The Nuclear Quadrupole Interaction of $^{187}W(\beta^-)^{187}Re$ in W(VI)-EDTA Complexes

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The nuclear quadrupole interaction of $^{187}W(\beta^-)^{187}Re$ in W(VI)-EDTA complexes at room temperature was determined by time differential perturbed angular correlations (TDPAC) to be $\nu_Q = 1270(8)$ MHz with an asymmetry parameter $\eta = 0.403(4)$. While the coordination geometry of the Mo(VI)-EDTA complex is known, there appears to be none for the W-analogue. The rather similar asymmetry parameters for the $^{187}W(\beta^-)^{187}Re$ in W(VI)-EDTA complex and for the $^{99}Mo(\beta^-)^{99}Tc$ in Mo(VI)-EDTA complex, determined previously, supports the idea that the coordination geometries in the Mo- and W-complexes are similar.

Key words: Nuclear Quadrupole Interactions; W-Complexes.

1. Introduction

Hexavalent tungsten ions form complexes with ethylenediaminetetraacetic acid (EDTA). EDTA and its salts are widely used as supporting electrolytes. Contrary to the Mo-analogues there appears to be no proposal for the structure of the W-complexes. Based on polarographic methods, a structure has been proposed [1] and was subsequently verified [2] for the Mo(VI)-complex which for the Na-salt predicts the formula $Na_4Mo_2O_{14}H_{12}C_{10}N_2 \cdot 8H_2O$, i.e. a molar ratio of metal to EDTA of 2. Both metal sites are equivalent, and the metal is six-fold coordinated by three terminal double-bonded oxygen atoms, two carbonyl and one nitrogen atom from the EDTA (see Fig. 1). This should result in a highly distorted octahedral first coordination shell, and rather large electric field gradients a the Mo-site are expected. We have previously determined the nuclear quadrupole interaction (NQI) of $^{99}Mo(\beta^-)^{99}Tc$ in the Mo(V,VI)-EDTA complexes, both in frozen solutions and in the crystalline state [3]. The observed NQI-parameters were ν_Q around 120 MHz and η around 0.45. If the W-analogue has the same coordination geometry, we should expect a high NQI-frequency and a similar asymmetry parameter. A first guess about ν_Q could be obtained by comparing ^{99}Mo- and ^{187}W-results for the Mo- and W-disulfides: for ^{99}Mo in MoS_2 in the form of bulk powder we observed $\nu_Q = 118$ MHz [4], and for ^{187}W in a WS_2 single crystal we observed $\nu_Q = 1083$ MHz [5] (both with axial symmetry). With the ratio $\nu_Q(W)/\nu_Q(Mo) = 9.18$ we expect an NQI-frequency for the W(VI)-EDTA complex of about 1100 MHz, an accessible frequency range for ^{187}W-TDPAC spectroscopy.

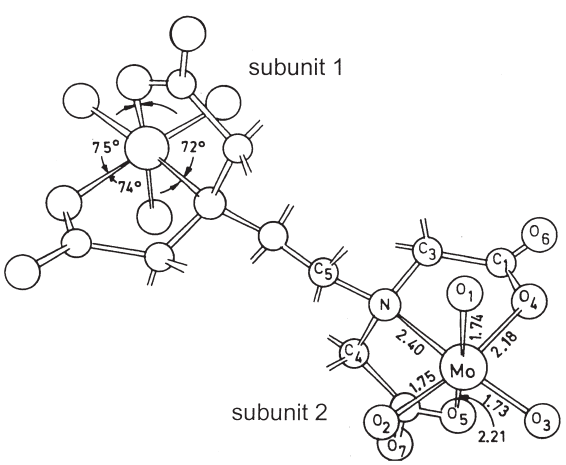

Fig. 1. Perspective view of the Mo(VI)-EDTA anion after [2].

