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NUCLEAR QUADRUPOLE RESONANCES OF α-$(CH_3)_2TeX_2$ (X=Cl, Br, I) AND $(CH_3)_2TeI_4$

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ABSTRACT

NQR spectra were observed for α-$(CH_3)_2TeX_2$ (X=Cl, Br, I) and $(CH_3)_2TeI_4$ at various temperatures The two ^{81}Br NQR lines were observed above 110 K in α-$(CH_3)_2TeBr_2$ The characteristic temperature dependence of the ^{127}I NQR line in α-$(CH_3)_2TeI_2$ can be explained by the 3c—4e bond of the linear I—Te—I group The positive temperature dependence of the lowest ^{127}I NQR line in $(CH_3)_2TeI_4$ is discussed on the basis of the electron population calculated from Townes—Dailey treatment.

INTRODUCTION

The X-ray structural analysis clarified that α-$(CH_3)_2TeX_2$ (X=Cl, I) molecules in the crystal are bound to each other by weak halogen bridges to form an infinite chain [1, 2] The tellurium atom is octahedrally surrounded by four halogen and two carbon atoms but the structures of α-$(CH_3)_2TeCl_2$ and α-$(CH_3)_3TeI_2$ differ because half the chlorine atoms in the former and all iodine atoms in the latter form weak intermolecular bonds. For α-$(CH_3)_2$-$TeBr_2$ the crystal structure is not yet known.

On the other hand, $(CH_3)_2TeI_4$ comprises α-$(CH_3)_2TeI_2$ and I_2 molecules [3]. The I_2 molecules are, on both sides, bound to $(CH_3)_2TeI_2$ iodine atoms and form a linear chain designated as an I_4 group. Only one iodine atom of $(CH_3)_2TeI_2$ is bound to the I_2 molecules.

In all the compounds mentioned above, the linear X—Te—X bond is considered to be formed by a 3c—4e bond [3] As the two bonds in the linear X—Te—X bond are strongly correlated, it is of interest to examine their bond character. In the present work, we tried to obtain information regarding the 3c—4e bond and intermolecular bond from the NQR spectra.

For α-$(CH_3)_2TeCl_2$, Kondo et al. [4] have already reported two ^{35}Cl NQR lines at several temperatures and assigned them to two chlorine atoms in the molecule from the Zeeman effect study.

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EXPERIMENTAL

Using the method of Vernon [5], α-$(CH_3)_2TeI_2$ was prepared from Te and CH_3I, and α-$(CH_3)_2TeX_2$ (X=Cl, Br) were prepared from α-$(CH_3)_2TeI_2$, $AgNO_3$, and HX. $(CH_3)_2TeI_4$ was prepared from α-$(CH_3)_2TeI_2$ and I_2 by the procedure in the literature [6] These compounds were identified by CHN elemental analysis as listed in Table 1.

The NQR spectrometers used were superregenerative oscillators with frequency modulation or Zeeman modulation. Resonance lines were observed on an oscilloscope or a recorder. The NQR frequencies were measured with a signal generator and a frequency counter with an estimated accuracy of ±0.002 MHz for ^{35}Cl and ±0.02 MHz for ^{81}Br and ^{127}I. The Zeeman effect on the NQR lines was observed using a magnetic field of about 25 mT and examined by means of the zero-splitting cone method at room temperature.

RESULTS AND DISCUSSION

Table 2 shows the ^{35}Cl and ^{81}Br NQR frequencies at room temperature. α-$(CH_3)_2TeCl_2$ yielded two ^{35}Cl NQR lines whose resonance frequencies are in good agreement with those reported by Kondo et al. [4]. α-$(CH_3)_2TeBr_2$ also yielded two ^{81}Br NQR lines. The difference in frequency between two halogen atoms is larger in the bromide than in the chloride. However, taking into account the quadrupole moment, the difference in electric field gradient between two halogen atoms is larger in the chloride than in the bromide. This reflects the fact that intermolecular Br···Te interaction is weaker than the Cl···Te interaction.

