^{81}Br Nuclear Quadrupole Resonance of Modifications of Titanium Tetrabromide

Tsutomu Okuda, Yoshihiro Furukawa, and Hisao Negita
Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima

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^{81}Br NQR of titanium tetrabromide has been observed at temperatures between −196°C and 35.5°C, and its Zeeman effect has been measured at room temperature. The cubic form of titanium tetrabromide shows two resonance lines, as has been reported previously; their temperature coefficients change from positive to negative when the temperature is raised. The bond angles, ∠Br–Ti–Br, are in the range of 108.7° to 110.3°. The asymmetry parameters are 2.0 and 2.5%. On the other hand, the monoclinic form shows four resonance lines; 39.175, 39.184, 39.454, and 39.800 MHz at 11°C. The temperature coefficient of the lowest line is positive at the lower temperature, whereas those of the remainder are negative. The bond angles, ∠Br–Ti–Br, are found in the range of 108.8° to 110.1°. The asymmetry parameters are 1.2, 4.6, 2.1, and 3.5% for the bromine atoms in the order of increasing resonance frequencies. The ionic and double-bond characteristics of the Ti–Br bond in both forms are about 60 and 16%. These findings suggest that, in titanium tetrabromide, the crystal field has little effect on the molecular shape, the bond character, and the asymmetry parameter.

It had been known for a long time that titanium tetrabromide has several modifications and that one of them is a cubic form isomorphous with stannic tetraiodide.1) Later, the presence of at least three modifications (Form 1, Form 2, and Form 3) was reported by Sackman *et al.*2) They found that Form 1, which is a cubic form and which is usually obtained by the solidification of the melt, is transformed into Form 2 over a period of several days at room temperature, and that Form 3, which is prepared on cooling the molten substance rapidly, is transformed into Form 1 at −5°C. Recently, the crystal structure of Form 2 has been determined by means of the X-ray analysis by Brand and Schmidt.3) They found that it is monoclinic and isomorphous with α-stannic tetrabromide. The crystal structure of the remainder has not yet been established. The NQR of Form 1 has been reported by Barnes and Engardt.4) They found two resonance lines and the positive coefficient of the temperature dependence for the stronger resonance line, while the Zeeman effect on NQR has not yet been observed. In the present experiment, the reasonance frequencies of Form 2 were determined for the first time, and the temperature dependence and the Zeeman effect in both modifications were observed, in order to discuss the nature of the Ti–Br bonds and the molecular structures.

Experimental

Form 1 was obtained on the distillation of commercial titanium tetrabromide (Wako Pure Chem. Ind., Ltd.), while Form 2 was obtained by cooling Form 1 melted at a temperature above 100°C. The single crystals of these substances were prepared by the Bridgeman-Stockbarger method. The spectrometer used in the present experiment was a super-regenerative oscillator, and the absorption lines were observed on an oscilloscope. The magnetic field used for the Zeeman study was provided by the Helmholtz coil5) with a field strength of about 200 gauss.

Results

The resonance frequencies of ^{81}Br in Form 1 were measured between −196°C and 35.5°C. Only two resonance lines (designated as ν_1 and ν_2) were observed in the whole temperature range studied. The temperature dependence of ν_2 was in good agreement with finding by Barnes and Engardt.4) The resonance frequencies observed at room temperature are listed in Table 1, and the temperature dependence is shown in Fig. 1. The resonance frequencies of both ν_1 and ν_2 increase and then decrease through

Table 1. ^{81}Br nuclear quadrupole resonance frequencies in titanium tetrabromide

Compound		Resonance frequency, MHz	
		20°C	−196°C
Form 1	ν_1	38.701	38.685
	ν_2	39.370	39.366
Form 2	ν_1'	39.162	39.209
	ν_2'	39.162	39.322
	ν_3'	39.428	39.641
	ν_4'	39.770	40.094

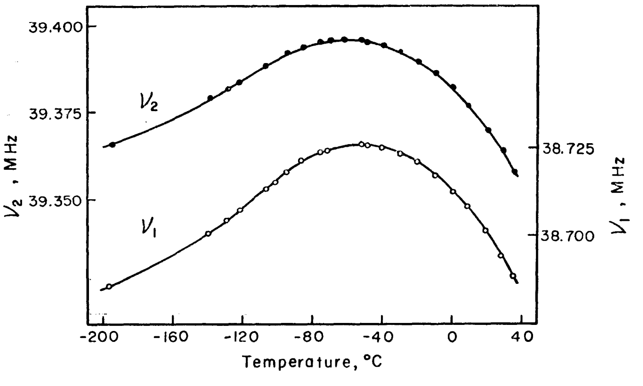

Fig. 1. Temperature dependence of ^{81}Br nuclear quadrupole resonance frequencies in Form 1.

