

Powder Zeeman NQR Study on ^{123}Sb in $\text{Sb}(\text{C}_6\text{H}_5)_3$

O. Ege, S. Maekawa, H. Akiyama, and H. Negita

Department of Physics, Faculty of Education and Culture, Miyazaki University,
Gakuen-kibanadai, Miyazaki 889-2192, Japan

Reprint requests to Prof. O. E.; Fax: 81-985-58-2892, E-mail: o.ege@cc.miyazaki-u.ac.jp

Z. Naturforsch. **57 a**, 304–306 (2002); received January 23, 2002

Presented at the XVth International Symposium on Nuclear Quadrupole Interactions,
Hiroshima, Japan, September 9-14, 2001.

Powder Zeeman NQR spectra of ^{123}Sb in $\text{Sb}(\text{C}_6\text{H}_5)_3$ were studied by means of a computer simulation and an experiment. The ^{123}Sb nucleus has spin $7/2$. There are two non-equivalent ^{123}Sb atoms in the crystal of $\text{Sb}(\text{C}_6\text{H}_5)_3$, so that there are two series of three transition lines (higher series: $\nu_{1h}, \nu_{2h}, \nu_{3h}$; lower series: $\nu_{1l}, \nu_{2l}, \nu_{3l}$). The powder Zeeman spectra for ν_{1h} , based on the transition between the levels $m_1 = \pm 1/2$ and $\pm 3/2$, were observed at 77 K under the two conditions that i) the oscillation coil and the static magnetic coil were set coaxially and parallel, and ii) they were set perpendicular to each other. The powder line shapes for ν_{1h} , which is the lowest line of the higher series due to ^{123}Sb nuclei, were in good agreement with those from a computer simulation under the conditions i) and ii), showing that the asymmetry parameter of the field gradient is very small ($\eta = 0$). The line shape from i) exhibits two shoulders (saddle type), as it appeared for nuclear spin $5/2$ and $\eta = 0$.

The quadrupole coupling constant for ν_{1h} , calculated from the resonance frequency 47.820 MHz and the observed η , is 669.480 MHz at 77 K.

Key words: NQR; Nuclear Quadrupole Resonance; Zeeman Effect; Powder Zeeman NQR; Spin $7/2$.

1. Introduction

Zeeman effects in NQR spectra of powders (PZNQR) were mainly studied for nuclear spin $3/2$ to investigate the asymmetry parameters of the electric field gradient (η) at nuclear sites [1 - 9]. These methods had sometimes difficulties in exactitude but were useful when single crystals of the specimens were not available. Our studies concerned nuclear spins of $3/2$ and $5/2$ [10 - 15].

In the present paper we report a spin $7/2$ PZNQR study of ^{123}Sb nuclei in $\text{Sb}(\text{C}_6\text{H}_5)_3$ by means of computer simulations and experiments. The ^{123}Sb nucleus has two NQR lines due to the basic transitions between the levels $m = \pm 1/2$ and $\pm 3/2$, as indicated by Barnes and Bray [16]. At 77 K, the lowest line ν_{1h} of the higher series, which we observed at 47.820 MHz, has about twice the intensity of the lowest line ν_{1l} of the lower series at 47.589 MHz. We observed the PZNQR absorption curves for ν_{1h} and could estimate the EFG, but could not get a clear enough curve to estimate η for ν_{1l} .

2. Experiment and Simulation

The NQR signals were detected in integral form, using a super-regenerative oscillator and a bridge circuit, their S/N ratio being improved with a signal averaging device. The PZNQR spectra were observed in two situations: i) with the oscillator coil producing H_r (the radio frequency field) and the Helmholtz coil for H_o (static magnetic field) set coaxially ($H_r \parallel H_o$), and ii) with the two set perpendicular to each other ($H_r \perp H_o$).

The computer simulations of the transition probability were carried out with the method of Toyama [1] and Brooker [5].

