorded on the analogue instrument for three different samples, see Table 1, and it is of the same magnitude, i.e. ~ 0.01 GHz. The short half-life ($t_{1/2} = 2.47$ ns) of the intermediate nuclear level of the γ - γ cascade used in $^{199\text{m}}\text{Hg}$ PAC spectroscopy dictates that only a limited time span of $R(t)$, *vide supra*, (typically 15-20 ns) may be recorded with decent signal-to-noise ratio. Thus, a high frequency signal, where several oscillations may be recorded, is required in order to achieve a small relative error on ν_Q and η . The current reference sample satisfies this requirement, see Table 1 and Figure 2, and the relative error is of the same magnitude ($< 1\%$) as the typical relative error on time calibration of an analogue PAC instrument. Other simpler thiols such as methanethiol, ethanethiol, etc. similarly give excellent $^{199\text{m}}\text{Hg}$

PAC spectra in complex with Hg^{2+} [8], but they were not selected for the current work, due to their rather unpleasant odour.

The obtained NQI parameters of $\nu_Q = 1.458(7)$ GHz and $\eta = 0.10(6)$ are in good agreement with literature reporting ^{199}mHg PAC data on distorted linear HgS_2 coordination geometries, and significantly differ from ^{199}mHg PAC data recorded for HgS_3 and HgS_4 [8-10] complexes. The fact that the asymmetry parameter, η , is slightly larger than zero, implies that perfect axial symmetry is not present, an observation also made for the crystal structure of bis-(L-cysteinato)mercury(II) [11]. This indicates that the coordination geometry of Hg^{2+} in the reference compound is distorted linear bis-(thiolato)mercury(II), as expected.

The relatively short lifetime of the ^{199}mHg mother isotope ($t_{1/2} = 43$ min) puts restraints on the time available for chemical sample preparation. Consequently, to keep the sample preparation fast and simple, we used rapid precipitation rather than careful crystallization. The rapid precipitation might give rise to considerable variability of the structure near the PAC probe. However, the small value of δ , Table 1, indicates that a very well defined coordination geometry for Hg^{2+} is achieved (δ reflects static variations of the NQI from one probe nucleus to the next). The PAC data therefore indicate that the sample is in fact microcrystalline with randomly oriented micro domains, even if it appears to be an amorphous precipitate. A similar but slightly lower value of ν_Q (1.41(2) GHz) has been reported for a Hg^{2+} -cysteinate species obtained by evaporation to dryness from a solution (with no precipitation) [10]. The difference between the value of ν_Q reported in this work, and that reported by Butz et al. [10] may be due to the differences in sample preparation, or – less likely – slight inaccuracies in the time calibration of the PAC instruments.

Table 1: Parameters fitted to ^{199}mHg PAC data for the reference compound recorded on analogue (3 measurements) and digital (1 measurement) PAC setups. The last line of the table shows fit values for the added ensemble of the analogue measurements. The digital and analogue added ensemble of $R(t)$ data with the corresponding theoretical fits and respective Fourier spectra are shown in Figure 2.

Instrument	ν_Q	η	δ	A	χ^2
	(GHz)		$\times 100$	$\times 100$	

Digital	1.450(8)	0.05(8)	0.0(7)	12.4(9)	0.51
Analogue 1 st	1.46(1)	0.15(4)	0.7(9)	14(1)	0.64
Analogue 2 nd	1.470(7)	0.11(3)	0.7(7)	15(1)	0.84
Analogue 3 rd	1.47(1)	0.16(4)	0.0(2)	15(2)	0.59
<Analogue>	1.466(5)	0.14(2)	0.4(5)	14.3(7)	0.83

