

## Raman Spectra of Hydroxo Complexes of Tin (II) and Lead (II) in Strongly Alkaline Solutions, and of Antimony (III) Fluoride in Various Solvents

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A number of studies have been carried out on the Raman spectra of metallic hydroxo complexes.<sup>1)</sup> However, it seems that there are no published data on the Raman spectra of the hydroxo complexes of tin (II) and lead (II) formed in very concentrated alkali solutions. Such ions (the so-called stannite and plumbite ions) were described formerly as  $[\text{MO}_2]^{2-}$ , and more recently as  $[\text{M}(\text{OH})_4]^{2-}$ , but recent literature tends to formulate them as  $[\text{HMO}_2]^-$  or  $[\text{M}(\text{OH})_3]^-$ . The last formulation seems to be the most reasonable, in view of a number of stability and solubility data<sup>2)</sup>. It is also in conformity with the structural expectation, that the inert electron pair ( $ns^2$ ) of  $\text{Sn}^{2+}$  or  $\text{Pb}^{2+}$  will tend to occupy a coordination site and favor the formation of the pyramidal (i. e.  $\text{NH}_3$ -like)  $[\text{M}(\text{OH})_3]^-$  complex in strongly alkaline solutions.

We have tried to observe the Raman spectra of such complexes, and, for the sake of comparison, also those of antimony (III) fluoride, which is isoelectronic with  $[\text{Sn}(\text{OH})_3]^-$ , in aqueous and organic solutions,

### Experimental

The chemicals and solvents used were "Guaranteed Grade" or "Spectro Grade" chemicals, except antimony (III) fluoride which was of "Chemical Reagent" Grade (Wako Pure Chemical Ind., Ltd.). The Raman spectra were measured with a JEOL JRS-S1 Raman Spectrophotometer, using an Argon laser (5145Å and 4880Å\*).

### Results and Discussion

*Hydroxo Complex Ions of Tin (II) and Lead (II)*—When sodium hydroxide pellets are dissolved in an aqueous solution of tin (II) chloride (0.5–2.5 M), tin (II) hydroxide naturally precipitates at first, but, with successive addition of the pellets it gradually dissolves, although a part of it still remains undissolved even when the molar ratio  $\text{OH}^-/\text{Sn}^{2+}$  in the mixture is as high as six. The

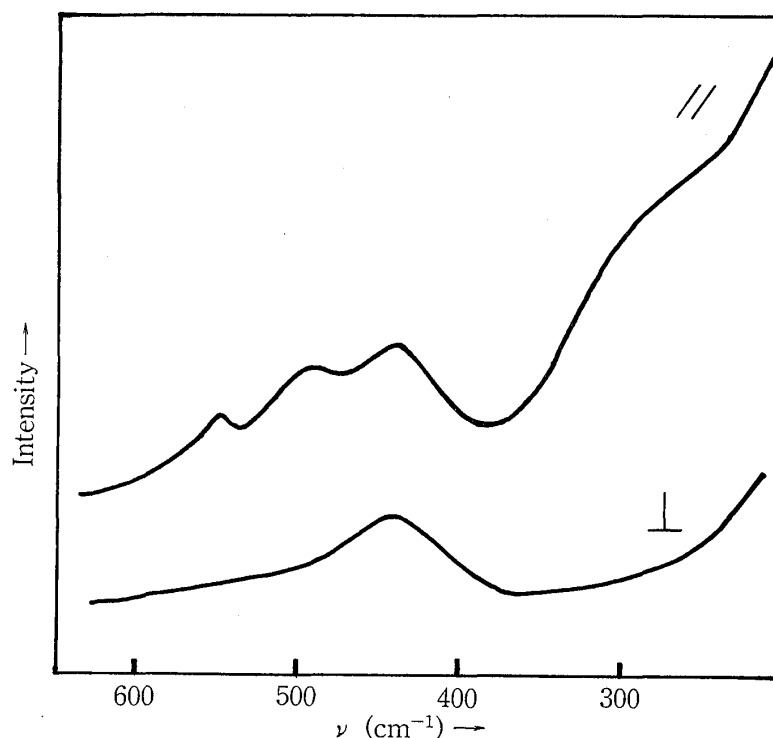


Fig. 1. Polarized Raman spectra of  $\text{Sn}^{2+}$  in a concentrated NaOH solution.

Raman spectra of such solutions, filtered with a sintered glass filter, were studied in some detail.

Fig. 1 shows a typical spectrum of such a solution (initial concentration of tin (II) chloride: 2.5M,  $\text{OH}^-/\text{Sn}^{2+}=6$ ). Among the four Raman lines observed, the strongly polarized one at  $480\text{ cm}^{-1}$  very probably corresponds to the totally symmetric stretching frequency ( $\nu_{sym}$ ) of the hydroxo complex (probably  $[\text{Sn}(\text{OH})_3]^-$ ; see above) formed predominantly in such a highly alkaline solution.

