figurational energy difference is given by eq 14, where the two

$$\Delta E_{av}(s \rightarrow d) \simeq \epsilon_{3d,f} - \epsilon_{4s,i} \qquad (14)$$

orbital energies are eigenvalues of two different Hartree–Fock Hamiltonians. The validity of this approximation is excellent for the lighter atoms and ions; it correctly predicts the 3d–4s crossover at carbon.

If $N \geq 2$, the conventional $\epsilon(Z)$ curves are no longer appropriate. Indeed, not two, but five different orbital-energy curves are to be considered. Yet, by the use of the frozen orbitals of the intermediate $d^{n+1}s^1$ configuration average, the Hartree–Fock $\Delta E_{av}(s \rightarrow d)$ curves could be reproduced rather satisfactorily. In this case, one finds eq 26, which is formally reminiscent of eq 14.

$$\Delta E_{av}(s \rightarrow d) \simeq \Delta E_{av}{}^1(s \rightarrow d) = \epsilon_{3d,f}{}^1 - \epsilon_{4s,i}{}^1 \qquad (26)$$

If *both* orbital energies are calculated in the initial configuration, eq 26 takes the alternative form

$$\Delta E_{av}(s \rightarrow d) \simeq \Delta E_{av}{}^1(s \rightarrow d) = (\epsilon_{3d,i}{}^1 - \epsilon_{4s,i}{}^1) + [(3d,3d)^1 - (3d,4s)^1] \qquad (28)$$

where the term in square brackets represents a (positive) threshold value.

In the neutral atoms, $\epsilon_{3d,i}{}^1 - \epsilon_{4s,i}{}^1$ is negative but smaller (in absolute value) than the threshold value (4s above 3d, but only slightly). Therefore, the ground state is characterized by 4s population. Dropping an electron from 4s into 3d would increase both orbital energies with no resulting energy gain. Upon ionization however, the resulting contraction causes a strong increase of the 4s–3d orbital-energy difference, accompanied by a much smaller increase of the valence repulsion so that, for positive ions, it does become favorable to depopulate the 4s orbital. As a consequence, the 4s electrons are "first ionized", although eq 14a shows they were also "first populated".

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Contribution from the Department of Chemistry, The College of Arts and Sciences,
The University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan

Relaxation Mechanism of Germanium-73 in Tetrabromogermane and Tetraiodogermane at High Temperature

Toshie Harazono, Katsumi Tanaka, and Yoshito Takeuchi*

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The spin–lattice relaxation time (T_1) and spin–spin relaxation time (T_2) of ^{73}Ge nuclei in $GeBr_4$ and GeI_4 have been measured at various temperatures. It has been shown that T_1 is almost exclusively dominated by the quadrupole relaxation mechanism, while T_2 is dominated by the combination of the scalar coupling and the quadrupole relaxation mechanisms in the high-temperature region.

Introduction

As is always the case with a quadrupole nucleus, the relaxation mechanism of ^{73}Ge nuclei with a spin of $^9/_2$ has not been extensively investigated. For the last few years, however, the relaxation mechanism of symmetric tetrasubstituted alkylgermanes and halogermanes were studied. Thus, the spin–lattice relaxation of ^{73}Ge in tetramethylgermane and tetraethylgermane was found to proceed via the quadrupole relaxation mechanism.[1,2] We also showed that both the spin–lattice and spin–spin relaxations of ^{73}Ge in GeR_4 (R = methyl (Me), ethyl (Et), *n*-propyl (Pr), *n*-butyl (Bu)) were solely through the quadrupole relaxation mechanism.[3]

On the other hand, there remain ambiguities concerning the relaxation mechanism of ^{73}Ge nuclei in tetrahalogermanes. Tarasov et al.[4] showed that the spin–lattice relaxation of ^{73}Ge in $GeBr_4$ was solely via the quadrupole relaxation mechanism while in $GeCl_4$ the relaxation occured mostly via the spin–rotation mechanism above 57 °C and mostly via the quadrupole relaxation mechanism below 57 °C. We found, however, that scalar coupling relaxation was involved in the spin–spin relaxation of ^{73}Ge in $GeCl_4$ and $GeBr_4$.[5,6] We investigated the scalar coupling relaxation of ^{73}Ge in $GeCl_4$ in detail in the temperature range between −50 and +50 °C.[6] In that temperature range, however, the temperature effect on the relaxation time of ^{73}Ge nuclei in $GeBr_4$ and GeI_4 was obscure. We thought that the temperature range investigated was so low for these heavier halogens that we failed to observe the temperature effect.

