

**A Model for Describing Paramagnetic Mössbauer Relaxation Spectra of Organometallic <sup>237</sup>Np Compounds**

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As shown first by Karraker [1], organometallic compounds of <sup>237</sup>Np yield Mössbauer spectra which are difficult to interpret. The magnetic behaviour of the compounds is paramagnetic down to 1.5 K. The resonance lines are strongly broadened by spin relaxation effects in the intermediate frequency range, where the use of any perturbation treatment of the relaxation theory is not allowed. A model was developed to fit the paramagnetic Mössbauer relaxation spectra. Anisotropic hyperfine coupling parameters and relaxation frequencies had to be introduced to find a satisfactory approximation to the spectra.

**Theory**

The theoretical treatment of the line shape of Mössbauer spectra in the presence of relaxation effects was worked out by many authors [2-6]. In the special case of organometallic <sup>237</sup>Np spectra, the hyperfine Hamiltonian, which splits the nuclear levels, is assumed to consist of an anisotropic paramagnetic hyperfine coupling term and an electric quadrupolar interaction term with an asymmetry parameter  $\eta \neq 0$ . Both tensor interactions need not coincide in their principle axes. The static hyperfine Hamiltonian has the form

$$\hat{H}_0 = \sum_{i=x,y,z} \hat{A}_i \hat{S}_i \hat{I}_i + \frac{eQV_z z'}{4I(2I-1)} \times (3\hat{I}_z^2 - \hat{I}^2 + \eta'(\hat{I}_x^2 - \hat{I}_y^2))$$

with  $I = 5/2$  in the excited and the ground nuclear state and  $S = 1/2$ , describing an isolated Kramers doublet. The coordinate system  $x'y'z'$  is transformed into the system  $xyz$  by the three Euler angles  $\alpha\beta\gamma$ . The possible transition energies and the intensities are given by the eigenvalues and the matrix of eigenvectors of the associated Liouville operator  $H_0^x$ . It is calculated from the static hyperfine Hamiltonian by

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$$\langle \mu m \nu n | \hat{H}_0^x | \mu' m' \nu' n' \rangle = \delta_{\nu\nu'} \delta_{nn'} \langle \mu m | \hat{H}_0 | \mu' m' \rangle - \delta_{\mu\mu'} \delta_{mm'} \times \langle \nu' n' | \hat{H}_0 | \nu n \rangle$$

Here  $|\mu m\rangle$  is a coupled electric-nuclear state.

The relaxation behaviour is assumed to be anisotropic, but independent of the hyperfine transition energies ('white noise approximation' [7]). Under these conditions the most general relaxation supermatrix is

$$\langle \mu m \nu n | \hat{R} | \mu' m' \nu' n' \rangle = \delta_{mm'} \delta_{nn'} \{ \delta_{\mu\mu'} \delta_{\nu\nu'} [W_z(2\langle \nu | \hat{S}_z | \nu' \rangle) \times \langle \mu' | \hat{S}_z | \mu \rangle - \frac{1}{2}] - \frac{1}{2}(W_x + W_y) + \frac{1}{2}(W_x + W_y)(\langle \nu | \hat{S}_+ | \nu' \rangle \langle \mu' | \hat{S}_- | \mu \rangle + \langle \nu | \hat{S}_- | \nu' \rangle \times \langle \mu' | \hat{S}_+ | \mu \rangle) + \frac{1}{2}(W_x - W_y)(\langle \nu | \hat{S}_+ | \nu' \rangle \times \langle \mu' | \hat{S}_+ | \mu \rangle + \langle \nu | \hat{S}_- | \nu' \rangle \times \langle \mu' | \hat{S}_- | \mu \rangle) \}$$

$W_z$ ,  $W_x$  and  $W_y$  are the anisotropic relaxation frequencies which describe the coupling of the electric-nuclear system to the time-dependent magnetic fields induced by neighbouring fluctuating spins.

With the terms explained above, the Mössbauer line shape is given by

$$I(\omega) = Re \{ \sum_m \hat{M}_{Lm}^+ \hat{U}(p)^{-1} \hat{M}_{Lm} \}$$

where  $M_{Lm}$  is a multipole operator describing the intensity distribution of the emitted or absorbed radiation of multipolarity  $L$  and polarization  $m$ , and  $\hat{U}(p)^{-1}$  is the inverse of the superoperator  $\hat{U}(p) = p\hat{1} - i/\hbar \cdot \hat{H}_0^x - \hat{R}$  where  $p = \Gamma/2 - i\omega$  with  $\Gamma$  as the natural linewidth.