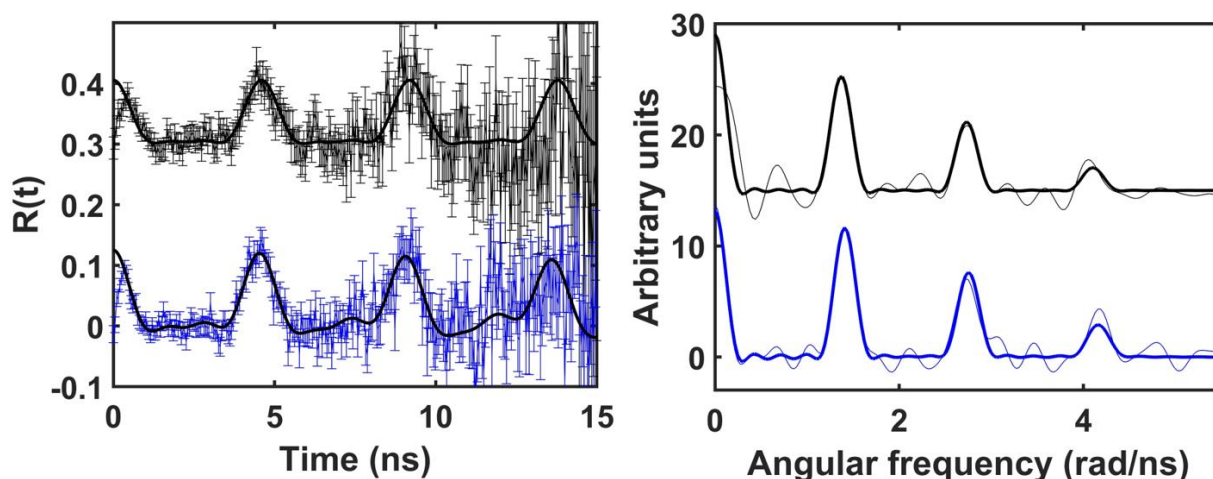


Figure 2 $^{199\text{m}}\text{Hg}$ PAC data for the reference compound recorded on a digital (black) and an analogue PAC instrument (blue; the sum of three measurements). Left: Experimental data and fit. Data points with error bars and fit as full line; Right: Fourier transformed data (thin line) and fit (bold faced line).

The maximum effective amplitude of the PAC signal, A_{22}^{eff} , is also a useful value for calibration. It depends on the properties of the nuclear decay as well as the sample-detector geometry [12,13].

In general, effective $A_{kk'}$ coefficients are defined as the product of a correction factor $Q_{kk'}$ multiplied by the theoretical $A_{kk'}$ factors solely depending of the decay cascade characteristics, i.e. the spins and multipolarity mixing of the emitted gamma rays. $A_{kk'}$ are the product of $A_k(\gamma_1) \times A_{k'}(\gamma_2)$, and similarly $Q_{kk'}$ are the product of $Q_k(\gamma_1) \times Q_{k'}(\gamma_2)$ [12, 13]. The Q_k attenuation factors have values between 0 and 1 and can be analytically estimated by integrating a normalized Legendre polynomial of order k within the solid angle covered by the detector, considering the efficiency for the photo peak creation that depends on the γ energy and the type of scintillator. Unfortunately, source size effects, the centering of the sample and other aspects taking into account the light yield of the

scintillator and photomultiplier characteristics make a simple analytic estimation of Q_k biased towards too large values. Therefore, experimental determination of A_{22}^{eff} may serve as a benchmark for theoretical evaluation of this property. The samples used in this work were approximately cylindrical (diameter 0.65 cm and height about 0.5 cm) and placed at the geometrical centre of the 6D PAC setup. The distance from the centre of the sample to the face of the detector housing was ~ 30 mm. In summary, A_{22}^{eff} is unique to a given instrument and PAC probe, but may vary even from sample to sample, if the sample volume varies or if the sample-detector distance is changed. However, using a fixed geometry, A_{22}^{eff} serves as a reference for the instrument. Thus, although the, A_{22}^{eff} , Table 1, reported here cannot be used for calibration of other PAC instruments, it may be applied as the total (fixed) amplitude in data analysis for data recorded on the two PAC instruments used in this work, respectively. That is, the reported values for A_{22}^{eff} are the total amplitudes that may be measured with these instruments in this sample-detector geometry, and therefore missing fractions may be identified if the amplitudes (of potentially several NQIs) do not add up to A_{22}^{eff} , if the sample-detector geometry is the same as for the reference compound.

Conclusions

With this work we present nuclear quadrupole interaction parameters, $\nu_Q = 1.458(7)$ GHz and $\eta = 0.10(6)$, for a reference compound, $\text{Hg}(\text{Cys})_2(\text{s})$, which is very simple to produce. The reference compound may be used to calibrate and test performance of instruments applied in $^{199\text{m}}\text{Hg}$ perturbed angular correlation of γ -rays experiments.

Declaration of competing interests

The authors have no competing interests.

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