Table I. Values of T_1(IR) and $T_2(\Delta\nu_{1/2})$ for ^{73}Ge in Tetrahalogermanes

compd	solvent	T_1(IR)/ ms	$T_2(\Delta\nu_{1/2})$/ ms	temp/°C	ref
$GeBr_4$	$CDCl_3$	160	130	30	6
	toluene-d_8	88	81	25	this work
GeI_4	CS_2–C_6D_6 (1:1)	80	80	30	6
	toluene-d_8	51	50	45	this work

In the present paper we describe the details of the relaxation of ^{73}Ge in $GeBr_4$ and GeI_4 in the high-temperature region. For this purpose we determined the ^{73}Ge spin–lattice relaxation times (T_1) and spin–spin relaxation times (T_2) of $GeBr_4$ and GeI_4 in the temperature range between 25 and 105 °C.

Experimental Section

Preparation of Compounds. $GeBr_4$ (bp 82–83 °C (32 mmHg)) and GeI_4 (mp 146 °C) were prepared by the procedures given in the literature.[7] The purity of the compounds was confirmed by the GLC (Shimadzu GC-3BT). $GeBr_4$ (50% v/v) and GeI_4 (0.5 g/1.5 mL) were dissolved in toluene-d_8. The solution was put in an egg-shaped cell and degassed by the freeze–thaw method.

^{73}Ge NMR Spectra. The ^{73}Ge NMR spectra were recorded on a JEOL FX-90Q instrument equipped with the low-frequency insert NM-IT10LF at 3.10 MHz. T_1 was determined by the inversion–recovery method (T_1(IR)), while T_2 was determined by the half-line-width method ($T_2(\Delta\nu_{1/2})$). The error in T_1 and T_2 thus determined was estimated to be about or less than 5%. Other conditions of the measurements have

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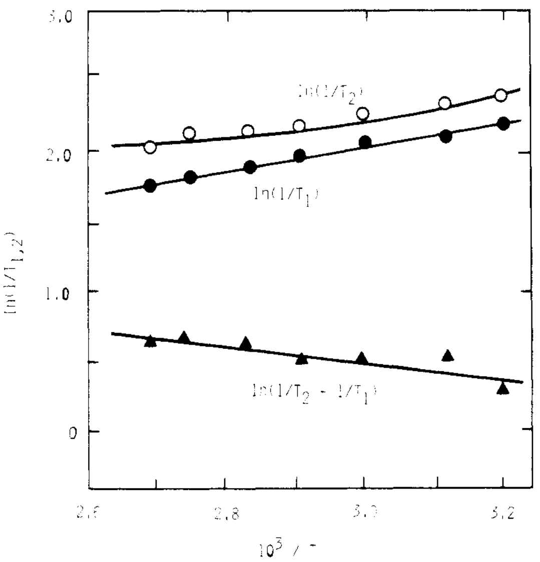

Figure 1. Plots of ln $(1/T_1)$, ln $(1/T_2)$, and ln $(1/T_2 - 1/T_1)$ vs $1/T$ for ^{73}Ge in $GeBr_4$.

been described in previous papers.[3,6]

Results and Discussion

Relaxation Time. As described in our previous papers,[3,6] ^{73}Ge relaxes mostly via the quadrupole mechanism. Indeed, in tetraalkylgermanes, T_1 was equal to T_2 within the experimental error.[3] On the other hand, it was shown that T_1 was longer than T_2 for tetrahalogermanes. This was most remarkable for $GeCl_4$ in $CDCl_3$ at low temperatures.[6] We further determined T_1(IR) and T_2($\Delta\nu_{1/2}$) of $GeBr_4$ and GeI_4 in toluene-d_8 at higher temperatures. Results for GBr_4 at 25 °C and GeI_4 at 45 °C in toluene-d_8 together with results for $GeBr_4$ in chloroform and GeI_4 in a CS_2/benzene mixture are tabulated in Table I. T_1 is slightly longer than T_2 for $GeBr_4$. On the other hand, for GeI_4, T_1 is identical with T_2 at 45 °C. The relaxation times of compounds in toluene-d_8 were shown to be shorter than those in chloroform-d_1 or a CS_2/benzene mixture.[6] This is likely to be due to the higher viscosity of toluene-d_8 than that of chloroform-d_1 or a CS_2/benzene mixture. We further investigated the temperature dependency on T_1 and T_2 of ^{73}Ge in $GeBr_4$ and GeI_4 in order to elucidate the relaxation mechanism.

