Re-determination of the nuclear quadrupole moment of the first excited $I = \frac{5}{2}$ state of ^{61}Ni with Mössbauer spectroscopy

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Abstract

The ^{61}Ni-Mössbauer spectra of the two compounds $BaNiO_2$ and $(As(C_6H_5)_4)_2$ $[Ni('^{bu}S_2')_2]$, where $'^{bu}S_2'^{2-}$ = 3,5-ditertiarybutyl-1,2-benzenedithiolate(2−), which exhibit large quadrupole splittings are used to calculate the ratio of the nuclear quadrupole moments of the $I = 3/2$ ground state (Q_g) and the first excited $I = 5/2$ state (Q_e), the result being $Q_g/Q_e = -0.47(-7/+5)$. From this the nuclear quadrupole moment of the first excited $I = 5/2$ state can be derived as $Q_e = -0.34 \pm 0.06$ b which is significantly different from the value used to evaluate Mössbauer spectra for the last 30 years ($Q_e = -0.20 \pm 0.03$ b).

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1 Introduction

After the 40th anniversary of ^{61}Ni Mössbauer spectroscopy (the first publications of Obenshain and Wegener[1, 2] are dating back to 1961) the nuclear quadrupole moment of the first excited $I = 5/2$ state of ^{61}Ni currently accepted and listed in Nuclear Data Sheets[3] and Atomic Data and Nuclear Data Tables[4] is still $Q_e = (-0.20 \pm 0.03) \times 10^{-24}\text{cm}^2 = -0.20 \pm 0.03$ b. It was calculated from the nuclear quadrupole moment of the $I = 3/2$ ground state ($Q_g = 0.162 \pm 0.015$ b) published by Childs and Goodman[5] in 1968 and the ratio of the nuclear quadrupole moments of the first excited $I = 5/2$ state and the ground state $Q_e/Q_g = -1.21 \pm 0.13$ derived from Mössbauer spectra of $NiCr_2O_4$ by Göring[6] in 1971. There was also a value of $Q_e/Q_g = -0.5 \pm 0.4$ derived from spectra of $NiCl_2 \cdot 6H_2O$ by Obenshain, Williams, and Houk[7] in 1976. In 1978 Göring, Wurtinger, and Link[8] summarized that Q_e/Q_g values in the range of −0.5 to −2.5 were reported.

The availability of Mössbauer spectra of two compounds with near square-planar coordination of Nickel(II), with a $3d^8$ low spin electron configuration, made a new determination of the Q_g/Q_e ratio possible.

In terms of crystal field theory, the V_{zz} component of the EFG tensor lacks a large positive valence contribution from the non-occupied $3d_{x^2-y^2}$-orbital resulting in a relatively

large negative value and the appropriate quadrupole splitting. (In the less-likely case of a high spin state the same would apply for large positive valence contributions from the half filled $3d_{x^2-y^2}$- and $3d_{xy}$-orbitals.) As this is a relatively rare case, this coordination is a textbook example[9, 10] for large quadrupole splitting in ^{61}Ni Mössbauer spectroscopy. More detailed investigations of the electronic structure of $BaNiO_2$ were subject to band structure calculations published in Ref. [11].
A complex with similar coordination but exhibiting smaller splitting was already subject to studies by Dale, Dickinson, and Parish[12]. Recent publications showed ^{61}Ni quadrupole splittings in emission spectra of ^{61}Cu doped high-T_c superconductors[13, 14, 15, 16].

2 Compounds

2.1 $BaNiO_2$

First described by Lander[17], the preparation and crystal structure of this compound were published by Kirschner, Torkar, and Kolbesen[18]. The actual preparation and characterization of the sample was described in Ref. [19] and previous results were also published in Refs. [20] and [11].
Puckered layers of parallel zig-zag chains consisting of edge-sharing NiO_4 units with near square-planar coordination of Nickel represent a solid state example of the d^8 low spin configuration mentioned before. A non-magnetic ground state at low temperatures was recently confirmed by μSR measurements[21] and neutron scattering[22].

2.2 $(As(C_6H_5)_4)_2[Ni('^{bu}S_2')_2]$

In $(As(C_6H_5)_4)_2[Ni('^{bu}S_2')_2]$, where $'^{bu}S_2'^{2-}$ = 3,5-ditertiarybutyl-1,2-benzenedithiolate(2−), which was prepared ^{61}Ni enriched according to Ref. [23] to compensate low concentration and the relatively small Lamb-Mössbauer factor of Ni, the bulky organic two dentate ligands lead to an almost square planar coordination of Nickel(II) by Sulfur with the same implications for the electronic structure as in the compound mentioned before.

