On the Raman Scattering Spectra of Complex Compounds Containing $\mathrm{SbCl_3}$ and $\mathrm{SnCl_4}$

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Abstract

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The study of the spectra of complex compounds is, in the case of complexes with metal halides, of considerable interest also for the theory of catalytic processes ([1]). Therefore an investigation was undertaken of compounds containing $SbCl_3$. Some of the results obtained were published earlier ([2,3]).

In the present work the results are set forth of a study of the spectra of crystals of complexes of naphthalene and diphenyl ether with $SbCl_3$ ($2SbCl_3 \cdot (C_6H_5)_2O$ and $2SbCl_3 \cdot C_{10}H_8$)*. The investigation of these compounds presented certain difficulties. For example, the compound of $SbCl_3$ with naphthalene always had a yellow coloration in our preparations, which, of course, hindered the obtaining of a complete spectrum of this compound and, perhaps, our data are insufficiently complete, especially near the exciting line (4358 Å).

The frequencies of the Raman spectra of the compounds studied are presented in Table 1. As is seen from these data, in the spectra of the complexes there is a series of characteristic changes as compared with the spectra of the components: first, a noticeable redistribution of intensities and a shift of frequencies are observed; second, new lines appear in different regions of the spectrum and splitting occurs of certain frequencies of the spectra of the components of the complexes. These features were noted by us earlier in studying the spectra of compounds of $SbCl_3$ with benzene and a number of its derivatives ([3]). First of all, let us point out that also in the case of compounds of $SbCl_3$ with naphthalene and diphenyl ether there occurs a lowering of the C—C frequencies, and new lines appear in this same region. As before, we are inclined to regard this as evidence that these complexes are formed with participation of π-electrons**. Further, there are changes also in the region of the C—H frequencies, especially noticeable in the case of the complex $2SbCl_3 \cdot C_{10}H_8$.

We shall dwell particularly on the complication of the spectrum in the region of the stretching frequencies of $SbCl_3$. Thus, for example, in the spectrum of the complex $2SbCl_3 \cdot (C_6H_5)_2O$ in this region there are 4 frequencies, whereas in the spectrum of pure $SbCl_3$ in the crystalline state two frequencies are observed: 313 and 349 cm^{-1}. The first frequency, owing to the symmetry of the molecule, is doubly degenerate. In the case of removal of the degeneracy, the $SbCl_3$ molecule cannot have more than 3 frequencies. Meanwhile, we have seen above that in the case of complex formation a larger number of lines is observed. As was already reported (^{3}), a similar phenomenon also occurs in the spectra of other compounds of $SbCl_3$.

The cause of the appearance of new lines in the region of the stretching frequencies of $SbCl_3$ cannot be reduced only to deformation of the molecules, as was done at one time Brigleb, in explaining the spectrum of $SnCl_4$ in complexes (4). Thus, evidently, only the appearance of 3 lines can be explained.

This complication of the spectrum cannot be connected with the second component of the complexes, since in some compounds the spectra of the components do not overlap (for example, in $2SbCl_3 \cdot C_6H_6$). These changes, as experiment shows, are not connected with the stoichiometric composition of the complex (3) and are not caused mainly by the crystal lattice, since in the spectra of some complex compounds in the molten state bands have been found instead of the sharp lines of the crystal in the region of the vibrations of $SbCl_3$. This broadening is noticeable even in the spectra of dilute solutions and appears where, in the spectra of the crystals, new frequencies appear in this region*.

Table 2

Frequencies of the Raman spectra of crystals of the complexes $2SbCl_3 \cdot (C_6H_5)_2O$ and $2SbCl_3 \cdot C_{10}H_8$

$(C_6H_5)_2O$ (crystal)	$2SbCl_3 \cdot (C_6H_5)_2O$	$(C_6H_5)_2O$ (crystal)	$2SbCl_3 \cdot (C_6H_5)_2O$	$C_{10}H_8$ (6)	$2SbCl_3 \cdot C_{10}H_8$	$C_{10}H_8$ (6)	$2SbCl_3 \cdot C_{10}H_8$
21 (5)	23 (3)	874 (1)	868 (1/2)		31 (4)	1258 (2)	
39 (3)	40 (7)	942 (1/2)	939 (0)		41 (4)	1280 (1/2)	
	48 (1)		995 (6)		47 (1)		1303 (<1/2)
69 (4)	66 (4)		1001 (1/2)		77 (2)	1324 (1/2)	
	88 (3)	1005 (7)	1006 (0)		141 (5)	1380 (20)	1377 (10)
100 (6)	126 (3)	1020 (3)	1018 (5)		162 (4)	1438 (1)	1447 (1)

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* L. N. Mukhina took part in obtaining the Raman spectra of the crystals.