Relaxation Mechanism. The quadrupole relaxation time of a nucleus with spin $I > {}^1/_2$ is given by eq 1,[8] where e^2Qq/h is the

$$\pi(\Delta\nu_{1/2}) = \frac{1}{T_1} = \frac{1}{T_2} = \frac{3\pi^2}{10}\,\frac{2I+3}{I^2(2I-1)}\left(\frac{e^2Qq}{h}\right)^2\left(1+\frac{\zeta^2}{3}\right)\tau_c \qquad (1)$$

quadrupole coupling constant, ζ is the asymmetry parameter, and τ_c is the correlation time. The reciprocals of the quadrupole relaxation time, $1/T_1{}^q$ and $1/T_2{}^q$, are reasonably represented by an Arrhenius-type equation as given in eq 2, where A is a constant,

$$1/T_1{}^q = 1/T_2{}^q = A\exp(\Delta E/RT) \qquad (2)$$

ΔE is an activation energy, and R is the gas constant. The superscript "q" indicates the quadrupole relaxation. If the relaxation occurs solely via the quadrupole relaxation mechanism, ln $(1/T_1{}^q)$ and ln $(1/T_2{}^q)$ are proportional to the reciprocal of the absolute temperature, $1/T$ (K). The plots of ln $(1/T_1{}^q)$ or ln $(1/T_2{}^q)$ against $1/T$ (K) should give a straight line with a positive slope. Plots of ln $(1/T_1)$ vs. $1/T$ and ln $(1/T_2)$ vs $1/T$ for $GeBr_4$ and GeI_4 are given in Figures 1 and 2, respectively. The plots of ln $(1/T_1)$ vs $1/T$ for both compounds gave straight lines with positive slopes, which indicate that the spin–lattice relaxation of ^{73}Ge in $GeBr_4$ and GeI_4 is dominated by the quadrupole relaxation mechanism. We have already described in detail the origin of the quadrupole relaxation in such highly symmetric tetrasubstituted germanes.[3,9]

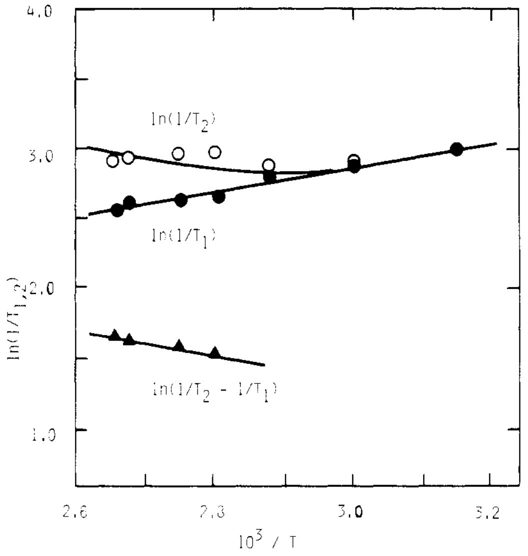

Figure 2. Plots of ln $(1/T_1)$, ln $(1/T_2)$, and ln $(1/T_2 - 1/T_1)$ vs $1/T$ for ^{73}Ge in GeI_4.

On the other hand, the difference between T_1 and T_2 increased, and hence the plot of ln $(1/T_2)$ vs $1/T$ deviated from the plot of ln $(1/T_1)$ vs $1/T$ as the temperature increased. This suggests that there is an involvement of another relaxation mechanism that has a temperature dependency opposite to the quadrupole relaxation. Indeed, the plot of ln $(1/T_2 - 1/T_1)$ against $1/T$ gave straight lines with negative slopes as indicated in Figures 1 and 2.

When there is an effective spin–spin coupling between spin I and spin S, and S varies with time, nucleus I will relax. This is referred to the scalar coupling contribution of the second kind,[8] which is found in the nucleus I bonded to the halogen atom. The scalar contribution of the second kind is given by eq 3,[8] where

$$(T_1{}^{sc})^{-1} = \frac{2}{3}A^2S(S+1)\left(\frac{\tau_2}{1+(\omega_I-\omega_S)2\tau_2{}^2}\right)N_S$$

$$(T_2{}^{sc})^{-1} = \frac{1}{3}A^2S(S+1)\left(\tau_1 + \frac{\tau_2}{1+(\omega_I-\omega_S)^2\tau_2{}^2}\right)N_S \qquad (3)$$

S is the nuclear spin of halogen atom, $\tau_{1,2}$ are the correlation times for the scalar interaction, ω_I and ω_S are the Larmor frequencies in Hz, and N_S is the number of halogen nuclei. The superscript "sc" indicates the scalar coupling relaxation, while A denotes the scalar coupling constant and is equal to $2\pi J$ where J is the coupling constant between germanium atom and halogen atom (in Hz).