Table 3 shows the ^{127}I NQR frequencies at room temperature. α-$(CH_3)_2TeI_2$ yielded six $\nu_1(1/2—3/2)$ NQR lines of ^{127}I, indicating the presence of six nonequivalent iodine atoms, i.e., three crystallographically nonequivalent $(CH_3)_2TeI_2$ molecules in the crystal This is consistent with its crystal structure [2]. The Zeeman effect on the lowest and the highest ν_1 NQR lines of ^{127}I were observed and their zero-splitting patterns are shown in Fig. 1. The angles between the crystal *b* axis and the principal *z* axes of electric field gradients at the two iodine atoms are 142.1° and 143.6° which are in good

TABLE 1

Melting point and analytical data

Compound	M.p (°C)	Found (Calc.)	
		C (%)	H (%)
α-$(CH_3)_2TeCl_2$	92	10.70(10.50)	2.61(2.62)
α-$(CH_3)_2TeBr_2$	91	7.71(7.56)	1.74(1.89)
α-$(CH_3)_2TeI_2$	127	5.88(5.83)	1.46(1.46)
$(CH_3)_2TeI_4$	89	3.66(3.61)	0.90(0.90)

TABLE 2

NQR frequencies in α-$(CH_3)_2TeCl_2$ and α-$(CH_3)_2TeBr_2$

Compound	Nucleus	Frequency (MHz)	T (K)
α-$(CH_3)_2TeCl_2$	^{35}Cl	15.309	292
	^{35}Cl	17.872	292
α-$(CH_3)_2TeBr_2$	^{81}Br	120.09	300
	^{81}Br	124.64	300

TABLE 3

^{127}I NQR parameters in α-$(CH_3)_2TeI_2$ and $(CH_3)_2TeI_4$ at about 300 K

Compound	Line	Frequency (MHz)		η (%)	e^2Qq_{zz}/h (MHz)
		ν_1	ν_2		
α-$(CH_3)_2TeI_2$	ν_a	119.72	239.12	3.03	797.25
	ν_b	135.76	268.98	8.53	897.93
	ν_c	145.87	286.01	10.02	961.98
	ν_d	149.65	299.02	2.69	996.87
	ν_e	167.54	335.06	0.04	1116.89
	ν_f	175.92	350.02	6.32	1167.69
$(CH_3)_2TeI_4$	ν_a	114.65	207.87	28.65	703.96
	ν_b	141.46	255.79	29.08	866.63
	ν_c	314.14	—	—	—
	ν_d	325.27	—	—	—

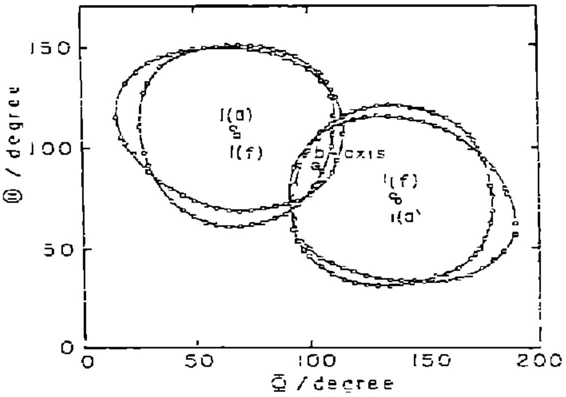


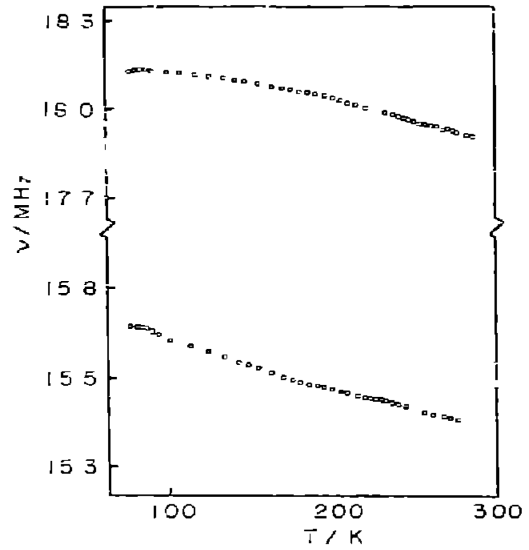
Fig. 1. The zero-splitting patterns of the lowest and the highest ν_1 NQR lines of ^{127}I in α-$(CH_3)_2TeI_2$

agreement with those from the X-ray crystal analysis [2]. The angle between the principal axes was 176.4° which is comparable with 178.3° from the X-ray crystal analysis. Therefore, the lowest and the highest NQR lines are assigned to two iodine atoms of a linear I—Te—I bond. The other NQR lines were also assigned to the iodine atoms from Te—I bond lengths, intermolecular I···Te distances, bond angles and NQR parameters. The results obtained are listed in Table 3. Six NQR lines are classified into three groups, ν_a, ν_f; ν_b, ν_e; ν_c, ν_d, and each of groups corresponding to one linear I—Te—I bond.