3 Experimental

3.1 Source preparation

To produce sources of the parent ^{61}Co nucleus with $T_{1/2}$ = 99 min, small platelets of $^{62}Ni_{0.85}Cr_{0.15}$ (97.7 % enriched) alloy[24, 9, 25] were transported to the activation site in front of the beam dump of the three spectrometer setup of the A1 collaboration of the MAinz MIcrotron with a pneumatic tube, allowing source activation during nuclear physics experiments. Bremsstrahlung including the giant resonance region of 20−25 MeV, necessary for the ^{62}Ni(γ, p) reaction, was produced from the electron beam (with up to 855 MeV energy and 100 μA current) directly before the activation area in a stack of air cooled gold foils. Immediately after activation, the sources, sealed in Aluminum containers, are transported to the Mössbauer setup.

3.2 Mössbauer setup

The spectra were recorded with a conventional vertical Mössbauer setup in transmission geometry with a helium bath cryostat. Samples were pressed into Teflon sample holders by screwing one part into the other, while the thread was sealed with Teflon tape. Source and Teflon absorber were immersed in liquid helium for the 4.2 K measurements. For rapid installation, the source was pushed through the 1.47 m hollow stainless steel drive rod, which was moved with a sine velocity profile because of it's length. On the other side of the transducer ^{57}Fe Mössbauer spectra of α-iron could be run simultaneously allowing velocity calibration.
The 67.4 keV radiation was detected with a 2 mm thick NaI(Tl) scintillator. To determine the effective thickness of the absorber, which was necessary for a correct calculation of linewidth, pulse height spectra were recorded several times during the measurements.

3.3 Mössbauer spectra

An absorber with $BaNiO_2$ equivalent to 153.9 mg Ni / 1.54 cm^2 was used to collect seven spectra from different source activations and partially different maximum velocities. One example is shown in Fig. 1(a).
Due to low concentration and Lamb-Mössbauer factor of Ni, enriched $(As(C_6H_5)_4)_2[Ni('^{bu}S_2')_2]$ was used to prepare an absorber with 13 mg ^{61}Ni / 1.54 cm^2. Three spectra from different source activations and with different v_{max} were recorded, exhibiting one of the largest pure quadrupole splittings ever found in ^{61}Ni Mössbauer spectra, one of the best is shown in Fig. 1(b).

4 Evaluation of the spectra

4.1 Background radiation

The components of pulse height spectra were fitted with Gaussian lines. Fitting the time dependence of the components' intensity with exponential decay functions allowed to estimate the integral background in the Mössbauer spectra. In cases where very accurate knowledge of the background is necessary a detection device with higher energy resolution like a Ge(Li) diode would be advisable.

4.2 Fit of the Mössbauer spectra

Evaluation of the parameters was performed with the fit program EFFI which in addition to calculation of the convolution integral solves the spin Hamiltonian for source and absorber and allows to fit several spectra simultaneously. The evaluation was based on a natural linewidth of $\Gamma_{nat} = \hbar/\tau = (\hbar \ln 2)/(5.34 \pm 0.16)$ ns $= (8.5 \pm 0.3) \times 10^{-8}$ eV $\hat{=}$ (0.380 ± 0.012) mm s^{-1} (Ref. [3], the average of values from Refs. [26] and [27]).

4.3 Fit of the ratio of the nuclear quadrupole moments

As the fit program EFFI did not allow to treat the natural constant Q_g/Q_e as a fit parameter, several fits were carried out assuming the old value and different values

around $(Q_g/Q_e)_0$ that corresponds to the minimum χ^2.
It was proved by Arndt and McGregor[28] that shifting a fixed parameter from it's minimum by it's variance σ (corresponding to a confidence interval of 68.3 % , the basis for all errors reported in this article) and fitting all free parameters to the new minimum results in a non-reduced χ^2 value that is higher by 1: $\Delta\chi^2_{nred} = 1$. The increase of the reduced χ^2-value calculated by the fit program is therefore 1 divided by the number of degrees of freedom ν, the number of data points n minus the number of free parameters n_p:

$$\Delta\chi^2 = \frac{1}{\nu} = \frac{1}{n - n_p} \tag{1}$$

A plot of reduced χ^2-values versus (Q_g/Q_e) allows to fit an asymmetric parabolic equation

$$\chi^2 = \begin{cases} a_l \left[\left(\frac{Q_g}{Q_e}\right) - \left(\frac{Q_g}{Q_e}\right)_0\right]^2 + \chi_0^2 & \text{if} \quad \left(\frac{Q_g}{Q_e}\right) < \left(\frac{Q_g}{Q_e}\right)_0 \\ a_r \left[\left(\frac{Q_g}{Q_e}\right) - \left(\frac{Q_g}{Q_e}\right)_0\right]^2 + \chi_0^2 & \text{if} \quad \left(\frac{Q_g}{Q_e}\right) \geq \left(\frac{Q_g}{Q_e}\right)_0 \end{cases} \tag{2}$$

from which the optimum $(Q_g/Q_e)_0$ and the asymmetric variance $\Delta(Q_g/Q_e)_{0l}$, $\Delta(Q_g/Q_e)_{0r}$ can be derived.

$$\Delta\left(\frac{Q_g}{Q_e}\right)_{0(l,r)} = \sqrt{\frac{1}{a_{(l,r)}(n - n_p)}} \tag{3}$$

5 Results and Discussion

5.1 Source properties

The source properties were calculated from spectra of a $Ni_{0.86}V_{0.14}$ absorber[29], the properties of which are known from the evaluation of spectra recorded with a new source of the same composition ($^{62}Ni_{0.86}V_{0.14}$). The source could be best described with a Lamb-Mössbauer factor of $f = 0.126 \pm 0.006$ and a Lorentzian broadening of 33 ± 9 % . The f-factor of the often used source was lower than reported in previous publications and also lower than in fresh $Ni_{0.86}V_{0.14}$ sources. As the amount of ^{61}Ni produced by nuclear decay is too low, self-absorption in the source can be ruled out as the reason for this effect. In cases of measurements where the knowledge of the Lamb-Mössbauer factor or slight broadenings is crucial, the source properties should be re-determined for the experiment.

5.2 Ratio of the nuclear quadrupole moments

After checking the equivalence of hyperfine parameters obtained from the single spectra, regarding their margins of error, simultaneous fits of seven spectra of $BaNiO_2$ were carried out. The effective thickness, isomer shift, quadrupole splitting, and asymmetry parameter of the absorber were correlated and fitted with one parameter each as well as the Lorentzian broadening of the source. The spectrum dependent baseline and geometry factor were fitted for each spectrum. The Lamb-Mössbauer factor of the source and Q_g/Q_e were set as well as known ratios of background radiation. Ratios of background radiations of spectra with recording times that were too long to estimate background radiations with sufficient accuracy were fit parameters. Q_g/Q_e was varied

in a grid around the minimum of χ^2 and Lamb-Mössbauer factor of the source and known ratios of background radiation were varied within their margins of error.
A fit of a plot of χ^2 versus Q_g/Q_e as described in 4.3 resulted in $Q_g/Q_e = -0.50(-0.18/+0.10)$. Simultaneous fits of three spectra of $(As(C_6H_5)_4)_2[Ni('^{bu}S_2')_2]$ as described before gave $Q_g/Q_e = -0.46(-0.08/+0.06)$ as the result. A common fit of all ten spectra was carried out to get an average value, the plot of χ^2 versus Q_g/Q_e is depicted in Fig. 2. The overall result turned out to be $Q_g/Q_e = -0.47(-0.07/+0.05)$ for every Lamb-Mössbauer factor of the source that was assumed. This value corresponds to $Q_e/Q_g = -2.1 \pm 0.3$ which is significantly different from the value obtained by Göring[6] $Q_e/Q_g = -1.21 \pm 0.13$ but within the range of earlier observations.
To calculate the nuclear quadrupole moment of the first excited $I = 5/2$ state, the value of Childs and Goodman[5] $Q_g = 0.162 \pm 0.015$b was used interpreting the error as the variance σ to get a combined error via Gaussian error propagation. The result is $Q_g(Q_g/Q_e)^{-1} = 0.162 \pm 0.015\text{b}[-0.47(-7/+5)]^{-1} \approx -0.34(-0.06/+0.05)\text{b} \approx -0.34 \pm 0.06$ b. Including the error of Q_g, this is still significantly different from the previous value $Q_e = -0.20 \pm 0.03$ b. The implications for the energy levels and the fits of spectra are visualized in Fig. 3.