It is expected that $(T_1{}^{sc})^{-1}$ is almost negligible as compared with $(T_1{}^q)^{-1}$ from the experimental result of relaxation times of $GeBr_4$ and GeI_4. $(T_2)^{-1}$ is expressed by a combination of two components of the relaxation rates as follows:

$$(T_2)^{-1} = (T_2{}^q)^{-1} + (T_2{}^{sc})^{-1} \qquad (4)$$

Since $(\omega_I - \omega_S)^2\tau_2{}^2$ is expected to be appreciably larger than 1 (extremely narrowing condition), the difference between $(T_2)^{-1}$ and $(T_1)^{-1}$ $(=1/T_1{}^q = 1/T_2{}^q)$ is given by

$$(T_2{}^{sc})^{-1} = (T_2)^{-1} - (T_1)^{-1} = A^2S(S+1)\tau_1N_S/3 \qquad (5)$$

Since τ_1 is equal to T_1 of halogen which relaxes via the quadrupole relaxation mechanism, $1/T_1$ for Br and I is proportional to τ_c (rotational correlation time). This means that the plot of ln $(1/T_2 - 1/T_1)$ of germanium relaxation vs $1/T$ should be a straight line with a negative slope. The activation energies obtained from the slopes of ln $(1/T_1)$ vs $1/T$ and ln $(1/T_2 - 1/T_1)$ vs $1/T$ were 7.0

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(correlation factor $R = 0.99$) and 6.1 kJ/(mol·K) ($R = 0.86$) for $GeBr_4$, and 6.8 ($R = 0.98$) and 7.0 kJ/(mol·K) ($R = 0.94$) for GeI_4, respectively. These values may be regarded as essentially identical within experimental errors and are reasonable compared with 7.6 kJ/(mol·K) for CCl_4[10] and 9.2 kJ/(mol·K) for $Sn(CH_3)_4$.[11] These results give a confirmative evidence that the scalar coupling relaxation is involved in the relaxation of ^{73}Ge in $GeBr_4$ and GeI_4.

Germanium–Halogen Coupling Constants. As described in our previous paper,[6] eq 5 for the two isotopes of Br, i.e., ^{79}Br and ^{81}Br, are converted to eq 6 and 7, where, τ_1^{81} and τ_1^{127} are T_1 of ^{81}Br

$$GeBr_4: \qquad (T_2^{sc})^{-1} = 4.04A_{81}^2\tau_1^{81} \qquad (6)$$

$$GeI_4: \qquad (T_2^{sc})^{-1} = 11.7A_{127}^2\tau_1^{127} \qquad (7)$$

and ^{127}I in $GeBr_4$ and GeI_4, respectively. However, no experimental results of τ_1 have been reported due to extremely broad signals for Br and I.

Johnson et al.[12] reported that T_2 values for ^{35}Cl in $GeCl_4$ and $SnCl_4$ were 4.1×10^{-5} and 2.2×10^{-5} s, respectively, while Sharp[13] reported that T_1 values for ^{81}Br and ^{127}I in $SnBr_4$ and SnI_4 were 7.5×10^{-7} (21 °C) and 1.5×10^{-7} s (150 °C), respectively. If the ratio $T_2(^{35}Cl)$ of $GeCl_4/T_{1,2}(^{35}Cl)$ of $SnCl_4$ is equal to $T_2(^{81}Br)$ of $GeBr_4/T_{1,2}(^{81}Br)$ of $SnBr_4$ or $T_2(^{127}I)$ of $GeI_4/T_{1,2}(^{127}I)$ of SnI_4, $T_2(^{81}Br)$ of $GeBr_4$ and $T_2(^{127}I)$ of GeI_4 will be 1.4×10^{-6} and 2.8×10^{-7} s, respectively. That is, we are using an analogy with X in SnX_4 to estimate $T_{1,2}(X)$ in GeX_4, and we found that $T_{1,2}$ becomes shorter in the order Cl → Br → I. Though there is no theoretical justification for this assumption, the similarity of the relaxation mechanism among these nuclei seem to allow our treatment at least in a semiquantitative manner. By substituting these values for τ_1 in eq 6 and 7, we estimate the coupling constants of J(Ge–Br) and J(Ge–I) as 64 and 220 Hz, respectively.