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1) O. Hassel and H. Kringstad, *Z. Physik. Chem.*, **B15**, 274 (1932).

2) H. Sackman, D. Demus, and D. Pankow, *Z. anorg. allg. Chem.*, **318**, 257 (1962).

3) P. Brand and J. Schmidt, *ibid.*, **348**, 257 (1966).

4) R. G. Barnes and R. D. Engardt, *J. Chem. Phys.*, **29**, 248 (1958).

5) K. Shimomura, *J. Phys. Soc. Jap.*, **12**, 657 (1957).

TABLE 2. THE BOND ANGLES ∠Br-Ti-Br IN FORM 2

	∠Br_1-Ti-Br_2[a)]	∠Br_1-Ti-Br_3	∠Br_1-Ti-Br_4	∠Br_2-Ti-Br_3	∠Br_2-Ti-Br_4	∠Br_3-Ti-Br_4
NQR	110.09°	109.26°	1.9.53°	109.95°	108.75°	109.74°
X-ray	110.57°	109.45°	109.27°	109.32°	111.97°	106.13°

a) The bromine atoms contributing to ν_1', ν_2', ν_3', and ν_4' are labelled as Br_1, Br_2, Br_3, and Br_4.

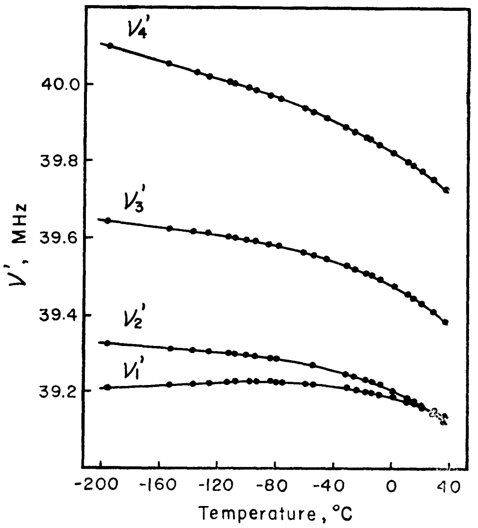

Fig. 2. Temperature dependence of ^{81}Br nuclear quadrupole resonance frequencies in Form 2.

peak at about −55°C, as the temperature rises from −196°C. The resonance frequencies of ^{81}Br in Form 2 were measured over the temperature range from −196°C to the melting point, as is shown in Fig. 2. Four resonance lines (designated as ν_1', ν_2', ν_3', and ν_4') were observed. When the temperature was lowered from room temperature to −196°C, no phase transition was observed. On the other hand, when the temperature was increased from −196°C, the resonance lines became broad around −20°C and disappeared at −15°C, while two lines with the same frequencies as those of Form 1 appeared. It is thus evident that the phase transition from Form 2 to Form 1 took place. The resonance frequencies are listed in Table 1, along with the results at the temperature of liquid nitrogen. The pattern of zerosplitting was obtained by measuring the Zeeman effect on each resonance line. Eight patterns were obtained for each of the two resonance lines, ν_1 and ν_2. Those for ν_1 are very similar to those for ν_2. The experimental results for ν_1 are shown in Fig. 3. In Form 2, two zerosplitting patterns were obtained for each of the two resonance lines, ν_3' and ν_4'. Since ν_1' and ν_2' cross each other at room temperature, it was difficult to identify four zerosplitting patterns. Accordingly, the assignment was done at 10°C, where each of the relevant lines was split into two.

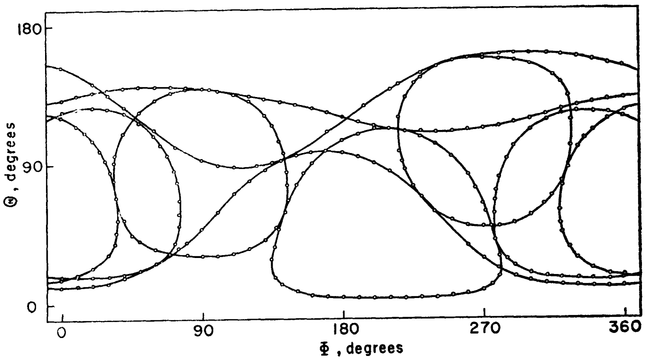

Fig. 3. Zerosplitting patterns of Zeeman lines of ν_1 in Form 1. Θ and Φ are polar and azimuthal angles, respectively, in the coordinate fixed to the sample.