The PZNQR energies and the eigenfunctions for the nuclear spin components of $m = (\pm \frac{7}{2}, \pm \frac{5}{2}, \pm \frac{3}{2}, \pm \frac{1}{2})$ are written as

$$E_Q + E_M = E_m \pm \left(I_{zm,m}^2 H_z^2 + I_{xm,-m}^2 H_x^2 + I_{ym,-m}^2 H_y^2 \right)^{1/2}, \quad (1)$$

$$\begin{aligned}\xi_m &= a_m \Psi_m + b_m \Psi_{-m}, \\ \xi_{-m} &= a_{-m} \Psi_m + b_{-m} \Psi_{-m},\end{aligned}\quad (2)$$

where E_Q and E_M are the pure NQR energy and the Zeeman energy representing reduced frequencies, respectively. Ψ_m and Ψ_{-m} are the state functions composed of spherical harmonics and coefficients including η . Other notations are according to those of Toyama and Brooker.

The transition probability of a PZNQR spectrum is calculated from the equation

$$T_{kl} = \sum_{i,j=x,y,z} H_{r_i} H_{r_j} J_{ij}(E_k, E_l), \quad (3)$$

where T_{kl} are the relative transition probabilities, H_{r_i} and H_{r_j} ($i, j = x, y, z$) are the radio frequency field components, and $J_{ij}(E_k, E_l)$ are the intensity parameters

$$J_{ij} = \frac{1}{2} [\langle \xi_k | \hat{I}_i | \xi_l \rangle \langle \xi_l | \hat{I}_j | \xi_k \rangle + \langle \xi_l | \hat{I}_i | \xi_k \rangle \langle \xi_k | \hat{I}_j | \xi_l \rangle], \quad (4)$$

represented in terms of the matrix elements: $\langle \xi_k | \hat{I}_i | \xi_l \rangle$, $\langle \xi_l | \hat{I}_j | \xi_k \rangle$, and so forth.

3. Result and Discussion

In the case of nuclear spin $7/2$ and the condition $\text{Hr} \parallel \text{Ho}$, the simulation curve of the PZNQR absorption line for $\eta = 0$ and the observed absorption curve for the lowest line ν_{1h} of the higher series due to ^{123}Sb nuclei are shown in Figs 1 and 2, respectively. In the vertical and horizontal directions the absorption intensities and reduced frequencies, respectively, are given in arbitrary units. G denotes the magnetic field strength (Gauss).

Both forms, exhibiting two symmetrical shoulders like a saddle, agree well with each other, so that η is estimated to be very small. They are also similar to the case of spin $5/2$.

Although implying less information for η , under the condition of $\text{Hr} \perp \text{Ho}$ the simulation curve and the observed curve for the ν_{1h} are shown in Figs. 3 and 4, respectively, for reference. They also are of the saddle-type but have broad mounds in the middle of the curves.

Under the condition $\text{Hr} \parallel \text{Ho}$, the observed curve for the ν_{1l} , which is the lowest line of the lower series due to ^{123}Sb nuclei, is exhibited in Figure 5.

Table 1. NQR constants for ν_{1h} of ^{123}Sb in $\text{Sb}(\text{C}_6\text{H}_5)_3$ at 77 K.

Compound	Nucleus	Frequency (MHz)	η	$e^2 Q q h^{-1}$ (MHz)
$\text{Sb}(\text{C}_6\text{H}_5)_3$	^{123}Sb	47.820	very small	669.480

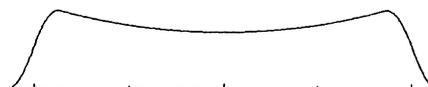


Fig. 1. PZNQR absorption curve simulated for $\eta = 0$ ($\text{Hr} \parallel \text{Ho}$).

