

# A Laser Raman Study of Metal-Metal Bondings in $X_3M-Mn(CO)_5$

(X=Cl and  $CH_3$ ; M=Ge and Sn)

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The nature of M-Mn bondings in a series of  $X_3M-Mn(CO)_5$  (X=Cl and  $CH_3$ ; M=Ge and Sn) compounds was studied by measuring the Raman intensities due to the M-Mn stretching vibration, and then calculating the M-Mn bond order. The M-Mn bond order of  $Cl_3M-Mn(CO)_5$  is much larger than those of methyl analogues and  $R_6M_2$  (R= $CH_3$  and  $C_6H_5$ , M=Si, Ge, Sn, and Pb). This finding can be interpreted in terms of a considerable degree of multi-bonding nature of M-Mn bonds for the  $Cl_3M-Mn(CO)_5$  compounds.

## Introduction

On account of the recent development of Raman spectrophotometers, many Raman studies have recently been reported on molecular and bond polarizability derivatives, and bond orders of inorganic compounds,<sup>1-8)</sup> which can be obtained from measured Raman intensities. As Raman lines due to metal-metal stretching vibrations are generally strong, it is easy to distinguish Raman lines due to metal-metal stretching vibrations from other Raman lines. Spiro et al. have particularly devoted their attention to the study of metal-metal interaction in polynuclear complexes by laser Raman spectroscopy,<sup>2-6)</sup> because of the potential utility of Raman spectroscopy for the study of metal-metal bonds. Though they have studied homonuclear systems, Raman spectroscopy is profitable for the study of heteronuclear metal-metal bonds. The present study was undertaken in order to obtain the extent of metal-metal interaction in  $X_3M-Mn(CO)_5$  (X=Cl and  $CH_3$ ,

M=Ge and Sn) compounds in terms of the bond order by measuring the Raman intensity due to the M-Mn stretching vibration.

*Intensities, Bond Polarizability Derivatives, and Bond Orders* The observed intensity of a totally symmetric ( $A_1$ ) Raman line, for the polarized incident light, is given by this formula;

$$I_i = \frac{KM(\nu_0 - \nu_i)^4 \cdot 45(\partial \bar{\alpha} / \partial Q_i)^2 \cdot 3(1 + \rho_i)}{\nu_i [1 - \exp(-h\nu_i/kT)] \cdot (3 + 4\rho_i)} \quad (1)$$

where K is an instrumental constant, M is the molar concentration of the scattering species,  $\nu_0$  is the frequency of the exciting line,  $\nu_i$  and  $Q_i$  are, respectively, the frequency and the normal coordinate of the i-th normal mode,  $\bar{\alpha}$  is the mean molecular polarizability,  $\rho$  is the depolarization ratio of the spectral line, and h, k, and T have their usual meanings.<sup>2)</sup> In order to eliminate K from the equation (1) and to place the intensities on an absolute scale, the following equation is used;

$$\frac{I_i}{I_s} = \frac{M_i \cdot (\nu_0 - \nu_i)^4 \cdot \nu_s [1 - \exp(-h\nu_s/kT)] (\partial \bar{\alpha} / \partial Q_i)^2 \cdot (1 + \rho_i) \cdot (3 - 4\rho_s)}{M_s \cdot (\nu_0 - \nu_s)^4 \cdot \nu_i [1 - \exp(-h\nu_i/kT)] (\partial \bar{\alpha} / \partial Q_s)^2 \cdot (1 + \rho_s) \cdot (3 - 4\rho_i)} \quad (2)$$

where the subscript i refers to the internal standard and s to samples, and other symbols have the same meanings as described above. According to Wolkenstein and Long,<sup>10,9)</sup> the

molecular polarizability derivatives,  $(\partial \bar{\alpha} / \partial Q_i)$ , are converted to bond polarizability derivatives,  $(\partial \bar{\alpha} / \partial u_j)$ , via the transformation

$$\frac{\partial \bar{\alpha}}{\partial Q_i} = \sum_j \sqrt{N_j} \cdot l_{ji} \cdot (\partial \bar{\alpha} / \partial u_j) \quad (3)$$