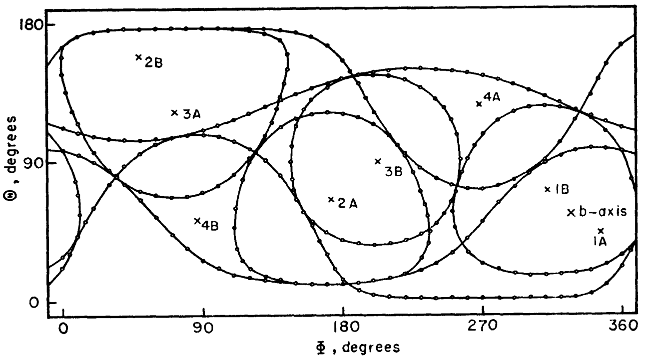

Fig. 4. Zerosplitting patterns of Zeeman lines of Form 2. Θ and Φ are polar and azimuthal angles, respectively, in the coordinate fixed to the sample.

The angles between any two Ti–Br bonds were calculated from the direction of the principal z axis of the field gradient. The bond angles, ∠Br–Ti–Br, in Form 1 are in the range of 108.8° to 110.3°; this indicates that the titanium tetrabromide molecule is nearly tetrahedral in the crystal. The results of Form 2 are listed in Table 2.

The values of the asymmetry parameter, η, were determined from the direction of the zerosplitting loci by means of the following relation:

$$\eta = 3(\sin^2\theta_{\max}-\sin^2\theta_{\min})/(\sin^2\theta_{\max}+\sin^2\theta_{\min}) \qquad (1)$$

where $\theta_{\max}$ and $\theta_{\min}$ are the maximum and minimum zerosplitting angles. Consequently, the quadrupole coupling constants may be calculated by the following equation:

$$\nu = (eQq_{zz}/2)(1+\eta^2/3)^{1/2} \qquad (2)$$

The values of η and eQq_{zz} derived in this way are listed in Table 3.

TABLE 3. QUADRUPOLE COUPLING CONSTANTS, ASYMMETRY PARAMETERS AND UNBALANCED p ELECTRONS OF ^{81}Br IN TITANIUM TETRABROMIDE AT ROOM TEMPERATURE (20°C)

Compound	ν	eQq_{zz}, MHz	η, %	Up, %
Form 1	ν_1	77.397	2.0±1.5	12.0
	ν_2	78.732	2.5±1.5	12.2
Form 2	ν_1'	78.323	1.2±1.0	12.2
	ν_2'	78.297	4.6±0.6	12.2
	ν_3'	78.850	2.1±0.3	12.3
	ν_4'	79.524	3.5±0.6	12.4

Discussion

Temperature Dependence. In Form 1, the temperature dependence of ν_1 is similar to that of ν_2 as shown in Fig. 1. The maximum of the frequency-temperature curve appeared near −55°C. The temperature coefficient of ν_1 is slightly larger than that of ν_2 below −55°C, but it is almost the same in the range above −55°C. The temperature dependence is expressed by the sum of the Bayer term and the effect of the pressure dependence.[6] As will be described later, the $d\pi$–$p\pi$ bond may be involved in the Ti–Br bond of Form 1. As the thermal vibrations increase with an increase in the temperature, the π-bond character decreases. This, in turn, causes the resonance frequency to increase. This effect is combined with that of averaging the field gradient due to the vibration, and so the absolute value of the Bayer term becomes small. Since the temperature dependence is positive at low temperatures, the effect of the pressure dependence dominates the Bayer term. In stannic tetraiodide, the absolute value of the temperature coefficient of the higher resonance line is larger than that of the remainder.[7] It was proved experimentally that the resonance line with a larger temperature coefficient came from the resonant atom in the more symmetrical position. This is also the case for Form 1.