5.3 Hyperfine parameters for the compounds under investigation

The new natural constant requires new fits of the compounds under investigation varying Q_g/Q_e and source parameters within their margins of error. The isomer shift δ (with reference to the source and not corrected for second order Doppler shift), the V_{zz} component of the EFG tensor, and the asymmetry parameter η for both compounds $BaNiO_2$ and $(As(C_6H_5)_4)_2[Ni('^{bu}S_2')_2]$ resulting from fits assuming ratios of the nuclear quadrupole moments within it's error margin are listed in table 1.
Depending on the Lamb-Mössbauer factor of the source and it's broadening, f-factors for valid fits (according to the criterion of Arndt and McGregor[28]) of $BaNiO_2$ were in the range of 0.135 ± 0.004 to 0.164 ± 0.004 and 0.0397 ± 0.0009 to 0.0498 ± 0.0012 for $(As(C_6H_5)_4)_2[Ni('^{bu}S_2')_2]$.
This shows that the determination of these parameters strongly depends on the errors of source parameters, background radiation and natural constants of the Mössbauer transition. Assuming the old Q_g/Q_e values leads to asymmetry parameters η close to 0 with the appropriate large influence on the calculation of V_{zz}. As we reported a value of $V_{zz} = (15.7 \pm 1.5) \times 10^{21}\,\mathrm{V\,m^{-2}}$ and $\eta < 0.4$ for $BaNiO_2$ based on the old constants in Ref. [11], the significantly different new values underline that there is still a considerable amount of uncertainty concerning absolute values and that, when comparing results of different measurements, the premises of the evaluation are important.
The relatively weak nuclear quadrupole moments in combination with a large natural linewidth and relatively rare cases of electronic configurations that produce a large EFG at the nucleus caused a situation where good statistics and a favourable case is required to measure an effect that is beyond the error range. In consequence investigations of ^{61}Ni quadrupole splittings are outnumbered by the well-established measurements of hyperfine magnetic fields. So after four decades and with a splitting of the ground state by quadrupolar interaction, conditions that are much more favourable than in the case of ^{57}Fe, there is still a considerable amount of uncertainty in calculations of absolute V_{zz} values.

6 Conclusions

The ratio of the nuclear quadrupole moments of the $I = 3/2$ ground state (Q_g) and the first excited $I = 5/2$ state (Q_e) were determined to be $Q_g/Q_e = -0.47(-7/+5)$. The corresponding inverse value of $Q_e/Q_g = -2.1 \pm 0.3$ is within the range of previous determinations (-0.5 to -2.5) but significantly different from the value that was currently accepted ($Q_e/Q_g = -1.21 \pm 0.13$). The nuclear quadrupole moment of the first excited $I = 5/2$ state is derived as $Q_e = -0.34 \pm 0.06$ b, also significantly different from the old value $Q_e = -0.20 \pm 0.03$ b.
The absolute values of V_{zz} depend on the assumed value of Q_g/Q_e and the error margin is considerable and in the examples shown far beyond statistical error. The influence of the asymmetry parameter η is also considerable.
To determine smaller pure quadrupole splittings the exact knowledge of Lamb-Mössbauer factor and broadening of the source and the amount of background radiation is crucial. Any absolute values of hyperfine parameters except an internal or external magnetic field and isomer shift without second order Doppler shift correction may strongly change with assumptions of natural constants and source properties and may not be comparable between different publications.

