Raman spectra of intermolecular compounds between antimony trichloride and methyl-group substituted benzenes (2:1)

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(Received 7 June 1988; in final form 1 February 1989; accepted 3 February 1989)

Abstract—Raman spectra of intermolecular complexes between antimony trichloride and methyl-group substituted benzene derivatives were recorded to investigate the complexation-induced frequency shifts of vibrations belonging to the aromatic complex partners. The shifts are discussed according to the reduction of electronic charge on the ring framework of the electronic donator molecules and higher amounts of vibrational coupling. Vibrational coupling appears between C=C stretching vibrations and internal modes of the substituted methyl groups and between C-H stretching vibrations of the ring and the methyl groups. The influence of the charge reduction is directly related to the affections of the C-H stretching vibrations and C-H out-of-plane vibrations of the ring, as well as the C=C stretching vibrations with tangential amplitude directions.

INTRODUCTION

Complexes between benzene derivatives and antimony trichloride have been well-known since MENSHUTKIN in 1911 confirmed their existence and stoichiometric relations by melting point curve [1]. Possible stoichiometric relations between halides and aromatic hydrocarbons are 1:1 and 2:1. The latter show two crystal configuration patterns in which two antimony trichloride molecules are located either on both sides or on one side of the ring planes. The halide molecules lose their C_{3v} symmetry and the antimony atoms are placed next to the aromatic ring planes [2-4]. In all investigated complexes, the shortest Sb-C distance is slightly smaller than the sum of the van der Waals radii, indicating a weak interaction between halides and aromatic molecules. Due to the classification of electron donator-acceptor complexes [5], these MENSHUTKIN complexes belong to the type $b\pi - v$ in which bonding π -orbitals of the aromatic hydrocarbons interact with vacant orbitals of the halide molecule.

In addition to intermolecular re-arrangements and geometry alterations of the halide molecules in the complexes, the complexation also modifies the molecular framework and charge distribution of the aromatic compounds. The subject of this work is to study how these modifications influence the Raman frequencies. We restrict our interest to the spectra of complexed benzene and its methyl-group substituted derivatives. These molecules have comparable force fields [6], so that general trends of complexationinduced effects on specific types of molecular vibrations can be expected.

EXPERIMENTAL

Benzene, benzene- d_6 and the liquid methyl-substituted benzenes were distilled over sodium. Their purity was gas-

chromatographically controlled and was at least 98%. The solid aromatic compounds were recrystallized in methanol, dried over SiccapentTM and checked by means of their melting points. Antimony trichloride (Merck, 99%) was distilled in a vacuum over antimony and then sublimed. The aromatic compounds were added to antimony trichloride in a nitrogen gas filled glove box with a residual humidity of 30-60 ppm. Deviations from the true stoichiometric relations show a percentage uncertainty of about 0.5%. The melts and the solid complex compounds were colourless which indicated the absence of σ -complex formation [7]. The reaction products were powdered and sealed up in glass tubes under vacuum. The samples were cooled to 253 K and their spectra were recorded by a spectrometer (Jarrell-Ash, model 25-400; Czerny-Turner type double monochromator, 1 m focal length) combined with a Peltier element-cooled photomultiplier (RCA, C31034) and a photocounting system (Photonic, PC07A). The fixed slit width setting was chosen to give a spectral resolution of 6 cm⁻¹ at 488 nm. The wavenumber shifts between the spectra of complexed and uncomplexed molecules were checked by simultaneous detection of laser plasma lines [8]. All samples were excited with the 488 nm emission line of an Ar⁺-ion laser (Spectra Physics, model 165). The scattered light was received at right angles to the excitation laser beam.

RESULTS AND DISCUSSION

The spectra of the Menshutkin complexes can be roughly divided into two parts. The first part $(10-400 \text{ cm}^{-1})$ contains lattice modes and Sb–Cl vibrations, whereas the second $(400-3100 \text{ cm}^{-1})$ shows the vibrations of the aromatic compounds. Tables 1 and 2 contain vibrational frequencies of complexed benzene and some methyl-substituted derivatives, as well as frequency shifts related to the non-complexed molecules. Although the molecular force fields are most likely modified by complexation, the vibrations in the complex spectra are still classified according to WILSON's numbering convention [9].