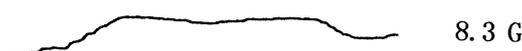


Fig. 2. PZNQR absorption curve observed for ν_1 of ^{123}Sb in $\text{Sb}(\text{C}_6\text{H}_5)_3$ ($\text{Hr} \parallel \text{Ho}$).

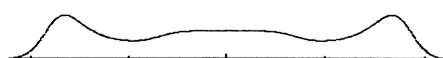


Fig. 3. PZNQR absorption curve simulated for $\eta = 0$ ($\text{Hr} \perp \text{Ho}$).

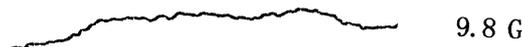


Fig. 4. PZNQR absorption curve observed for ν_1 of ^{123}Sb in $\text{Sb}(\text{C}_6\text{H}_5)_3$ ($\text{Hr} \perp \text{Ho}$).



Fig. 5. PZNQR absorption curve observed for ν_2 of ^{123}Sb in $\text{Sb}(\text{C}_6\text{H}_5)_3$ ($\text{Hr} \parallel \text{Ho}$).

Although its η could not be estimated from the noisy curve due to its small intensity, it might be seen that the curve has two dips on the shoulders, and so η was not very small.

In the case of spin $7/2$, when $\eta \neq 0$, the computer simulation shows that two symmetrical dips appear near the shoulders, as it is seen for spin $3/2$ and $5/2$. It is known that the dips become largest at $\eta = 0.185$.

The quadrupole coupling constant, calculated with the resonance frequency of 47.820 MHz and the obtained η , is 669.480 MHz.

The NQR constants for ν_{1h} of ^{123}Sb in $\text{Sb}(\text{C}_6\text{H}_5)_3$ are shown in Table 1.

It is considered that there are two non-equivalent molecules in a unit cell of $\text{Sb}(\text{C}_6\text{H}_5)_3$ crystal.

Although η values can only be obtained from NQR frequencies except for the nuclear spin of $3/2$, the PZNQR measurement is useful for two reasons: i) the

frequency range for research is relatively low and not wide, and ii) the assignment of the lines to the non-equivalent nuclei is not necessary.

- [1] M. Toyama, J. Phys. Soc. Japan **14**, 1727 (1959).
- [2] Y. Morino and M. Toyama, J. Chem. Phys. **35**, 1289 (1961).
- [3] J. D. Graybeal and P. J. Green, J. Phys. Chem. **73**, 2948 (1969).
- [4] J. Darville, A. Gerard, and M. T. Calende, J. Magn. Reson. **16**, 205 (1974).
- [5] H. R. Brooker and R. B. Creel, J. Chem. Phys. **61**, 3658 (1974).
- [6] R. B. Creel and E. D. von Meerwall, J. Magn. Reson. **20**, 328 (1975).
- [7] G. M. Muha, J. Magn. Reson. **53**, 85 (1983).
- [8] P. J. Bryant and S. Hacobian, Z. Naturforsch. **41a**, 141 (1986).
- [9] T. Varty, R. J. C. Brown, and F. P. Temme, Z. Naturforsch. **45a**, 550 (1986).
- [10] O. Ege, J. Sci. Hiroshima Univ. A **46**, 21 (1982).
- [11] O. Ege and H. Negita, Z. Naturforsch. **45a**, 141 (1986).
- [12] O. Ege and H. Negita, Mem. Fac. Educ. Miyazaki Univ., Nat. Sci. **63/67**, 1 (1990).
- [13] O. Ege, S. Hamai, and H. Negita, Z. Naturforsch. **47a**, 401 (1992).
- [14] O. Ege, S. Hamai, and H. Negita, J. Mol. Struct. **345**, 139 (1995).
- [15] O. Ege, S. Nishijima, E. Kimura, H. Akiyama, S. Hamai, and H. Negita, Z. Naturforsch. **53a**, 314 (1998).
- [16] R. G. Barnes and P. J. Bray, J. Chem. Phys. **23**, 1177 (1955).