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# Contribution of Scalar Coupling Pathway in the Relaxation of Germane and Tetrahalogermanes

Toshie HARAZONO, Katsumi TANAKA, Yoshito TAKEUCHI,* and Norihiro KAKIMOTO+

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

+ASAI Germanium Research Institute, Komae, Tokyo 201

$^{73}$Ge relaxation in $GeH_4$, $GeCl_4$, and $GeBr_4$, and $^{1}$H relaxation in $GeH_4$ have been studied, and found to contain a scalar coupling mechanism in a spin-spin relaxation. Furthermore, a scalar spin coupling constant, $J(^{73}Ge - ^{35}Cl)$ = 24Hz, was obtained.

Magnetic relaxation of nuclei of group IVB elements with I = 1/2(i.e., $^{13}$C, $^{29}$Si, $^{119}$Sn, and $^{207}$Pb) has been extensively investigated. Thus, it has been shown that in $CCl_4$[1] and $SnCl_4$[2] the spin-lattice relaxation of $^{13}$C and $^{119}$Sn are solely via spin-rotation mechanism, and in such tetrahalides as $SnBr_4$,[3] $SnI_4$,[2] and $PbCl_4$,[4] the spin-lattice relaxation of $^{119}$Sn or $^{207}$Pb occurs via a combination of two mechanisms , i.e., spin-rotation and scalar coupling, while the spin-spin relaxation of these nuclei in the above tetrahalides occurs solely via scalar coupling mechanism. Furthermore, in $Sn(CH_3)_4$[5] and $Pb(CH_3)_4$,[5] $^{119}$Sn and $^{207}$Pb spin-lattice relaxations were dominated by the spin-rotation mechanism.

On the contrary, only a limited amount of informations is available on the relaxation of $^{73}$Ge nuclei mostly because of the difficulties of measurement associated with their electric quadrupole moment with I = 9/2. It was shown that $^{73}$Ge spin-lattice relaxation in $Ge(CH_3)_4$ and $Ge(C_2H_5)_4$ were predominated by the quadrupole relaxation because a plot of $\ln(1/T_1)$ vs. 1/T (T is the absolute temperature(K)) gave a straight line with a positive slope.[6] The quadrupole relaxation was also found to be the main relaxation pathway of $^{73}$Ge nuclei

Table 1. $^{73}Ge$ and $^{1}H$ relaxation data for germanium compounds and coupling constant, J(Ge-H), in germane at 303 K[9)]

| | $^{73}Ge$ | | $^{1}H$ | | |
|---|---|---|---|---|---|
| | $T_1$ / ms | $T_2$ / ms | $T_1$ / s | $T_2$ / s | J(Ge-H) / Hz |
| $GeH_4$ | 570 | 320 | 65 | 12 | 97.7 |
| $GeCl_4$ | 280 | 120 | | | |
| $GeBr_4$ | 160 | 130 | | | |

of $Ge(C_4H_9)_4$ and other tetraalkyl germanes.[7)]

Since a contribution of scalar coupling has been detected in the relaxation of other IVB elements when the nuclei are bonded to halogens, a similar contribution may be detected in the relaxation of $^{73}Ge$ nucleus bonded to halogens or to any other nuclei which spin-couple with germanium. With this in mind, we determined the $^{73}Ge$ and $^{1}H$(when appropriate) spin-lattice relaxation times($T_1$) and spin-spin relaxation times($T_2$) of $GeH_4$, $GeCl_4$, and $GeBr_4$ at various temperatures. $T_1$ and $T_2$ were determined by the inversion-recovery and Carr-Purcell-Meiboom-Gill methods, respectively,[8)] with a JEOL FX-90Q spectrometer at 3.10 MHz($^{73}Ge$) and 89.56 MHz($^{1}H$). The data at 303 K are tabulated in Table 1, which indicate that $T_2$ are generally shorter than $T_1$ in both $^{73}Ge$ and $^{1}H$ resonances.

A plot of $\ln(1/T_1)$($^{73}Ge$) of $GeCl_4$ against 1/T(Fig. 1a) gave a straight line (R=0.999) with a positive slope which indicates that the spin-lattice relaxation of $^{73}Ge$ is predominantly via quadrupole mechanism.

On the other hand, a plot of $\ln(1/T_2)$ of $GeCl_4$ against 1/T(Fig. 1b) gave a concave curve with a minimum, which is an evidence that at least two pathways with a different temperature dependency were involved, while the plot of $\ln(1/T_2 - 1/T_1)$ against 1/T(Fig. 1c) gave a straight line(R=0.979) with a negative slope.

On the contrary, for $GeH_4$, the similar procedure(Fig. 2) gave straight lines with a positive slope for $\ln(1/T_2-1/T_1)$ vs. 1/T (R=0.973; Fig. 2c). These observations can be explained in a following manner.

Generally speaking, the contribution of scalar coupling is observed for the relaxation of nuclei which are bonded to such quadrupole nuclei as $^{35(\mathrm{or}\ 37)}Cl$ or $^{79(\mathrm{or}\ 81)}Br$, or which spin-couple with other nuclei.[10,11)]

When

$$1 + (\omega_I - \omega_S)^2 \tau_{sc}^2 \quad >> \quad 1,$$

where $\omega_I$ and $\omega_S$ are the resonance frequencies of nuclei I(in this case Ge) and S(nucleus bonded to Ge), respectively, and $\tau_{sc}$ is the correlation time of scalar coupling, the difference between $1/T_1$ and $1/T_2$ is given by:

$$1/T_2 - 1/T_1 = (2\pi J)^2 I_S(I_S + 1)\tau_{sc}N_S/3$$

where J is the spin-spin coupling constant, $I_S$ is the nuclear spin of the nucleus S and $N_S$ is the number of nucleus S.

