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Abstract

Full Text

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ON THE RAMAN SPECTRA OF LIGHT SCATTERING OF $AgClO_4$ AND ITS COMPLEX WITH BENZENE

(Presented by Academician A. N. Terenin, 13 VII 1961)

$AgClO_4$, like $SbCl_3$ and certain other complex-forming agents, forms compounds with benzene and its derivatives. It is significant that in recent years the structure of the crystal and of the complex $AgClO_4 \cdot C_6H_6$ has repeatedly been studied by X-ray methods (^{1,2}), and in work (^{2}) it proved possible to establish the deformation of the carbon skeleton of the benzene ring, and also to give an estimate of the energy of the donor-acceptor bond in this complex. Up to the present time, a number of investigations have been carried out on the spectra of $AgClO_4$ complexes. For example, in work (^{3}) the infrared spectra were studied not only of $AgClO_4 \cdot C_6H_6$, but also of the compound $2SbCl_3 \cdot C_6H_6$ in the solid phase, previously studied by us. The results obtained confirm the data of our investigations on the Raman spectra of complexes of $SbCl_3$ with benzene and its derivatives (^{4}). Since the character of the spectral changes, in the opinion of the author of (^{3}), is not identical in these two complexes, a conclusion is drawn about the different type of bond in them.

Fig. 1. Records of the Raman spectra of anhydrous (1) and hydrated (2) $AgClO_4$ on a DFS-12 spectrometer.

In the present work the Raman spectrum of the polycrystalline complex $AgClO_4 \cdot C_6H_6$ was studied on a DFS-12 instrument —a double-monochromator with gratings and photoelectric recording of the spectrum (dispersion 5.2 Å/mm, relative aperture 1 : 5.3). The spectrum was excited by the 4358 Å line obtained from a low-pressure mercury spiral arc with cooled elec-

Fig. 2. Recordings of Raman spectra of the polycrystalline complex $AgClO_4 \cdot C_6H_6$ (1) and liquid benzene (2) on the DFS-12 spectrometer

Figure 2: Fig. 2. Recordings of Raman spectra of the polycrystalline complex $AgClO_4 \cdot C_6H_6$ (1) and liquid benzene (2) on the DFS-12 spectrometer

trodes, made in the laboratory; the short-wavelength part of the arc spectrum was filtered out by a saturated solution of $NaNO_2$.

At the same time, the spectra of anhydrous $AgClO_4$ and of its monohydrate were also studied. The frequencies of the spectra obtained are presented in Table 1; recordings of the spectra on the DFS-12 are reproduced in Figs. 1 and 2. The spectra of anhydrous and hydrous $AgClO_4$ differ noticeably from one another, as is evident from Table 1. First of all, it should be noted that the frequencies 1045 and 1130 cm^{-1}, upon hydration, become a triplet band with maxima at 1050, 1085, and 1130 cm^{-1}. Further, the two frequencies 610 and 645 cm^{-1} of anhydrous $AgClO_4$ become a band at 625 cm^{-1} (possibly with structure). Let us also note that the frequencies 440—485 cm^{-1} of anhydrous $AgClO_4$, upon hydration, come closer together and form a band with broad maxima at 540 and 475 cm^{-1}.

Fig. 2. Recordings of Raman spectra of the polycrystalline complex $AgClO_4 \cdot C_6H_6$ (1) and liquid benzene (2) on the DFS-12 spectrometer

When the spectrum of the $AgClO_4 \cdot C_6H_6$ complex is considered in the frequency region of $AgClO_4$, as is evident from Table 1, it more closely resembles the spectrum of hydrated $AgClO_4$ than that of the anhydrous compound. It should be noted that two new intense frequencies, 130 and 215 cm^{-1}, appear, and that the frequency of the intense (Cl—O) line at 925 cm^{-1} is lowered by 10 cm^{-1}. As for the frequencies in the region of the vibrations of the second component of the complex, we point to the lowering of the 995 cm^{-1} frequency of C_6H_6 upon formation of the complex by 15 cm^{-1}, and to an analogous lowering of the frequencies of the doublet 1586—1608 cm^{-1} by approximately 25 cm^{-1}. Frequencies of C—H (from λ 4047), marked in Fig. 2 with an asterisk, were also observed. In the spectrum of the complex they are represented by a blurred band, possibly with two maxima at 3050 and 3075 cm^{-1}, not very different in intensity, whereas in the spectrum of pure C_6H_6 there are two lines of different intensity with frequencies 3045 and 3063 cm^{-1}.

The results we have obtained may usefully be compared with data on the Raman spectra of single crystals of intermolecular compounds of $SbCl_3$ with benzene and its derivatives (^{4}). As was shown,

upon formation of these complexes, the following changes occur in their spectra: first, in the region of the valence vibrations of $SbCl_3$, a larger number of lines is observed in the spectra of the complexes than can be attributed to the $SbCl_3$ molecule (even in the case of the complex $2SbCl_3 \cdot C_6H_6$, where the spectra of the components of the complex do not overlap). It was suggested that these lines should probably be assigned to new bonds formed in the complex. Second, new lines are observed in the region of the organic component of the complex which, as we have proposed, are associated with a violation of the selection rules. Third, splitting and displacement of a number of lines in the spectra occur.