In Form 2, the absolute value of the temperature coefficient decreases in the order of the decreasing resonance frequency, and the temperature coefficient of ν'_1 is positive below the temperature of −80°C, as is shown in Fig. 2. In many halogenides, a lower resonance line has a smaller temperature dependence. This may be interpreted in terms of an intermolecular bond, such as the Sb-Cl binding in the crystal of antimony trichloride.[8] However, in titanium tetrabromide, the intermolecular interaction between Ti and Br atoms must be weak, because the Ti atom is surrounded tetrahedrally by Br atoms. The intermolecular interaction may be caused only by the neighboring Br atoms. Since the bond length has not been reported in the results of the X-ray analysis, we calculated the bond length on the basis of the atomic parameter which was used in the calculation of the structure parameter, $|F_o|$.[3] The results were 2.43, 2.35, 2.34, and 2.31 Å. The bond contributing to ν'_1 is the longest and is parallel to the b axis, whereas that for ν'_4 is perpendicular to the b axis, as Table 4 shows. It is of interest to note that the temperature coefficient of ν'_1 is the smallest.

Quadrupole Coupling Constant and Asymmetry Parameter. The results of the X-ray analysis[1] indicate that the crystal of Form 1 is isomorphous with that of stannic tetraiodide. According to the NQR study of stannic tetraiodide by Shimomura,[9] the lower resonance line is three times as strong as the higher. This relative intensity is reversed in Form 1 and α-stannic tetrabromide.[5] There is a pair of tetrahedral molecules in the crystal of both stannic tetraiodide and α-stannic tetrabromide; six atoms face each other in the former, but only two atoms in the latter. It was revealed recently that no such atoms exist in α-stannic tetrabromide, as had been presumed by Shimomura. Therefore, a crystal structure like that of stannic tetraiodide may show an NQR spectrum of Form 1. In order to clarify this point, we calculated the field gradient due to external atoms, using a point-charge model on the basis of the X-ray analysis.[1,7] The z axis was chosen along a metal-halogen bond, while the x and y axes were in an arbitrary direction perpendicular to the z axis. The charges on the metal and halogen atoms were assumed to be $4e_x$ and $-e_x$ respectively. The scanning radius was 30 Å. The results are shown below:

$TiBr_4$

Br_1—ν_1	Br_2—ν_2
$q_{xx}=-0.2959e_{Br}$ Å^{-3}	$q_{xx}=-0.2906e_{Br}$ Å^{-3}
$q_{yy}=-0.2959e_{Br}$ Å^{-3}	$q_{yy}=-0.3157e_{Br}$ Å^{-3}
$q_{zz}=0.5918e_{Br}$ Å^{-3}	$q_{zz}=0.6063e_{Br}$ Å^{-3}

SnI_4

I_1—ν_2	I_2—ν_1
$q_{xx}=-0.2377e_I$ Å^{-3}	$q_{xx}=-0.1172e_I$ Å^{-3}
$q_{yy}=-0.2397e_I$ Å^{-3}	$q_{yy}=-0.2946e_I$ Å^{-3}
$q_{zz}=0.4774e_I$ Å^{-3}	$q_{zz}=0.4119e_I$ Å^{-3}

It is evident that the results make possible a qualitative interpretation of the differences in the NQR spectra between Form 1 and stannic tetraiodide. Taking account of Sternheimer's antishielding effect,[10] the agreement between the calculation and observed values may be improved. One of the defects of the present calculation is the fact that the x and y axes are chosen arbitrarily. Accordingly, in calculating the field gradients for Form 1, we chose x and y axes in various directions perpendicular to the z axis. The value of the field gradients at the bromine atom contributing to ν_1 did not vary. On the other hand, at the atom contributing to the other line the values of q_{xx} and q_{yy} varied slightly, while q_{zz} remained as the same. The results of the X-ray analysis for stannic tetraiodide[11] show that the intramolecular distance, I–I, is slightly larger than the intermolecular distance. On the contrary, the intramolecular distance, Br–Br, in Form 1 is smaller than the intermolecular distance. The difference in the NQR spectra may be caused by this discrepancy.

Brand and Schmidt have reported that the crystal structure of Form 2 is isomorphous with that of α-stannic tetrabromide. In fact, Form 2 shows four resonance lines, in analogy with the spectrum of α-stannic tetrabromide. The lowest resonance line in α-stannic tetrabromide is lower by about 3 MHz than the other; this is ascribed to the presence of intermolecular interaction.[5] In Form 2, however, the spacing ν'_1 and ν'_4 was about 900 kHz. If Form 2

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[6] H. S. Gutowsky and G. A. Williams, *Phys. Rev.*, **105**, 464 (1957).

[7] R. W. Ward, Thesis, Virginia Polytechnic Institute, (1968).