C-H vibrations

C-H stretching vibrations. In the spectra of complexed benzene, mono-substituted and di-substituted

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						a	re assigned	d accordin	g to [12]								
			Stretchir	ig modes				C-H and (Out-of	C-CH ₃ vi f-plane mo	brations odes				In-plane 1	modes		
	3	7a	7b	20a	20b	13	5	10a	10b	17	11	3	15	9a	96	18a	18b
sence	3074	9 9 9)65					862	877					1179			
	(9+)	+	· 12)					(+10)	(9+)					(+2)			
Benzene-d ₆	2303	52	278					681						877	856		
ł	(+)	+)	·10)					(+1	(-					(+2)	(+ 4)		
Toluene		3069	3061					868					1001	1181	1161	1028	
		(6+)	(+18)					(-)					(-3)	(+3)	(+4)	(-3)	
Xylene	3051	1224	3062	3086	3076		0 66				272						1051
	(+19)	(-2)	(+12)	(+3)	(+4)		(+4)				(+13)						(-3)
n-Xylene	3064	3048							161		228				1173	1093	
•	(+11)	(+8)							(+21)		(+21)				(+2)	(-2)	
Xylene	3067	1201	3043				952	827				1317		1187			
	(+ 8)	(-2)	(6+)				(+20)	(+16)				0		(+ 5)			
Mesitylene	3038	Π	169			1304		246		668				281			
	(+20)	<u> </u>	- 2)			(+1)		(+1	5)	(+18)				(+3)			

benzene derivatives, the C-H stretching vibrations show significant shifts to higher wavenumbers. Parallel to this, the C-H out-of-plane vibrations of these molecules also shift to higher frequencies after complexation. Both frequency changes are attributed to charge reductions on the hydrogen-bonded carbon atoms. This can be established by using linear correlations between charge and vibrational frequencies [10,11] in which semi-empirically calculated charge densities are compared to the recorded group frequencies. The C-H stretching modes 20a/b of complexed oxylene increase less compared to all other C-H stretching vibrations of the mono, di and tri-substituted molecules. This indicates either a different sensitivity to charge reduction or a vibrational interaction with C-H stretching modes of the methyl groups. The latter effect can be identified in higher methyl-substituted benzenes. The C-H stretching vibrations of higher methyl-substituted benzenes have lower frequencies after complexation. The frequency shifts amount to 2-4 cm⁻¹ in the complex spectra of durene, 1,2,3,4tetramethylbenzene and pentamethylbenzene. Equivalent data concerning the C-H out-of-plane vibrations could not be obtained because these vibrations are difficult to assign. According to the frequency/ charge correlation, the complexation apparently generates a weak increase in the charge of the hydrogen carrying atoms in higher methyl-substituted molecules. This assertion is inconsistent with an electron transfer from the aromatic compound to the halide and conflicts with the affections of the C=C stretching modes with tangential amplitude directions (Table 2). The frequency decrease of the C-H stretching vibrations may alternatively be created by complexationenhanced vibrational interactions with internal C-H stretching modes of the substituted methyl groups. This assumption is supported by the molecule-specific frequency shifts of the symmetric and asymmetric C-H stretching vibrations of the methyl groups in the complex spectra (Table 2). Additionally, the methyl group modes are directly affected by the molecular charge transfer: this can be seen from the complex spectrum of hexamethylbenzene, in which the C-H stretching vibrations show considerably different frequencies in comparison with those recorded in the spectrum of pure hexamethylbenzene. These shifts cannot be caused by vibrational coupling since vibrations which are capable of interacting with these C-H stretching modes have frequencies which are too low.