2. Experimental

W(VI)-EDTA complexes were formed by mixing dissolved neutron activated ammonium-paratungstate with EDTA adjusting the pH to 6. The resulting solution was evaporated and ethanol was added until turbidity appeared. A white precipitate was formed in an ice-bath. These samples were used for room temperature TDPAC-measurements on the 24 h-halflife nuclide ^{187}W using the longlived $I = 9/2$ isomeric state. Several samples were prepared, and a total of 1.5 billion coincidence counts had to be collected in order to obtain a reasonable signal-to-noise ratio.

We used a high-efficiency 6-detector TDPAC-camera equipped with BaF_2-scintillators because spectral components at rather high frequencies were expected. The time resolution was about 1.5 ns at the γ-energies of 480 keV/72 keV. The time-spectra were cosine-transformed and then analyzed by a cross-correlation analysis [6]. Finally, a non-linear least-squares fit was performed with start parameters deduced from the cross-correlation analysis.

3. Results

The time spectrum for $^{187}W(\beta^-)^{187}Re$ in W(VI)-EDTA is shown in Figure 2. Oscillations are visible only for the first 100 ns, i.e. they were severely damped. Despite the time resolution of 1.5 ns, the first 5 ns are corrupted by a strong prompt contribution. In addition, roughly 50% of the expected anisotropy of about $A_{22} = -2\%$ is lost within the first 10 ns, indicating that under the preparation conditions described above a substantial fraction of ^{187}W is in a rather ill-defined environment leading to a very broad distribution of electric field gradients.

The cosine-transformed TDPAC spectra (see Fig. 3) revealed a prominent peak at $\omega = 635(4)$ Mrad/s and no spectral intensity below this peak. Since this peak is also the strongest spectral component, an asymmetry parameter close to the "magic" asymmetry parameter of about 0.39, where the lowest two lines of the $I = 9/2$ spectrum happen to coincide [7, 8], is expected. The cross-correlation analysis shows indeed (see Fig. 4) that the prominent peak consists of two nearly overlapping lines close to the

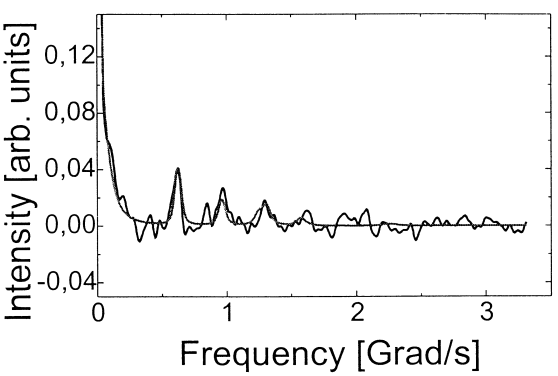

Fig. 3. Cosine-transform of the TDPAC time spectrum for $^{187}W(\beta^-)^{187}Re$ in W(VI)-EDTA. The noisy line represents the data, the smooth line the fitted theoretical function.

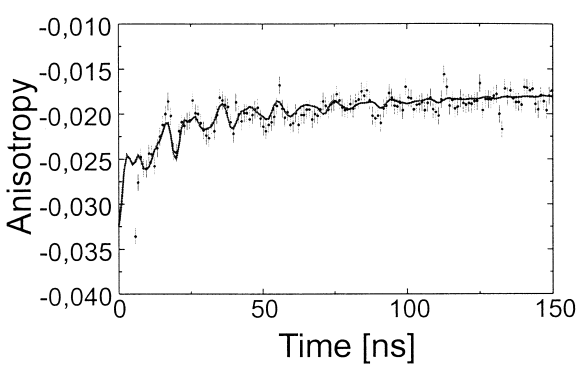

Fig. 2. TDPAC time spectrum for $^{187}W(\beta^-)^{187}Re$ in W(VI)-EDTA at room temperature. The solid line is the result of a least squares fit to the data points.

