

Germane 과 Stannane 의 원자 극성텐서

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Atomic Polar Tensors In Germane and Stannane

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Polar tensors have been calculated for most of the molecules for which all of the infrared fundamental intensities are known.¹ Germane and stannane are prominent exceptions, however. Besides their obvious chemical significance these molecules are important from a spectroscopic point of view. Hence we report in this NOTE the polar tensors of these molecules.

The polar tensors (P_x) of these molecules were calculated via²

$$P_x = P_Q L^{-1} U B, \quad (1)$$

the rotational contributions to P_x , $P_{\rho}\beta$, being zero because of the null equilibrium dipole moments (see ref. 1 for the detailed implication of Eq. (1)). The Cartesian coordinate axes and numbering of atoms are shown in Fig. 1. The B matrix elements were calculated using the equations relating the internal coordinates as defined by Kim² to this space-fixed system. Internuclear distances were taken from ref. 3 and 4. The U matrix applied for these T_d molecules corresponds to the one given in ref. 5. The L^{-1} matrix of germane was calculated using the force fields suggested by Duncan *et*

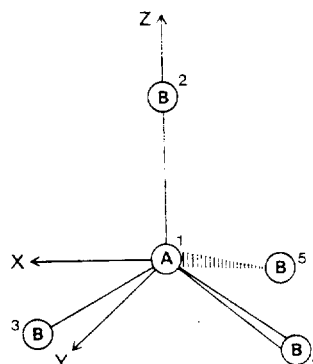


Fig. 1: Coordinate axes and molecular orientation used in normal coordinate calculation. A is either Ge or Sn and B is either H or D atom.

*al.*⁶ The P_Q values for this molecule were obtained from the intensity data in ref. 7. For stannane the infrared intensities and normal coordinates were taken from ref. 8.

Table 1 contains the polar tensor elements as a function of sign choice for the dipole moment derivatives with respect to the normal coordinates constituting P_Q matrices. The experimental errors for the individual polar tensor elements are given in parenthesis. In fact, we need to

Table 1. The polar tensor elements of germane and stannane in multiples of e^a

Molecules	Sign choices ^b	$\partial P_z/\partial X_A^c$	$\partial P_z/\partial X_B^d$	$\partial P_z/\partial Z_B^d$
GeH ₄	$\begin{pmatrix} ++ \\ -- \\ -+ \end{pmatrix}$	$\pm 0.154(0.008)^e$	$\mp 0.196(0.001)$	$\pm 0.276(0.003)$
	$\begin{pmatrix} +- \\ -+ \end{pmatrix}$	$\mp 0.858(0.008)$	$\pm 0.178(0.001)$	$\pm 0.287(0.003)$
	$\begin{pmatrix} ++ \\ -- \\ -+ \end{pmatrix}$	$\pm 0.115(0.004)$	$\mp 0.190(0.001)$	$\pm 0.295(0.001)$
GeD ₄	$\begin{pmatrix} ++ \\ -- \\ -+ \end{pmatrix}$	$\pm 0.115(0.004)$	$\mp 0.190(0.001)$	$\pm 0.295(0.001)$
	$\begin{pmatrix} +- \\ -+ \end{pmatrix}$	$\mp 0.850(0.004)$	$\pm 0.174(0.001)$	$\pm 0.290(0.001)$
	$\begin{pmatrix} ++ \\ -- \\ -+ \end{pmatrix}$	$\pm 0.245(0.011)$	$\mp 0.328(0.003)$	$\pm 0.473(0.004)$
SnH ₄	$\begin{pmatrix} ++ \\ -- \\ -+ \end{pmatrix}$	$\pm 0.245(0.011)$	$\mp 0.328(0.003)$	$\pm 0.473(0.004)$
	$\begin{pmatrix} +- \\ -+ \end{pmatrix}$	$\mp 1.460(0.011)$	$\pm 0.299(0.003)$	$\pm 0.498(0.004)$
	$\begin{pmatrix} ++ \\ -- \\ -+ \end{pmatrix}$	$\pm 0.259(0.030)$	$\mp 0.336(0.010)$	$\pm 0.478(0.003)$
SnD ₄	$\begin{pmatrix} ++ \\ -- \\ -+ \end{pmatrix}$	$\pm 0.259(0.030)$	$\mp 0.336(0.010)$	$\pm 0.478(0.003)$
	$\begin{pmatrix} +- \\ -+ \end{pmatrix}$	$\mp 1.471(0.030)$	$\pm 0.308(0.010)$	$\pm 0.488(0.003)$
	$\begin{pmatrix} ++ \\ -- \\ -+ \end{pmatrix}$			