** Possibly this gives additional confirmation to M. Usanovich' s suggestion (^{5}) that in the case of diphenyl ether, unlike ethers of the aliphatic series, oxygen does not participate in the formation of the complex.

$(C_6H_5)_2O$ (crystal)	$2SbCl_3\cdot(C_6H_5)_2O$	$(C_6H_5)_2O$ (crystal)	$2SbCl_3\cdot(C_6H_5)_2O$	$C_{10}H_8$ (6)	$2SbCl_3\cdot C_{10}H_8$	$C_{10}H_8$ (6)	$2SbCl_3\cdot C_{10}H_8$
	143 (5)	1076 (1)	1068 (<1/2)	191 (1)	316 (7)	1462 (6)	1462 (1)
	162 (2)	1160 (1)	1152 (2)		346 (9)	1576 (6)	1570 (7)
223 (1)	222 (1)		1160 (3)	395 (2)	353 (3)		1587 (1/2)
	243 (1)		1188 (1/2)	512 (10)	508 (4)		1605 (1/2)
254 (1)		1195 (4)	1195 (4)	726 (1)		1625 (1)	1636 (2)
309 (1/2)	314 (3)		1384 (1)	762 (10)	764 (5)	3004 (1)	
	326 (7)		1417 (2)	778 (1)		3027 (0)	
	336 (1/2)		1435 (1/2)	940 (1)	948 (<1/2)	3055 (10)	3051 (8)
	341 (10)		1458 (1)	1022 (10)	1025 (2)		3065 (8)
	350 (5)	1592 (3)	1580 (3)		1062 (<1/2)	3244 (2)	
616 (1/2)	612 (1/2)		1596 (3)	1146 (4)	1146 (1)		
746 (2)	744 (2)	1603 (3)		1168 (2)			
	761 (<1/2)	3059 (4)	3053 (4)		1185 (<1/2)		
798 (1)	796 (1)	3068 (4)	3073 (7)		1215 (<1/2)		
841 (1/2)	841 (1/2)			1240 (2)	1241 (1)		

The appearance of these new frequencies, apparently, is also not connected with traces of H_2O, since experiments carried out have shown that, for example, in the system $2SbCl_3 \cdot C_6H_6 \cdot nH_2O$ in the liquid state there is neither the appearance of new frequencies nor broadening of the lines, whereas in dilute solutions of $SbCl_3$ in C_6H_6 broadening of the lines of the valence vibrations is clearly manifested*.

Thus, it should be considered that the new frequencies in the region of the valence vibrations of $SbCl_3$ should most probably be attributed, in the case of the compounds investigated in the present work, as in other cases investigated by us, to new bonds formed by $SbCl_3$ with the molecules of the second components of the complexes.

Of interest is the question of whether a similar effect occurs in the spectra of other compounds of metal halides. A preliminary investigation of the Raman spectrum of one of the crystal hydrates of $SnCl_4$ ($SnCl_4 \cdot 5H_2O$) in the solid state showed that its spectrum contains sharp lines which, in the spectrum of the supercooled melt, are shifted and strongly broadened. In the spectrum of the supercooled melt of $SnCl_4 \cdot 5H_2O$ the following 5 frequencies were found: 99; 155; 228; 280 and 335 cm^{-1}.

Furthermore, in the spectrum of the solid crystal hydrate, in the region of the hydrogen-bond frequencies, two sharp lines, 3515 and 3545 cm^{-1}, were found. An analogous pic– was found in the same frequency region in the case of a crystal of the complex $2SbCl_3 \cdot C_6H_5OH$ ([3]), where a sharp line with frequency 3530 cm^{-1} was found, whereas pure phenol has a broad hydrogen-bond band ($\sim$ 300 cm^{-1}) lying in the region 3200–3400 cm^{-1}. These facts can apparently be explained by the rupture of the hydrogen bond upon formation of the complex.

At present we have undertaken a further study of the spectra of crystalline hydrates of $SnCl_4$, as well as the spectra of complexes of $SnCl_4$ and other metal halides with various organic compounds.

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* This broadening of the lines occurs only in that concentration region of $SbCl_3$ where, according to B. N. Menshutkin (7), the existence of a complex has been proved.

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Note: Figure translations are in progress. See original paper for figures.