Table 1

Raman spectra of $AgClO_4$ **and of the complex** $AgClO_4 \cdot C_6H_6$

$AgClO_4$ anhydrous	$AgClO_4$ hydrate	$AgClO_4 \cdot C_6H_6$	C_6H_6
		130(7)215(6)	
440(1/2)	265(< 1/2)	445(1/2)	
	450(> 1)475(< 1)	475(1/2)	
485(1)610(< 1)		600 (1)	609(< 1)
645(< 1)	625(1)	625(< 1)	850(1/2)
925(10)	925(10)	915($4^{1/2}$)	
1045(1)	1050(1/2)*1085(1/2)	1130(1/2)980(10)	995 (10)
1130(1/2)		1175 (1)1475	1178
		(1/2)1560	(1)1483(1/2)1586
		($1^{1/2}$)1580 (1)	(1/2)1608(1/2)
		3050	3045(1/2)*3063($1^{1/2}$)
		(1)3075(< 1)	

* Band with maxima.

Thus, for example, the frequency 995 cm^{-1} mentioned above in the spectrum of the intermolecular compound $2SbCl_3 \cdot C_6H_6$ is lowered by 4 cm^{-1}, and the doublet 1586–1608 cm^{-1} by 6–7 cm^{-1}. Despite the relatively small magnitude of these shifts, and proceeding from the fact that it is observed systematically in a number of other complexes, we earlier proposed (^{4}) that such a lowering of the frequencies of these lines for benzene and its derivatives is characteristic upon formation of π-complexes. As we have seen, in analyzing our data on the Raman spectra of $AgClO_4 \cdot C_6H_6$, in this case the same characteristic changes are also observed, but to a greater degree*. The natural question arises: is it possible, since the above-mentioned shifts of lines in the spectra of the compounds $AgClO_4 \cdot C_6H_6$ and $2SbCl_3 \cdot C_6H_6$ are known, and since the estimate of the bond energy Ag—C_6H_6 is known from work (^{1}), to express any assumptions about the bond energy in the catalytic complex $2SbCl_3 \cdot C_6H_6$. It seems to us that this cannot be done on the basis only of the known results. First, there are no X-ray data on the structure of the crystal and of the complex; second, there are indirect indications suggesting that the interaction in this intermolecular compound is not so very small. Some qualitative indications of this kind are available in the work of Menshutkin (^{5}), as well as in our experiments. In addition, for compounds of this kind the question of the correspondence between the interaction of the components in the complex and the observed spectroscopic changes is still unclear.

In conclusion we would like to point out the following. In recent years new studies have appeared on the spectra of $SbCl_3$ and its complexes ([6,7]); in particular, in work ([7]) our investigations of the Raman spectra

[*] It therefore seems to us that the conclusion made in work ([3]) that the compounds $2SbCl_3 \cdot C_6H_6$ and $AgClO_4 \cdot C_6H_6$ have different character, because the changes in their spectra are different, is at least premature. The question cannot be confidently resolved without X-ray data on the structure of the crystal and of the compound.

scattering of $SbCl_3$ with benzene and its derivatives ([4]), confirming all our experimental results.

According to the authors ([7]), in the spectrum of pure liquid $SbCl_3$, near the intense band at 357–380 cm^{-1} there are weak additional maxima, which explain the appearance of new lines in the spectrum of the complex $2SbCl_3 \cdot C_6H_6$. However, repeated studies of the contour of the 357–380 cm^{-1} band, both by the photographic and by the photoelectric methods (on a DFS-12), did not confirm the existence of such weak maxima.

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CITED LITERATURE

[1] R. E. **Rundle**, J. H. **Goring**, J. Am. Chem. Soc., **72**, 5337 (1950).
[2] H. G. **Smith**, R. E. **Rundle**, J. Am. Chem. Soc., **80**, 5075 (1958).
[3] L. W. **Daasch**, Spectrochim. Acta, No. 9, 726 (1959).
[4] Sh. Sh. **Raskin**, DAN, **100**, No. 3, 485 (1955); Optics and Spectroscopy, **1**, issue 4, 516 (1956); DAN, **123**, No. 4, 645 (1958).
[5] B. N. **Menshutkin**, *On the Influence of Substituents on Certain Reactions of Benzene and Its Substituted Derivatives*, St. Petersburg, 1912.
[6] A. **Tramer**, Bull. Acad. Polon. Sci., ser. math., astron., phys., **6**, No. 10, 659 (1958); P. W. **Davis**, R. A. **Octjen**, J. Molec. Spectrosc., **2**, 253 (1958); L. W. **Daasch**, J. Chem. Phys., **28**, 1005 (1958); **Watari Fumio**, **Kimaki Susumi**, Bull. Chem. Res. Inst. Non-Aqueous Solit. Tohoku Univ., **9**, No. 1 (1959); K. **Wilmshurst**, J. Molec. Spectrosc., **5**, 343 (1960).
[7] P. **Simova**, R. **Angelieva**, Izv. na Bŭlgarsk. akad. na naukite, ser. fiz., **7**, 333 (1959).

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