$(CH_3)_2TeI_4$ gave four ν_1 NQR lines of ^{127}I, indicating the presence of four nonequivalent iodine atoms in the crystal. This is consistent with the molecular structure of $(CH_3)_2TeI_2\cdot I_2$ determined by X-ray crystal analysis. From comparison of the ^{127}I NQR frequencies of α-$(CH_3)_2TeI_2$ in the present work and I_2 in the literature [7], the two lower ν_1 NQR lines are assigned to the $(CH_3)_2TeI_2$ moiety and the two higher lines, to the I_2 moiety.

Temperature dependence of NQR frequency in α-$(CH_3)_2TeX_2$ (X=Cl, Br)

The temperature dependence of NQR frequencies in α-$(CH_3)_2TeCl_2$ is shown in Fig 2. The NQR frequencies at 77 K and 205 K are in good agreement with those reported by Kondo et al. [4] who observed the NQR lines at several temperatures Both ^{35}Cl NQR line frequencies decreased monotonously with increasing temperature although one of the two chlorine atoms in the molecule forms an intermolecular Cl···Te bond [1]. The difference



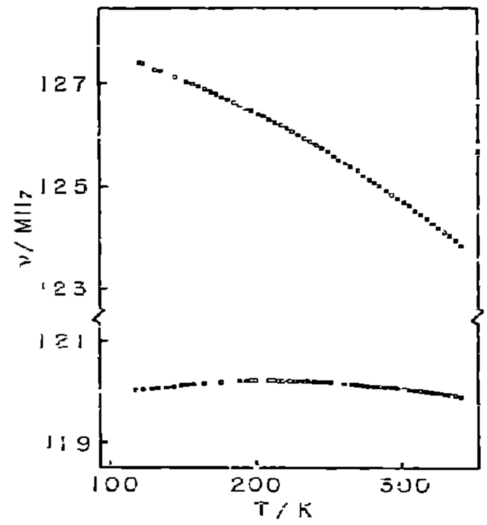


Fig 2 The temperature dependence of ^{35}Cl NQR lines in α-$(CH_3)_2TeCl_2$

Fig 3 The temperature dependence of ^{81}Br NQR lines in α-$(CH_3)_2TeBr_2$.

in frequency between two ^{35}Cl NQR lines seems to be almost independent of temperature, as shown in Fig. 2. This finding cannot be explained on the basis of the crystal structure from X-ray diffraction [1]; the structure leads us to expect a temperature dependence as shown for the bromide in Fig. 3.

For α-$(CH_3)_2TeBr_2$, no NQR lines were observed at 77 K. As the temperature was raised, two ^{81}Br NQR lines were detected at 110 K. The lower NQR line frequency increased slightly up to about 220 K and then decreased whereas the higher NQR line frequency decreased with increasing temperature. This feature of the temperature dependence of NQR frequencies suggests that the crystal structure is analogous to that of the chloride reported by Christofferson et al [1].

The temperature dependence of ^{127}I NQR frequencies in α-$(CH_3)_2TeI_2$ is shown in Fig. 4. The curves have a characteristic feature, i.e., six curves are symmetrical with respect to the frequency of about 149 MHz. This temperature dependence can be explained by assuming that the linear I—Te—I bond is formed by the 3c—4e bond. The validity of the 3c—4e bond was suggested by the X-ray crystal analysis [2], which indicated that the axial Te—I bonds are considerably longer compared with the sum of the covalent radii [8]. The two Te—I bonds in the linear I—Te—I bond are strongly correlated. When one iodine atom in the I—Te—I bond forms intermolecular bonds, one I—Te bond is weakened and lengthened and this results in a shortening of the