^aThe atomic polar tensors can be constructed with the elements given in this table. For the details, see refs. 1 and 2. ^bThe signs are those of the dipole moment derivatives with respect to the normal coordinates, $\partial P/\partial Q_i$'s. For example, $(+-)$ would mean that the sign of $\partial P/\partial Q_3$ is positive and that of $\partial P/\partial Q_4$ is negative, where Q_3 and Q_4 are the normal coordinates corresponding to the triply degenerate stretching and bending modes, respectively. ^cA is either Ge or Sn atom. For A, the atomic polar tensor is diagonal with the elements being isotropic. ^dB is either H or D atom. In specific, B corresponds to the atom numbered as 2 in Fig. 1, for which the atomic polar tensor is diagonal and $\partial P_y/\partial Y_B = \partial P_z/\partial X_B$. ^eThe value with upper sign ($+0.154$) is, for example, the tensor element obtained from the signs of $\partial P/\partial Q_i$'s corresponding to the upper sign combination $(++)$ in two sets of sign choices $(\pm\pm)$. The values in parenthesis represent the uncertainties based on the estimated errors in the reported intensities.

consider 4 possible sign combinations since the IR active vibrational modes in T_d molecules are triply degenerate. As is well known, all of the derivatives in P_x must be isotopically invariant within experimental error for the correct sign combination. Other combinations normally do not adhere to this invariance principle.

Inspection of the values of the polar tensor elements in Table 1 suggests for germane that only the $(\pm\pm)$ sets for GeH₄ and the $(\pm\mp)$ choice for GeD₄ are isotopically invariant within experimental error. The differences between the respective polar tensor elements of these sets are either smaller than the sum of the experimental errors of these elements or they are slightly larger. The error estimates reported here are minimum values as they contain no contributions due to errors in the normal coordinates. Consideration of these errors could easily increase

our error estimates for each of the polar tensor elements by 0.001e which is sufficient to obtain agreement between all the individual elements of these sets.

On the other hand it is seen from Table 1 that the isotopic invariance rule seems rather difficult to be applied to stannane in removing the sign ambiguities. However, since the choice of the $(\pm\mp)$ sets for germane appears reasonably secure, the same choices probably hold for stannane, particularly since the chemical nature and electronic environment of both species are quite similar.

Nevertheless, we have to reach some decision about which of the two possible polar tensors corresponding to the $(+-)$ and $(-+)$ sign choices is correct for germane and stannane. For that purpose it may be appropriate to explore the properties of diatomic hydride

molecules, GeH and SnH. According to Bruns *et al.*⁹, the equilibrium dipole vector for GeH (SnH) points to the negative Z-direction when the Ge(Sn) atom is located at the origin and the other atom, H, on the positive Z-axis. Furthermore, Bruns *et al.*⁹ reported for these diatomic species that as the H atom displaces from its equilibrium position to the positive Z-direction, the bond dipole vector directs to the negative Z-direction with more magnitude of dipole moment compared to that with equilibrium geometry.

For tetrahedral molecules, as one terminal atom displaces from its equilibrium position, the central-to-terminal-atom bond dipoles should change from their equilibrium values. Then, it may be appropriate to assume that the bond dipole comprising the displacing atom would vary more significantly compared with those of other three bonds. Based on the present assumption along with the characteristics of diatomic hydrides, it now appears that the H-atom polar tensor elements ($\partial P_x/\partial X_B$ and $\partial P_x/\partial Z_B$ in Table 1) should be negative suggesting that the $(-+)$ sign choice is more probable than others for both molecular species, germane and stannane. This sign choice is, indeed, one of the two sets $(\pm\pm)$ regarded above as proper sign sets.

It is of interest to compare one another the polar tensor elements of the group IV tetrahydrides. Values of the isotropic polar tensor elements for central atoms of these hydrides are 0.014(methane)¹⁰, 0.915(silane)², 0.854(germane), and 1.466e(stannane). The values for silane and germane are nearly equal, a possible reflection of the similarities in bond lengths and electronegativities of the two systems. In comparison, the value of methane(stannane) is much smaller(larger) than those of silane and ger-

mane. This may indicate that the electrons of C atom are more rigid, while those of Sn atom are more flexible than those of Si and Ge atoms. Although the systems of silane and germane appear to possess similar electronic characters, their detailed structures may not be same each other. Indeed, the elements of H(2) atom polar tensor in silane are nearly isotropic², while those of germane are highly anisotropic. More charge-redistribution during molecular vibration is thus expected for silane than for germane. On the other hand, it can be noticed from Table 1 that the degrees of anisotropy in germane and stannane are rather comparable each other even though the electrons of Sn atoms are more flexible than those of Ge atom.

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