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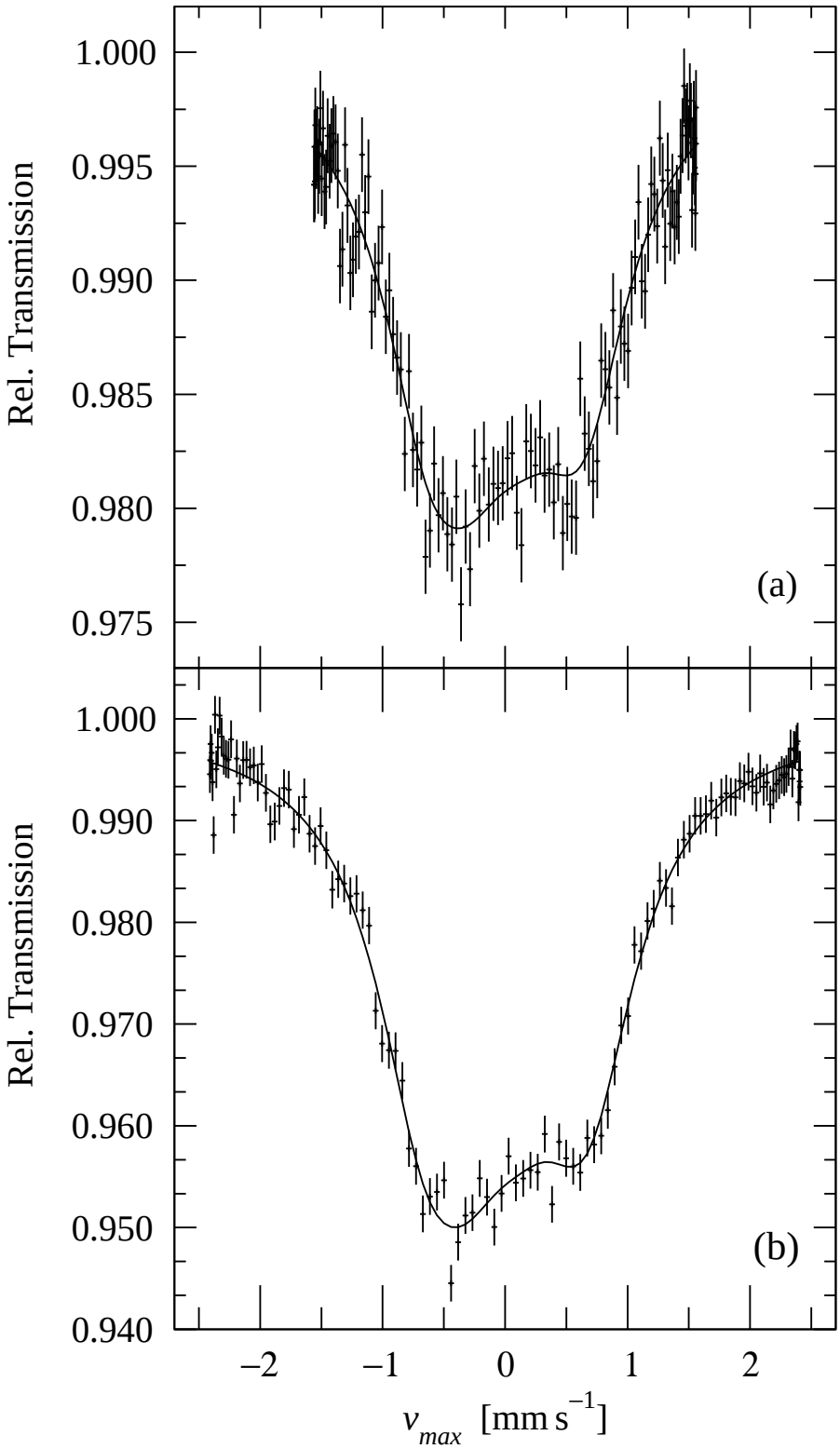

Figure 1: Mössbauer spectra and best fits of $BaNiO_2$ (a) and $(As(C_6H_5)_4)_2[Ni('^{bu}S_2')_2]$, where $'^{bu}S_2'^{2-}$ = 3,5-ditertiarybutyl-1,2-benzenedithiolate(2−), (b) with low v_{max}. Four channels were summed up to one for better visual impression.