When $(2\pi J) << 1/T_1$ or $1/T_2$, $\tau_{sc}$ is equal to $T_1$ of nucleus S.[10,11] Since it is reported that $T_2$ of $^{35}Cl$ of $GeCl_4$ is $4.1\times10^{-5}$ s,[12] the above requirement is fulfilled for the relaxation of germanium in $GeCl_4$. Since $1/T_1$ of $^{35}Cl$ is predominantly quadrupole pathway, and hence proportional to $\tau_c$ (rotational correlation time), 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 which is in line with the experimental results. By substituting $\tau_{sc}$ with $T_2$ of $^{35}Cl$ of $GeCl_4$ in the above equation, the scalar spin coupling constant, $J(^{73}Ge-^{35}Cl)$=24 Hz is calculated.

In the case of $GeH_4$, $(2\pi J) >> 1/T_1$, which is contrary to the case of $GeCl_4$, and similar to such cases as $^{13}CH_3I$ and $^{13}CH_3COOCD_3$.[13] The plot of $\ln(1/T_2)$ of germanium relaxation vs. 1/T is a straight line with a positive slope. Temperature dependency of this kind is also observed for the slow chemical exchange($\tau_{sc} = \tau_{ex}$, where $\tau_{ex}$ is the chemical exchange time).[10,11] Thus, when the line-broadening is essentially governed by the chemical exchange, the plot of $\ln(\tau_{ex})$ vs. 1/T gives a straight line with a positive slope.

In conclusion, to the best of our knowledge we have experimentally first demonstrated that a significant contribution of scalar coupling pathway is operative in the $^{73}Ge$ and $^1H$ spin-spin relaxation of such highly symmetric germanes as $GeH_4$ or $GeCl_4$.

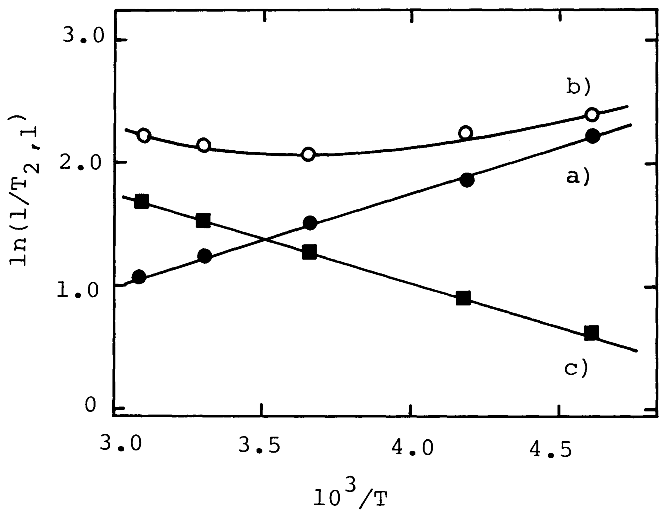


Fig.1. Plots of $\ln(1/T_1)$, $\ln(1/T_2)$, and $\ln(1/T_2-1/T_1)$ of $^{73}$Ge vs. 1/T in tetrachlorogermane. ○: $\ln(1/T_2)$; ●: $\ln(1/T_1)$, R=0.999; ■: $\ln(1/T_2 -1/T_1)$, R=0.979.

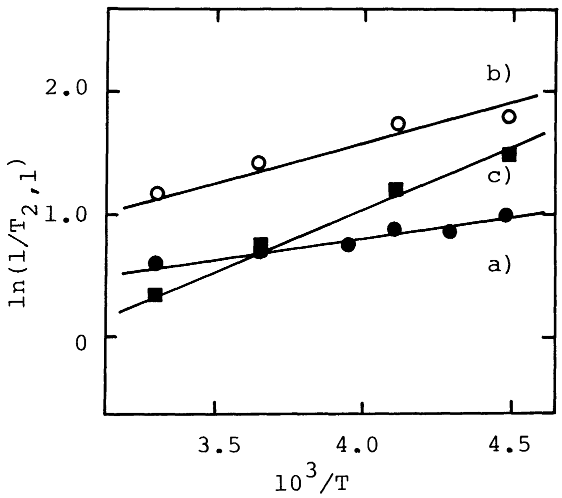


Fig.2. Plots of $\ln(1/T_1)$, $\ln(1/T_2)$, and $\ln(1/T_2-1/T_1)$ of $^{73}$Ge vs. 1/T in germane. ○: $\ln(1/T_2)$ R=0.973; ●: $\ln(1/T_1)$ ,R=0.973; ■: $\ln(1/T_2-1/T_1)$, R=0.973.

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8) From various measurements the accuracy of relaxation times is estimated to be within +5%.
9) The samples of $GeCl_4$ and $GeBr_4$ are in $CDCl_3$(1:1) and that of $GeH_4$ is a saturated solution in $CD_3COCD_3$. The samples were degassed by the freeze-thaw method.
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