The contribution of scalar coupling relaxation to the relaxation mechanism decreases in the order $GeCl_4 \rightarrow GeBr_4 \rightarrow GeI_4$; i.e., the scalar coupling mechanism appears at high temperature in that order. This is because T_1 becomes shorter in the order Cl → Br → I.

In conclusion, the contribution of scalar coupling in the spin–spin relaxation of ^{73}Ge in all halogermanes is now established. The extent of this contribution is, however, a function of temperature, and hence at room temperature this is observed only for $GeCl_4$ and $GeBr_4$.

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Registry No. $GeBr_4$, 13450-92-5; GeI_4, 13450-95-8; ^{73}Ge, 15034-58-9.

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Contribution from the Institut für Anorganische Chemie, Universität Bern, CH-3000 Bern 9, Switzerland,
Institut für Anorganische Chemie, Universität Mainz, D-6500 Mainz, West Germany,
Laboratorium für Kristallographie, Universität Bern, CH-3012 Bern, Switzerland,
and Physik Department, Technische Universität München, D-8046 Garching, West Germany

Mössbauer Spectra and Electronic Ground-State Calculations of Strongly Coupled Ruthenium Ammines Bridged by Pyrazine and *p*-Benzoquinone Diimine

Stefan Joss,[1a] Kai M. Hasselbach,[1b] Hans-Beat Bürgi,*[,1c] Rainer Wordel,[1d] Friedrich E. Wagner,[1d] and Andreas Ludi*[,1a]

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The electronic structure of the ligand-bridged binuclear ions $[(NH_3)_5Ru{-}pyz{-}Ru(NH_3)_5]^{n+}$ (n = 4–6; pyz = pyrazine) and $[(NH_3)_5Ru{-}bqd{-}Ru(NH_3)_5]^{m+}$ (m = 4, 5; bqd = benzoquinone diimine) is discussed in terms of a self-consistent-charge extended Hückel (SCCEHMO) approach. One-electron molecular orbitals are obtained by using valence-state ionization potentials for all of the atoms. Configurational energies are adjusted to the experimentally determined g values. The resulting wave functions were used to calculate isomer shifts and quadrupole splittings for the ^{99}Ru Mössbauer spectra of the various ruthenium dimers. Observed isomer shifts for the two mixed-valence ions are −0.535 (pyz) and −0.507 mm s^{-1} (bqd), and quadrupole splittings are 0.513 and 0.571 mm s^{-1}, respectively. The generally good agreement between calculated and observed quantities in conjunction with results deduced from the molecular structures is fully compatible with a symmetric structure for the two mixed-valence ions.

Introduction

Discussion of the electronic structure of ligand-bridged binuclear mixed-valence compounds continues to deal with the question whether a given compound $[M{-}L{-}M]^{\mu+\nu}$ is best described as localized, $[M^{\mu+}{-}L{-}M^{\nu+}]$ (class II), or delocalized $[M^{(\mu+\nu)/2}{-}L{-}M^{(\mu+\nu)/2}]$ (class III).[2] This classification scheme, as well as the approach by Hush,[3] has evolved from theoretical treatments of outer-sphere electron-transfer reactions. Neither these approaches nor the vibronic coupling model developed by Schatz[4] consider the electronic structure of the bridging ligand L explicitly. This may not present problems for the description of the weakly coupled metal ions typical for outer-sphere electron-transfer reactions, but it is a shortcoming for cases with strong metal–metal coupling mediated by bridging ligands.

The most prominent example of a stable mixed-valence dimer is the Creutz–Taube ion,[5] $[(NH_3)_5Ru{-}pyz{-}Ru(NH_3)_5]^{5+}$, abbreviated as [II-pyz-III].[6] Most experimental results for this compound may be explained in terms of a delocalized description, e.g. the crystallographic results for the complete electron-transfer series.[7] Taken together with structural data for [II-bqd-III],[8] they show a significant dependence of the Ru-N(bridge) distance on the oxidation state and on the electronic properties of the bridge.

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[1] (a) Institut für Anorganische Chemie, Universität Bern. (b) Universität Mainz. Present address: Dr. K. Thomae GmbH, Biberach, West Germany. (c) Laboratorium für Kristallographie, Universität Bern. (d) Technische Universität München.

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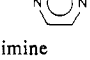
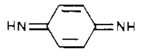


bqd is *p*-benzoquinone diimine



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