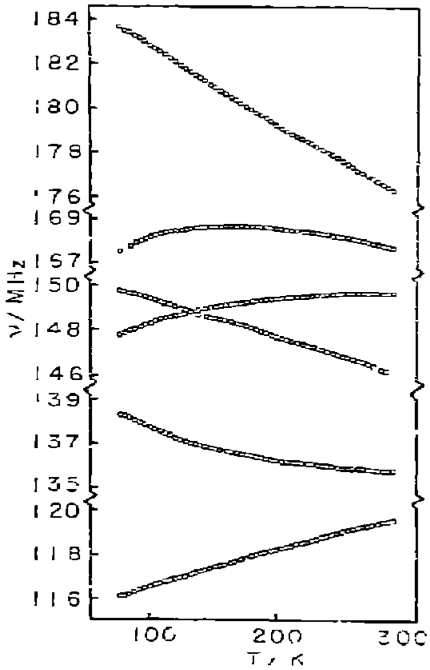


Fig 4 The temperature dependence of ν_1 NQR lines of ^{127}I in α-$(CH_3)_2TeI_2$

other. ^{127}I NQR frequencies of the two iodine atoms in the I—Te—I bond are also strongly correlated. When one iodine atom in the I—Te—I bond forms an intermolecular bond, its NQR frequency decreases; the intermolecular bond is formed by electron transfer from a *p* orbital of the iodine atom to an empty orbital of the tellurium atom. The frequency decrease for one iodine atom results in a frequency increasing for the other. When the temperature rises, the intermolecular bond will partly break and the NQR frequency of the iodine atom participating in the intermolecular bond will increase. However, the frequency of the other will decrease although these effects are modified somewhat by the lattice vibration effect. The curves of the two iodine atoms are thus symmetrical about a certain frequency.

Temperature dependence of NQR frequency in $(CH_3)_2TeI_4$

The temperature dependence of ^{127}I NQR frequencies in $(CH_3)_2TeI_4$ is shown in Fig. 5. The two higher NQR lines, which are assigned to the I_2 moiety, decreased their frequencies with increasing temperature; the two curves are almost parallel. With respect to the remaining two lines which are assigned to $(CH_3)_2TeI_2$ moiety, the frequency of the lower NQR line increased but that of the other decreased as the temperature was raised. Since the lower NQR line arises from the triply-bridging iodine atom, its positive

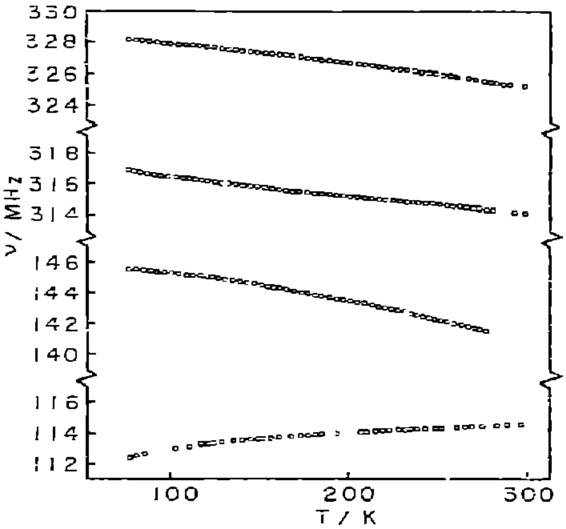


Fig 5 The temperature dependence of ν_1 NQR lines of ^{127}I in $(CH_3)_2TeI_4$.

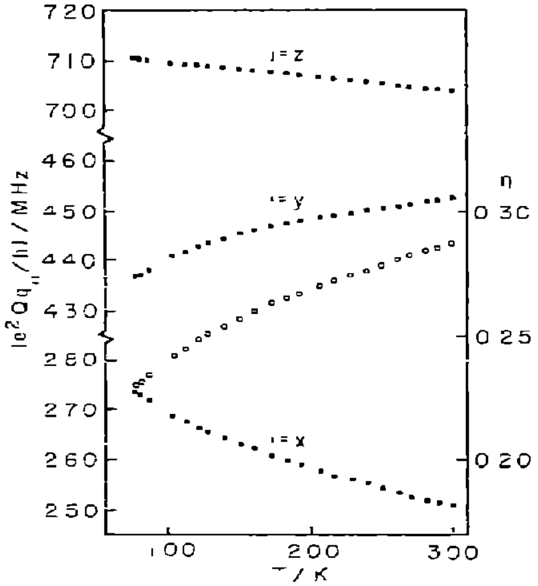


Fig 6 The temperature dependence of e^2Qq_{ii}/h and η of the lowest ^{127}I NQR line in $(CH_3)_2TeI_4$