The other three lines, however, do not seem to be all of the same origin. The polarized one at  $553\text{ cm}^{-1}$  is due to the hydroxo complex of tin (IV) produced by the oxidation, since an alkaline solution of tin (IV) chloride also gives the same line. The one at ca.  $300\text{ cm}^{-1}$ , also polarized, appears also in the Raman spectra of concentrated sodium hydroxide solutions with no tin salt, so it must be due to some characteristic vibration of the alkali solution itself.<sup>3)</sup> The depolarized one at  $440\text{ cm}^{-1}$ , which is the strongest, may correspond to the antisymmetric stretching frequency ( $\nu_{asym}$ ) of the predominant complex, although its intensity is seemingly too high. The spectral pattern in the range  $400\text{--}500\text{ cm}^{-1}$  does not change appreciably when the ratio  $\text{OH}^-/\text{Sn}^{2+}$  is changed from 4 to 7, or when the initial tin (II) chloride concentration is lowered to 0.5M at the  $\text{OH}^-/\text{Sn}^{2+}$  ratio 6, but the two lines at 480 and  $440\text{ cm}^{-1}$  both disappear, and a weak depolarized one at ca.  $425\text{ cm}^{-1}$  appears instead, in solutions containing less alkali ( $\text{OH}^-/\text{Sn}^{2+}=3$ ). Thus the line at  $440\text{ cm}^{-1}$  may contain some contributions from other coexisting complex species with less  $\text{OH}^-$  ions per one  $\text{Sn}^{2+}$ , although their nature is by no means

Table 1. Raman frequencies ( $\text{cm}^{-1}$ ) and approximate stretching force constants ( $\text{dyn cm}^{-1}$ ) of antimony (III) fluoride in various solvents.

Solvent	$\nu_1^a$	$\nu_2^a$	$\nu_3^a$	$\nu_4^a$	$k/10^{-5}$	DN <sup>5)</sup>
Water	580	225	527	150	3.26	18.0
CH <sub>3</sub> CN	620		575		3.72	14.1
CH <sub>3</sub> CO <sub>2</sub> CH <sub>3</sub>	615	225	570		3.66	16.5
Dioxane	612		560		3.63	—
DMF	593	265	545		3.40	26.6
Pyridine	587	275	535		3.34	33.1
DMSO	580	225	530		3.26	29.8

a In general,  $\nu_1$  is strong and polarized,  $\nu_3$  is weak to medium and depolarized. The other two lines are both weak and their polarization states are hardly discernible.

clear as yet.

As to the hydroxo complex of lead (II), the situation is much simpler. Sample solutions prepared by using lead (II) nitrate instead of tin (II) chloride, but else in the same manner as above, showed only one polarized Raman line at  $415\text{--}420\text{ cm}^{-1}$ , to be ascribed to  $\nu_{sym}$  of the predominant complex (probably  $[\text{Pb}(\text{OH})_3]^-$ ), when the initial concentration of  $\text{Pb}^{2+}$  is  $0.5\text{--}1.5\text{ M}$  and a sufficiently large amount ( $\text{OH}^-/\text{Pb}^{2+} \geq 5$ ) of alkali is added to it.

Thus we could observe only the  $\nu_{sym}$  of the predominant hydroxo complexes of tin (II) and lead (II) with certainty, and although the apparent stretching force constants  $k$  calculated from them with the simple two-body equation are of reasonable magnitude ( $2.02$  and  $1.63 \times 10^5\text{ dyn cm}^{-1}$ , respectively) we could not confirm their geometry by this study.

*Antimony (III) Fluoride*—Available data on the infrared and Raman spectra of this substance are as yet scanty<sup>4)</sup>. Although partial hydrolytic decomposition with precipitation and hydrogen fluoride formation disturbed the measurements, we could obtain a reasonably good Raman spectrum of its concentrated aqueous solution\*\*, with four frequencies at  $580$  (p, vs),  $527$  (dp, s),  $225$  (w) and ca.  $150$  (w)\*\*\* which can be assigned to the  $\nu_1(A_1)$ ,  $\nu_3(E)$ ,  $\nu_2(A_1)$  and  $\nu_4(E)$  of the trigonal pyramidal molecule.

Organic solutions were generally easier to handle, although the solubilities in them are often limited.\*\* Table 1 summarizes some of the obtained data. In general,  $\nu_4$  (and sometimes  $\nu_2$ ) could not be located with certainty, but the appearance of  $\nu_1$ (p) and  $\nu_3$ (dp) indicates that this molecule retains its pyramidal shape in all the solvents studied. These frequencies, and the value of  $k$  calculated from  $\nu_1$  as before, tend to decrease with increase of the coordination ability of the solvent, which can be expressed in terms of the donor number

\*  $1 \text{ \AA} = 10^{-8}\text{ cm}$ .

\*\* In general it was tried to prepare sample solutions of ca.  $2.5\text{ M}$ , but the actual concentrations were somewhat lower owing to partial decomposition or solubility limit.

\*\*\* p=polarized, dp=depolarized, vs=very strong, s=strong and w=weak.

of Gutmann<sup>5)</sup>. The data in Table 1 show that, with water as a notable exception, there is a roughly linear relation between  $k$  and DN, and the coordination of donor solvent molecules around the antimony atom weakens the strength of the Sb-F bond considerably, ca. 12% in going from acetonitrile to DMSO<sup>6)</sup>.

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### References

- 1) For a review, see R. Tobias: "The Raman Effect" (A. Anderson, Ed.), Vol. 2, p. 482, Dekker, New York (1973).
- 2) Cf. e. g., the data in M. Pourbaix: "Atlas of Electrochemical Equilibria in Aqueous Solutions", pp. 475, 485, Pergamon, London (1966) and G. Charlot, "Les Réactions Chimiques en Solution", pp. 298, 326, Masson, Paris (1969).
- 3) S.K. Sharma and M.D. Reed: *J. Inorg. Nucl. Chem.*, **38**, 1971 (1976) also reported similar data.
- 4) As for the data on related compounds, cf. D. J. Reynolds: "Advances in Fluorine Chemistry" (J. C. Tatlow et al., Ed.), Vol. 7, p. 1, Butterworths, London (1973).
- 5) V. Gutmann: "Coordination Chemistry in Non-Aqueous Solutions", Springer, Wien (1968).
- 6) A somewhat similar relation between  $k$  and DN was described by K. Sone, M. Aritaki, K. Hiraoka and Y. Fukuda, *Bull. Chem. Soc. Jpn.*, **49**, 2015 (1976).