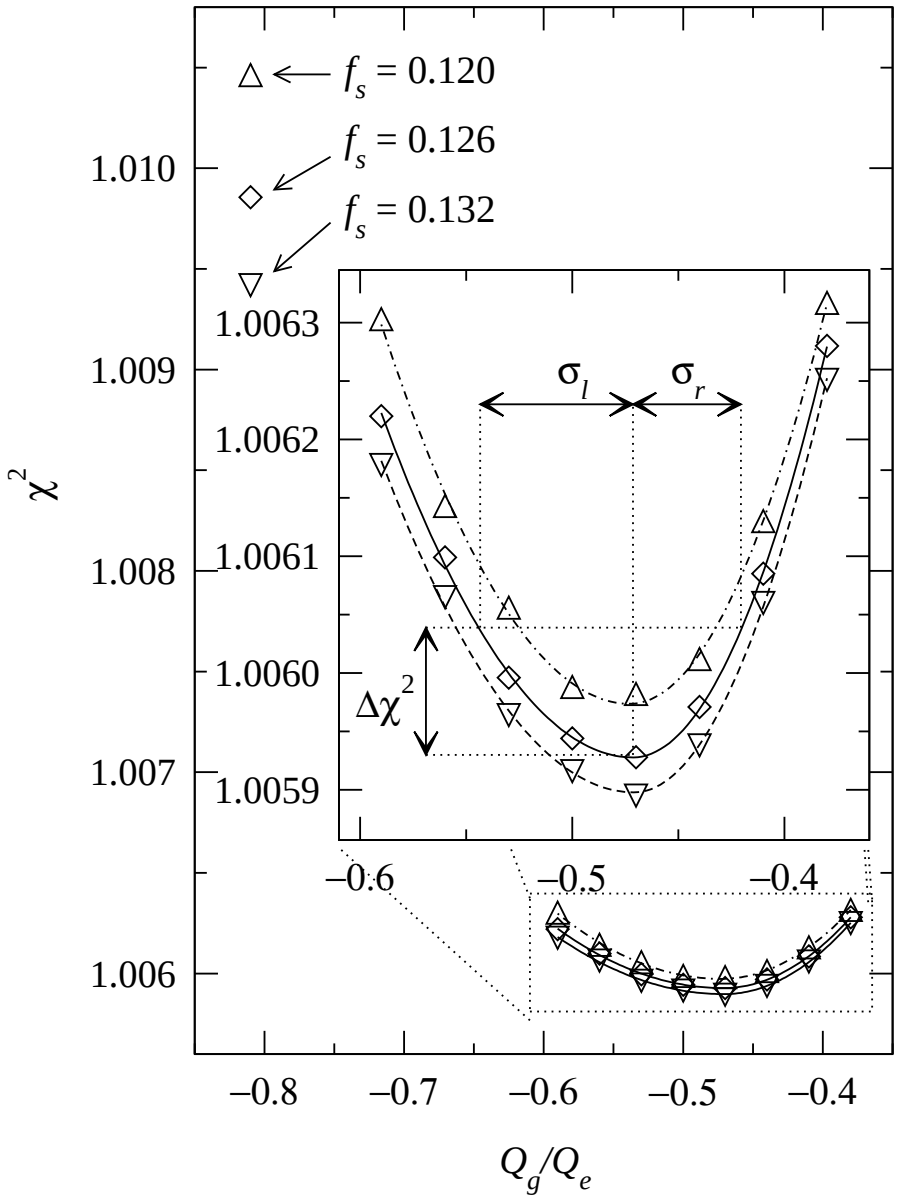

Figure 2: Plot of χ^2 versus Q_g/Q_e of simultaneous fits of all Mössbauer spectra assuming Lamb-Mössbauer factors of the source of $f_s = 0.120(\bigtriangledown)$, $f_s = 0.126(\Diamond)$, and $f_s = 0.132(\bigtriangleup)$, the curve and distances displayed represent the results of fitting an asymmetric parabolic function. The single symbols on the left correspond to the old ratio measured by Görig[6]