The white noise approximation was not dropped, because in this case the frequency of the radiation occurs in the mean diagonal of the matrix  $\hat{U}(p)$  only. By diagonalizing the matrix  $\hat{U}(p) + i\omega$  the numerical solution of the problem can be simplified. If  $\hat{\lambda}$  is the diagonalized form of the matrix  $\hat{U}(p) + i\omega$  and  $\hat{V}$  is the matrix containing the eigenvectors, the spectrum is given by [6]

$$I(\omega) = Re \{ \sum_m (\hat{M}_{Lm}^+ \hat{V})(\hat{\lambda} - i\omega)^{-1} (\hat{V}^{-1} \cdot \hat{M}_{Lm}) \}$$

The calculation of a spectrum with 512 points needs about 8 s on the Siemens 7890 computer. Without the diagonalization the computing time for a least-squares fit is intolerably long (25 min for simulating one spectrum).

TABLE I. Evaluated Parameters for the Spectra of  $\text{Np}(\text{C}_5\text{H}_5)_4$ ,  $(\text{Np}(\text{C}_5\text{H}_5)_3)_2\text{C}_2$  and  $[(\text{C}_5\text{H}_5)_3\text{Np}(\text{NCCH}_3)_2]^+[\text{AlCl}_4]^-$ 

	$A_z$ (mm/s)	$A_x$ (mm/s)	$A_y$ (mm/s)	$eQV_{zz}$ (mm/s)	$\alpha$ (°)	$\beta$ (°)	$\gamma$ (°)	$\eta$	$W_z$ (MHz)	$W_x$ (MHz)	$W_y$ (MHz)	$\delta^a$ (mm/s)
$\text{Np}(\text{C}_5\text{H}_5)_4$	71.9	71.9	66.9	15.9	-164	-13	-101	0.90	235	222	224	31.75
$(\text{Np}(\text{C}_5\text{H}_5)_3)_2\text{C}_2$	1.11	0.39	-0.26	66.61	-210	-49	-90	0.005	0	13.3	2.1	20.04
$[(\text{C}_5\text{H}_5)_3\text{Np}(\text{NCCH}_3)_2]^+[\text{AlCl}_4]^-$	98.5	72.7	-32.7	75.4	192	35	25	0.91	0	0	1036	26.72

<sup>a</sup>The isomeric shift  $\delta$  is given versus Am metal.

## Experimental

The spectra of  $^{237}\text{Np}$  bound in the compounds having the general formula  $\text{Np}(\text{C}_5\text{H}_5)_3\text{X}$  with  $\text{X}^- =$  halide, pseudohalide or alkyl were taken in standard transmission geometry. The source was  $^{241}\text{Am}$  metal, which was kept at 4.2 K or below. The absorbers were encapsulated in aluminium and brought into a helium bath. With a heating coil the temperature of the absorbers could be varied between 1.5 K and 40 K. The transmitting radiation was detected by a lead-loaded plastic scintillator. The spectra were fitted by introducing the parameters  $A_z$ ,  $A_x$ ,  $A_y$ ,  $eQV_{zz}$ ,  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\eta$ ,  $W_z$ ,  $W_x$ ,  $W_y$ , the natural line width  $\Gamma$  and the isomeric shift  $\delta$ .

## Results and Discussion

Three compounds are chosen to demonstrate how the individual parameters typically influence the spectra.

### (a) $\text{Np}(\text{C}_5\text{H}_5)_4$

From crystallographic data of the isostructural  $\text{U}(\text{C}_5\text{H}_5)_4$  [8] the molecular symmetry is known to be  $S_4$ . Therefore the Mössbauer spectra are expected to deviate from those expected for isotropic hyperfine interaction produced by a cubic environment. Indeed the best fit of the spectra yields the anisotropic parameters given in Table I. The spectrum is shown in Fig. 1 together with the fit (solid line). The dashed line is an approximation to the spectrum with the assumption of an ideal isotropic hyperfine interaction, *i.e.* with  $A_z = A_x = A_y = 70.2$  mm/s,  $eQV_{zz} =$

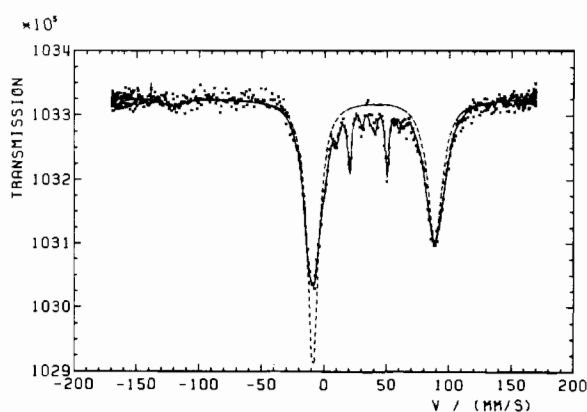


Fig. 1. Mössbauer spectrum of  $\text{Np}(\text{C}_5\text{H}_5)_4$  with two unidentified impurities (narrow lines with low intensities). The solid line shows the best fit assuming anisotropic behaviour. It takes into consideration two additional quadrupole spectra to describe the superposed spectrum. The dashed line is a simulation of isotropic hyperfine coupling without considering the impurities.