[8] H. Chihara, N. Nakamura, and H. Okuma, *J. Phys. Soc. Jap.*, **24**, 306 (1968).

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[10] R. Sternheimer, *Phys. Rev.*, **80**, 102 (1950).

[11] F. Meller and I. Fankushen, *Acta Crystallogr.*, **8**, 343 (1955).

has the same structure as α-stannic tetrabromide, the difference in the NQR spectrum may be caused by the contribution of the 3*d* orbital of the titanium atom to the Ti–Br bond. When the $d\pi$–$p\pi$ bond is formed, the resonance frequency becomes lower. Since the bromine-atom contribution to the ν'_1 is considered to take part in the interaction, as has been described above, the spacing of the highest and lowest resonance lines will be smaller.

As Table 3 shows, the values of the asymmetry parameters in Form 1 are small. This suggest that titanium tetrabromide is nearly tetrahedral in the solid state and that the Ti–Br bond is along the three-fold symmetry axis. The asymmetry parameter for ν_1 is similar to that for ν_2. It may be attributed to the fact that the angle of zerosplitting could not be determined definitely, since one resonance line gives rise to eight zero-splitting patterns and the lines of the Zeeman component are so weak. The asymmetry parameters in Form 2 are small because the molecule is tetrahedral, as is shown in Table 2. The difference between the asymmetry parameters of Form 1 and Form 2 is small. This suggests that the contribution to the field asymmetry from external ionic charges is so small that the molecular shape and the bond character of the Ti–Br in both crystal forms are almost unaffected.

Directions of the Ti–Br Bonds. The Zeeman measurements can determine the relative orientation of the Ti–Br bonds. Every angle between the Ti–Br bond and the crystal *b* axis in Form 1 is found to be equal to 54°44′; this value is in good agreement with that of the X-ray analysis. On the other hand, the results in Form 2 are listed in Table 4. The results of the X-ray analysis were calculated by using the atomic parameter of α-stannic tetrabromide, as has been described above. The agreement between the present results and those of the X-ray analysis is good. If the molecule in Form 2 will rotate around the axis perpendicular to the *b* axis in such a way that all the angles are the same with respect to the *b* axis, Form 2 will be transformed into Form 1. The bond angle, ∠Br–Ti–Br, is shown in Table 2. The results of the Zeeman analysis are in fairly good agreement with the results of the X-ray analysis, although the final decision should be made on the basis of a more accurate X-ray analysis.

TABLE 4. THE ANGLES BETWEEN THE CRYSTAL *b* AXIS AND THE PRINCIPAL *z* AXIS OF THE FIELD GRADIENT IN FORM 2

	Ti-Br$_1$	Ti-Br$_2$	Ti-Br$_3$	Ti-Br$_4$
NQR	19.54°	61.90°	61.63°	90.0°
X-Ray	19.40°	61.78°	61.17°	90.0°

Bond Character. Although the Ti–Br bond may be expected to be considerably ionic on the basis of the electronegativity difference between Ti and Br atoms, the observed resonance frequency is much lower than that estimated only in terms of the ionic character. Accordingly, the bond may involve a $d\pi$–$p\pi$ bond, by which the asymmetry parameter of the bromine atom is little affected. The number of unbalanced *p* electrons, *Up*, can be obtained using the following relation:[12]

$$Up = (1-s)(1-i-\pi) - \pi/2 \qquad (3)$$

where i and π are the extents of the ionic and π-bond characters respectively, and where s is the s electron character, which is assumed to be 0.15.[13] The value of *Up* is evaluated from the observed quadrupole coupling constant:

$$Up = (eQq_{zz})_{\rm obs}/(eQq_{zz})_{\rm atom} \qquad (4)$$

where $(eQq_{zz})_{\rm atom}$ is 643.0 MHz.[14] In order to obtain the extent of the π-bond character, the value of the ionic character must be estimated first. Although a number of authors have reported procedures for estimating the degree of ionic character, we made use of Gordy's relation[15] and obtained an ionic character about 60% for both Form 1 and Form 2. Next, using this value of the ionic character, the value of the π-bond character was calculated to be about 16% by means of Eq. (3). Judging from these values of the bond character, the Ti–Br bond seems to be somewhat extraordinary among the various metal-bromine bonds.

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[12] R. Ikeda, D. Nakamura, and M. Kubo, *J. Phys. Chem.*, **69**, 2101 (1965).

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