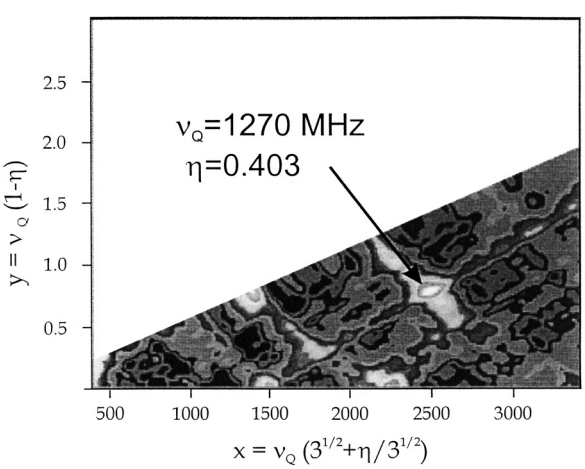

Fig. 4. Cross-correlation map of the spectrum of Figure 3. A single prominent spot is visible (arrow) which indicates a unique W-site.

"magic" asymmetry parameter of 0.403(4). There is a single high-intensity spot on the cross-correlation map. Hence, the data could be analyzed assuming a single W-site, in agreement with the proposed structure. This yields a quadrupole frequency of $\nu_Q = 1270(8)$ MHz.

4. Discussion and Outlook

The observed frequency ω and its harmonics are by far the highest observed, thus far for any ^{187}W nuclear quadrupole interaction. First, the observation of one equivalent W-site only is in agreement with the proposed structure. Secondly, both the strength and the large asymmetry parameter for the electric field gradient are also consistent with the proposed coordination for the following reasons: The asymmetry parameter $\eta = 0.403(4)$ obtained in the present study compares well with that obtained for the Mo-analogue of η around 0.45. Moreover, the ratio of the observed NQI-frequencies is 10.8, very close to the expected ratio of 9.2 (with an uncertainty of about 10%) based on the comparison of data on the Mo/W-disulfides (see introduction). This high ratio is not unexpected when comparing nuclear quadrupole moments: estimated $Q_{5/2}(^{99}Mo) = 0.3b$, $Q_{9/2}(^{187}W) = 3.04(5)b$ [7]. Of course, the difference in the averaged radial wave functions for the electrons of the two elements $\langle r^{-3} \rangle$ also plays an important role.

A line-broadening of $\Delta\omega/\omega = 1.6(5)\%$ was observed, which limits the observation of oscillations in the time spectrum to about 200 ns (the halflife of the $I = 9/2$ state is 555 ns, and for undamped oscillations the time window for observation would be about 7 halflifes, i.e. about 4000 ns). The line-broadening is not unexpected because of the lower stability of the W-EDTA complexes compared to their Mo-analogues [9].

At present we cannot unambiguously identify the reason for the fact that roughly 50% of the expected anisotropy are lost within the first 20 ns. There are two possible reasons: first, the preparation conditions could have been far from ideal, and apart from the desired EDTA-complex other unspecific W-complexes were formed which could result in a rather broad distribution of electric field gradients; secondly, the recoil energy of the β-decay and/or of the 480 keV γ-emission could have been sufficient to break a nearest neighbour chemical bond which is not reformed immediately. Considering the fact that EDTA is a strong chelator, the latter possibility appears less likely.

It would be interesting to extend these studies to W(V)-EDTA complexes because different and conflicting structures were proposed for the Mo- and the W-complex: for Mo(V)-EDTA the same as for Mo(VI)-EDTA, but two terminal oxygens instead of three [1]; for W(V)-EDTA a structure was reported [10] in which each W is surrounded in a slightly distorted plane of four oxygens, two of which are shared in a dioxo-bridge, the other ligands being a distant nitrogen and a terminal oxygen. The W–W-distance is sufficiently short to allow for direct metal–metal interactions. We propose the same structure for the Mo(V)-EDTA complex. The ^{99}Mo(V)-EDTA nuclear quadrupole frequencies were by about a factor of 2.55 higher than those for ^{99}Mo(VI)-EDTA [3], and it would be interesting to see the same ratio for W(V)/W(VI). However, due to the expected ultrahigh frequencies there is little hope that TDPAC-experiments with ^{187}W(V)-EDTA will be feasible.

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