where  $N_j$  is the number of internal coordinates,  $u_j$ , in the symmetry coordinates  $S_j$ , and  $l_{ji}$  is the eigenvector element connecting  $S_j$  with the normal coordinate  $Q_i$ . Their treatments of polarizability derivatives (the Wolkenstein theory) are based on the following assumptions: (1) the bond polarizability of interest is affected only by the stretching of that bond and does not depend on the stretching of other bonds, (2) the molecular polarizability is additive of bond polarizabilities, and (3) bond polarizabilities are not affected by the angle bending vibrations. The bond polarizability derivatives are related to bond orders, via the Long and Plane equation<sup>11)</sup>

$$\frac{n}{2} = \frac{3Z \cdot a_0}{2g \cdot \sigma \cdot r^3} \cdot \left( \frac{\partial \bar{\alpha}}{\partial u_j} \right) \quad (4)$$

where  $n$  is the number of electrons in the bond ( $n/2$  is the bond order),  $a_0$  is the Bohr radius,  $Z$  is the effective nuclear charge (taken as the atomic number minus the number of inner shell electrons),  $\sigma$  is the Pauling covalent bond character,  $g$  is the  $\delta$ -function strength, and  $r$  is the bond distance. For a heteronuclear bond A-B,  $Z$  is taken to be the geometric mean of  $Z_A$  and  $Z_B$ ,  $\sqrt{Z_A \cdot Z_B}$ ,  $g$  is taken to be  $(\chi_A^{1/2} \cdot \chi_B^{1/2})^{1/2}$ , where  $\chi$  is the Pauling electronegativity, and the Pauling covalent bond character,  $\sigma$ , is  $\exp \left[ -\frac{1}{4} (\chi_A - \chi_B)^2 \right]$ .

## Experimental

All the compounds were prepared by the literature methods.<sup>12-14)</sup> Raman spectra were recorded on a JASCO Model R-300 Laser Raman Spectrophotometer with a NEC GLG 108 He-Ne ion laser source ( $\sim 50$  mW at  $6328 \text{ \AA}$ ). The scattered radiation was collected at  $90^\circ$  and focused by a lens onto the entrance slit of the monochromator. The incident light from the laser was plane polarized and depolarization ratios were measured with an analyzer. Raman intensities were measured for 0.05-0.1 mol solutions ( $\text{CH}_2\text{Cl}_2$  solvent) using the  $283\text{cm}^{-1}$  line ( $A_1$ ) of the solvent as an internal standard, which in turn was compared with  $\nu_1$  of  $\text{CCl}_4$  ( $459\text{cm}^{-1}$ ,  $A_1$ ) in a 50:50(v/v) mixture of the two solvents. The intensity and depolarization ratio measurements were made at least three times for each solution. Peak areas were determined by cutting out the band and weighing the paper.

## Results and Discussion

The results of intensity measurements on  $\text{X}_3\text{M-Mn}(\text{CO})_5$  are presented in the Table, along with the M-Mn stretching force constant, the eigenvector element associated with the M-Mn stretching coordinate,<sup>15-17)</sup> and a number of parameters to be discussed below. Molecular and bond polarizability derivatives were calculated using eq 2 and 3. These were placed on an absolute scale using  $\partial \bar{\alpha} / \partial Q_1$  values of  $0.685 \text{ \AA}^2(\text{amu})^{-1/2}$  for  $459\text{cm}^{-1}$  line of  $\text{CCl}_4$ . Only the contribution of the M-Mn stretching to the molecular polarizability derivatives was considered to obtain the bond polarizability derivatives by the use of eq 3.<sup>18)</sup>

Table. Raman and IR Data

| Compound                                   | $\nu(\text{M-Mn})$<br>$\text{cm}^{-1}$ | $\rho$ | $l_{ji}$ | $\frac{\partial \bar{\alpha}}{\partial Q_i} / Q_i$<br>$\text{\AA}^2(\text{amu})^{-1/2}$ | $\frac{\partial \bar{\alpha}}{\partial u_j} / \text{\AA}^2$ | Bond<br>orders | K(M-Mn),<br>$\text{mdyne}/\text{\AA}$ |
|--|--|--------|----------|---|---|----------------|---------------------------------------|
| $\text{Cl}_3\text{Ge-Mn}(\text{CO})_5$     | 230                                    | 0.12   | 0.1278   | 0.547   | 4.27 <sub>7</sub>   | 0.98           | 1.23                                  |
| $\text{Cl}_3\text{Sn-Mn}(\text{CO})_5$     | 197                                    | 0.092  | 0.1175   | 0.629   | 5.35 <sub>4</sub>   | 1.02           | 1.0                                   |
| $(\text{CH}_3)_3\text{Ge-Mn}(\text{CO})_5$ | 195                                    | 0.22   | 0.1226   | 0.352   | 2.87 <sub>0</sub>   | 0.66           | 0.56                                  |
| $(\text{CH}_3)_3\text{Sn-Mn}(\text{CO})_5$ | 177                                    | 0.13   | 0.1203   | 0.370   | 3.07 <sub>6</sub>   | 0.53           | 0.70                                  |