temperature dependence is of interest. The temperature dependence of the nuclear quadrupole coupling constants, e^2Qq_{ii}/h $(i = x, y, z)$ and the asymmetry parameter, η were derived from the temperature dependence of the ν_1 and ν_2 NQR lines, as shown in Fig. 6. e^2Qq_{yy}/h shows a positive temperature dependence and e^2Qq_{zz}/h shows a large negative temperature dependence, η increases with increasing temperature. Since the ν_1 NQR frequency of ^{127}I is expressed approximately by

$$\nu_1 = (3e^2Qq_{zz}/20h)(1 + 1.0926\eta^2 - 0.6340\eta^4) \tag{1}$$

the frequency varies with η and e^2Qq_{zz}/h. In the present case, as the temperature is raised, e^2Qq_{zz}/h decreases slightly but η increases considerably Therefore, the contribution from the latter overcomes that from the former and the ν_1 frequency increases with increasing temperature.

Then, the positive temperature dependence of η is discussed in terms of the variation of electron population The triply-bridging iodine atom forms three bonds with a tellurium atom in the $(CH_3)_2TeI_2$ moiety and iodine atoms in the I_2 moieties on each side. The I—Te distance is 3.082 Å and I···I distances are 3.456 and 3.404 Å. The Te—I···I angles are 84.65° and 95.75° and the I···I···I angle is 140.45° [3]. Therefore, the iodine atom forms a triply-bridging bond by p_z and sp^2 hybrid orbitals. One p orbital is used to form one I—Te bond. Two sp^2 hybrid orbitals are used to form two equivalent I···I bonds and the last is a lone pair nonbonding orbital. When the direction of the lone pair orbital is chosen to be the z axis, the orbitals are given by

$$\begin{aligned}
\psi_1 &= \phi_{p_z}\\
\psi_2 &= (1-A)^{1/2}\phi_s - A^{1/2}\phi_{p_y}\\
\psi_3 &= (1/2)^{1/2}(A^{1/2}\phi_s - (1-A)^{1/2}\phi_{p_y} + \phi_{p_x})\\
\psi_4 &= (1/2)^{1/2}(A^{1/2}\phi_s - (1-A)^{1/2}\phi_{p_y} - \phi_{p_x}),
\end{aligned} \tag{2}$$

where $A = (1 - \cot^2\theta)$ and 2θ is the I···I···I angle. The electron populations of ψ_1, ψ_2, ψ_3, and ψ_4 are represented by a, 2, b, and b, respectively. Then, e^2Qq_{ii}/h and η are expressed as follows

$$\begin{aligned}
e^2Qq_{zz}/h &= [(A/2)(b-2) + (a-b)]e^2Qq_0/h\\
e^2Qq_{yy}/h &= (1/2)[A(b-2) + (b-a)]e^2Qq_0/h\\
e^2Qq_{xx}/h &= [(A(2-b) + (1/2)(b-a)]e^2Qq_0/h
\end{aligned} \tag{3}$$

$$\eta = 3(b-2)/[2A(a-b) + (b-2)] \tag{4}$$

where e^2Qq_0/h is the quadrupole coupling constant of one p electron The values of a and b are calculated from the observed e^2Qq_{zz}/h and η The results are listed in Table 4. The variation of electron populations is larger in b than in a Thus, the variation of the population with temperature is smaller in the I—Te bond than in the I···I···I bond, indicating that the I···I···I

TABLE 4

The values of *a* and *b* at various temperatures

T (K)	*a*	*b*
77	1.659	1.945
122	1.657	1.941
173	1.656	1.938
229	1.655	1.934
270	1.655	1.933
300	1.655	1.933

bond is weaker than the I—Te bond. This is consistent with the results of the X-ray analysis [3]. When the temperature is raised, the I···I···I bond is partly broken by the enhanced thermal vibration and only small amounts of electrons migrate to the I_2 moiety; the I_2 moiety charges negatively. The reduction of *b* results in an increase in η, as shown in Fig. 6.

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