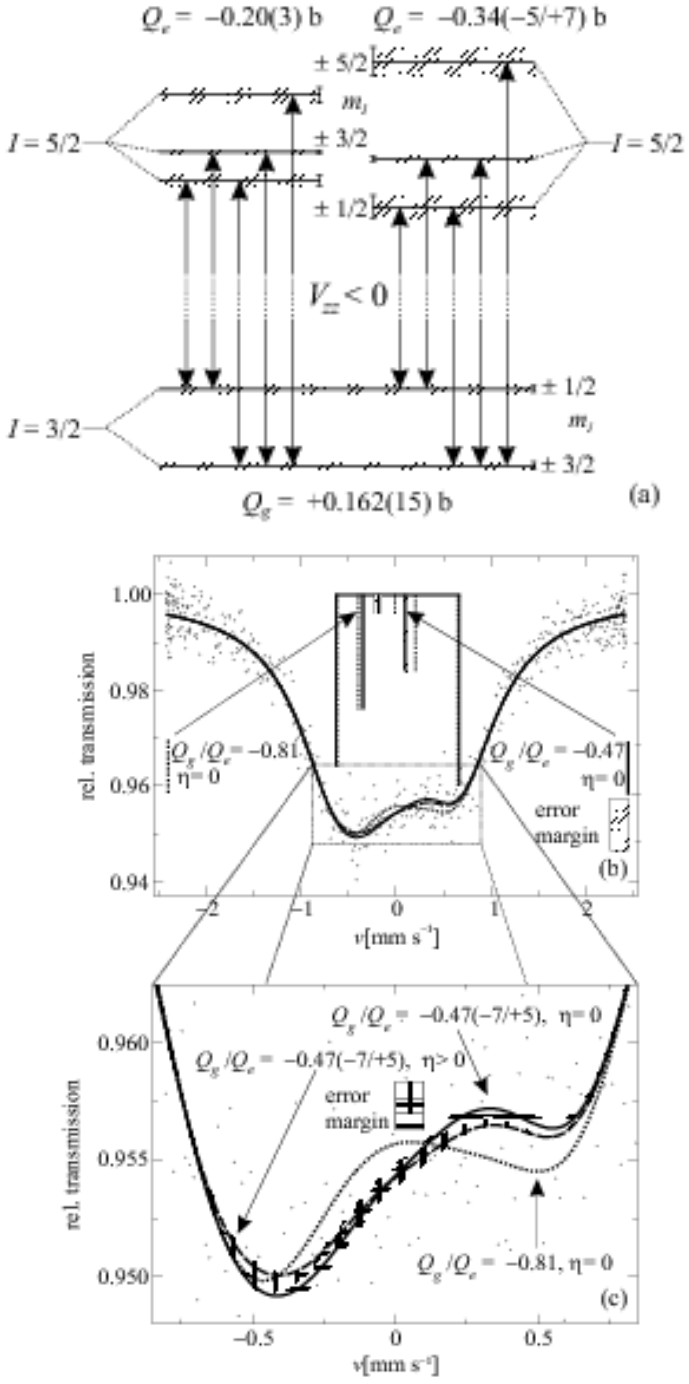

Figure 3: Enegery levels and transitions of a quadrupole pentet for the old and new values of Q_e (a) and best fits of an $(As(C_6H_5)_4)_2[Ni(^{'bu}S_2{}')_2]$, $^{'bu}S_2{}'^{2-}$ = 3,5-ditertiarybutyl-1,2-benzenedithiolate(2−), spectrum assuming (Q_e = 0.20 b, $\eta = 0$), (Q_e = 0.34 b, $\eta = 0$), and (Q_e = 0.34 b, $\eta > 0$) (b) and the area with significant differences in spectrum shape (c).

Table 1: Isomer shift δ (with reference to the source and not corrected for second order Doppler shift), V_{zz} component of the EFG tensor, and asymmetry parameter η for the compounds $BaNiO_2$ and $(As(C_6H_5)_4)_2[Ni('^{bu}S_2')_2]$ assuming ratios of the nuclear quadrupole moments within the error margin, the variation of source parameters is included in the parameter errors.

	$Q_g/Q_e = -0.47$	$Q_g/Q_e = -0.54$	$Q_g/Q_e = -0.42$
$BaNiO_2$			
$\delta(10^{-3}\mathrm{mm\,s^{-1}})$	$-32.0(-10/8)$	$-31.0(-10/8)$	$-33.0(-9/8)$
$V_{zz}(10^{21}\mathrm{V\,m^{-2}})$	-11.4 ± 0.2	$-13.5(-0.4/0.3)$	$-9.52(-0.19/0.22)$
η	$0.50(-0.15/0.10)$	$0.46(-0.21/0.11)$	$0.53(-0.13/0.09)$
$(As(C_6H_5)_4)_2[Ni('^{bu}S_2')_2]$			
$\delta(10^{-3}\mathrm{mm\,s^{-1}})$	$-29.0(-8/5)$	$-39.0(-9/8)$	$-30.0(-7/5)$
$V_{zz}(10^{21}\mathrm{V\,m^{-2}})$	$-12.28(-0.19/0.15)$	$-14.68(-0.23/0.21)$	$-10.26(-0.14/0.12)$
η	$0.37(-0.16/0.09)$	$0.23(-0.23/0.16)$	$0.42(-0.11/0.07)$