$r(\text{Ge-Mn}) = 2.44 \text{ \AA}$ ,<sup>20)</sup>  $r(\text{Sn-Mn}) = 2.67 \text{ \AA}$ ,<sup>21,22)</sup> for  $(\text{CH}_3)_3\text{Sn-Mn}(\text{CO})_5$ , and  $r(\text{Sn-Mn}) = 2.59 \text{ \AA}$ ,<sup>23)</sup>  
 $\chi_{\text{Mn}} = 1.55$ ,  $\chi_{\text{Ge}} = 2.01$ ,  $\chi_{\text{Sn}} = 1.96$ ,  $Z_{\text{Mn}} = 7$ ,  $Z_{\text{Ge}} = Z_{\text{Sn}} = 4$ .

Spiro et al. have recently studied metal-metal interactions in a series of compounds,  $\text{Hg}_2(\text{H}_2\text{O})_2^{2+}$ ,  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Re}_2(\text{CO})_{10}$ ,<sup>2)</sup>  $(\text{CH}_3)_6\text{M}_2$  ( $\text{M} = \text{Si}$ ,  $\text{Ge}$ , and  $\text{Sn}$ ),<sup>3)</sup> and  $(\text{C}_6\text{H}_5)_6\text{M}_2$  ( $\text{M} = \text{Sn}$

and  $\text{Pb}$ )<sup>4)</sup> by Raman intensities, and obtained a conjecture that a metal-metal bond of single metal-metal bond order will give  $n/2 = 0.3-0.5$ , though the bond orders are not reliable in an

absolute sense. [The bond orders obtained from eq 4 for  $X_3M-Mn(CO)_5$  fall in the range 0.5–1.0, and those values of chlorine derivatives are fairly larger than those obtained by Spiro et al.<sup>2-4, 19)</sup> Considering the conjecture by Spiro et al. that a metal-metal bond of unit bond order will give  $n/2=0.3-0.5$ , single bonding nature is expected for methyl derivatives, while considerable degree of multi-bonding nature ( $\pi$ -interaction) is expected for chlorine derivatives. Indeed, this expectation is substantiated by the present author's reports that the  $\pi$ -interaction between the IV b metal and manganese atoms for  $Cl_3M-Mn(CO)_5$  is stronger than those of methyl analogous.<sup>17-15)</sup> The Ge-Mn bond order of  $Cl_3Ge-Mn(CO)_5$  is larger than that of  $(CH_3)_3Ge-Mn(CO)_5$  by a factor of 1.5, while that of  $Cl_3Sn-Mn(CO)_5$  is larger than that of  $(CH_3)_3Sn-Mn(CO)_5$  by a factor of 1.9. The ratio of the metal-metal stretching force constants of  $Cl_3Ge-Mn(CO)_5$  vs. that of  $(CH_3)_3Ge-Mn(CO)_5$  is 2.2 and that of  $Cl_3Sn(CO)_5$  vs. that of  $(CH_3)_3Sn-Mn(CO)_5$  is 1.4. Therefore, it is one plausible conclusion that the extent of multi-bonding nature or  $\pi$ -interaction is well expressed in bond orders in a similar order as those of the metal-metal stretching force constants, since the metal-metal stretching force constant,  $K(M-Mn)$ , expresses the degree of the  $\pi$ -interaction between two metal atoms in a present series of compounds.<sup>17-15)</sup> Roughly speaking, the Raman intensity of the line associated with a metal-metal stretching vibration is a convenient tool to compare the extent of the metal-metal interaction of interest in a qualitative manner so long as the component metal atoms are same in the compounds of question, although great caution must be paid for doing such comparison in some cases.

#### References and footnotes

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