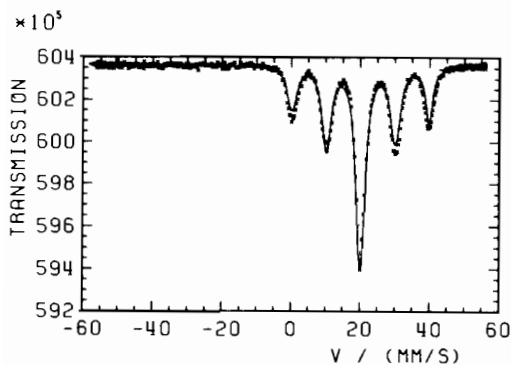


Fig. 2. Spectrum of  $(\text{Np}(\text{C}_5\text{H}_5)_3)_2\text{C}_2$ .

0 and  $W_z = W_x = W_y = 225$  MHz. Point-lattice calculations show that the measured electric field gradient can be reproduced, if an orthorhombic distortion is assumed, which turns the cyclopentadienyl rings out of their cubic position by approximately  $3^\circ$ .

(b)  $(\text{Np}(\text{C}_5\text{H}_5)_3)_2\text{C}_2$

Within the compound  $(\text{Np}(\text{C}_5\text{H}_5)_3)_2\text{C}_2$  the Np ions are only separated by a small distance. The magnetic moment of the compound decreases strongly with decreasing temperature and is nearly zero at  $T = 0$  K [9]. The Mössbauer spectrum reveals a distorted quadrupole splitting (Fig. 2). It can be reproduced by a small magnetic coupling together with the quadrupole interaction in the slow relaxation limit. This means that the density of unpaired spins is close to zero at the sites of the Np nuclei. The fitting parameters are given in Table I.

(c)  $[(\text{C}_5\text{H}_5)_3\text{Np}(\text{NCCH}_3)_2]^+[\text{AlCl}_4]^-$

The parameters fitting the spectrum are given in Table I. They are highly anisotropic in the hyperfine coupling tensor, the electric field gradient and the relaxation frequencies, which seems to be typical for the assumed  $D_{3h}$  symmetry of the molecule. Figure 3 shows the spectrum together with the fit (solid line) and a simulation with isotropic relaxation (dashed line).

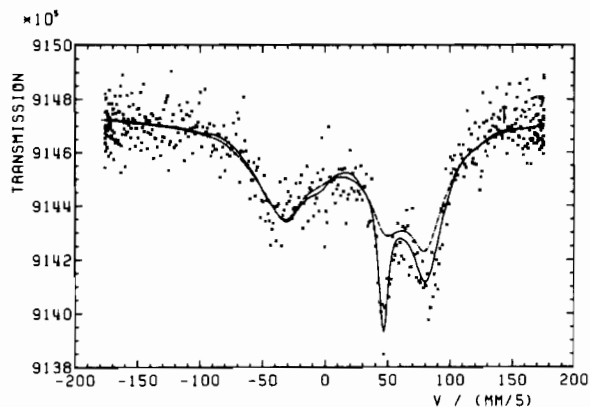


Fig. 3. Spectrum of  $[(\text{C}_5\text{H}_5)_3\text{Np}(\text{NCCH}_3)_2]^+[\text{AlCl}_4]^-$  with the best fit (solid line) and a simulation with isotropic relaxation frequencies (dashed line).

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### References

- 1 D. G. Karkaker, in T. J. Marks and R. D. Fischer (eds.), 'Organometallics of the f-Elements', Reidel, Dordrecht, 1979, p. 395.
- 2 J. Sivadriere, M. Blume and M. J. Clausser, *Hyp. Int.*, **1**, 227 (1975).
- 3 M. J. Clausser and M. Blume, *Phys. Rev. B*, **3**, 583 (1971).
- 4 F. Gonzales-Jimenez, P. Imbert and F. Hartmann-Boutron, *Phys. Rev. B*, **9**, 95 (1974).
- 5 G. K. Shenoy and B. D. Dunlap, *Phys. Rev. B*, **13**, 3709 (1976).
- 6 G. K. Shenoy and B. D. Dunlap, *Phys. Rev. B*, **13**, 1353 (1976).
- 7 G. K. Shenoy, B. D. Dunlap, S. Dattagupta and L. Asch, *Phys. Rev. Lett.*, **37**, 539 (1976).
- 8 J. H. Burns, *J. Organomet. Chem.*, **69**, 225 (1974).
- 9 R. Bohlander, *Thesis*, KfK Report No. 4152, Karlsruhe, 1986.