C-H bending vibrations. The recorded C-H in-plane bending modes 9a/b and 18a/b respond non-uniformly to complexation. Complexation allows the increase of the frequencies of the mode 9a/b while the frequencies of pair 18a/b are down-shifted. This behaviour is generated by the different character of both modes. Mode 9a/b is the most pure bending vibration [6] while pair 18 has a large amount of C=C stretching vibrations [6, 12]. Since C=C stretching modes with tangential amplitude directions have smaller frequencies in the complex spectra (Table 2), the large portion

Table 1. The wavenumbers of the C-H and C-CH₃ vibrations of the complexed benzene derivatives. The frequency shifts (in parentheses) are relative to the non-complexed molecules. The modes

				an	d [12]					
	Rac	C=(C stretching modes Tangential				Internal methyl-grou Stretching modes		up vibrations Bending modes	
	1	12	8a	8b	19a	19b	sym.	asym.	sym.	rock
Benzene	989 (1580	1600	14	78 - 9)				
Benzene-d ₆	945 (-3)		15 (-	53 8)	,	~)				
Toluene	784 (-2)	1001 (-3)	1596 (-11)	1577 (9)	1493 (-5)		2934 (+11)	2981 (-6)	1382 (+2)	
o-Xylene	733'	. ,	1571 (-13)	1598 (12)	1451 (-1)		2991 (+10)	2930 2962 (+7) (+16)	1389 (+1)	
m-Xylene	723 (-3)	999 (-1)	1582 (-12)	1605 (-11)	. ,		2927 (+5)	2862 (-5)	1383 (+3)	1039 (+3)
p-Xylene	822' (-8)	. ,	1610 (-9)	1568 (-12)			2990 (+10)	2958 (+2)	1395 (+11)	. ,
Mesitylene	582' (+5)	998 (0)	1592 (16) 1604 11)			2927 (+6)	2869 2956 (-2) (+6)	1391 (+9)	1044 (+3)
Durene	731 (-10)	(-)	1613 (-12)	1554 (-15)			/	*	1387 (-7)	,

Table 2. The wavenumbers of the C=C stretching modes and the internal vibrations of the substituted methyl groups. The frequency shifts (in parentheses) are relative to the non-complexed molecules. The modes are assigned according to [6] and [12]

*The stretching vibrations of the methyl groups could not be assigned.

of C=C stretching motion apparently lowers the wavenumbers of pair 18. This interpretation is confirmed by the behaviour of pair 19a/b which has lower frequencies in the complex spectra. These vibrations are dominantly formed by C-H bending motions, although they are usually assigned as C=C stretching vibrations [6] (Table 2). The behaviour of modes 9, 18 and 19 indicate that C-H bending motions are not greatly influenced by the modified force field in the complexed state.

C=C modes

Radial stretching modes. In benzene, the character of the radial stretching mode 1 is confined to C=C stretching motions and C-H bending motions [6, 12]. Since C-H bending motions are rather unaffected by complexation, evident from the behaviour of modes 9, 18 and 19, the frequency shift of mode 1 in the spectrum of complexed benzene can be regarded as an effect on a pure C=C stretching mode. The small shift shows that pure radial stretching vibrations are only slightly affected by the charge alteration in the complexed state. Similar frequency shifts of mode 1 are observed in the complex spectra of toluene, o-xylene and m-xylene. This indicates that complexation-enhanced interactions between modes of methyl groups and C=C stretching modes can be neglected for these molecules. In the spectra of complexed p-xylene and durene, mode 1 shifts more to lower wavenumbers and in a manner different from all recorded complex spectra, this mode rises for 5 cm^{-1} in the spectrum of complexed mesitylene. This non-uniform affection of mode 1 is attributed to a higher amount of vibrational interaction with CH₃-C stretching vibrations induced by the complexation. Since the magnitude of coupling

depends on the substitution pattern of the ring, most emphasized coupling conditions arise for p-substitution and symmetric tri-substitution with equal substituents [6]. The vibrational interaction must also cause a frequency shift of the CH₃-C stretching vibrations (spectral range 1130-1310 cm⁻¹, Table 1). These vibrations have smaller wavenumbers in the complexed state, complexed p-xylene and durene in particular. An opposite frequency shift appears in the spectrum of complexed mesitylene. The internal bending and rocking methyl-group vibrations are apparently involved in the vibrational coupling. These vibrations have altered wavenumbers in the spectra of the complexed molecules (Table 2). The bending vibrations normally rise a few wavenumbers. Again, for p-xylene and mesitylene, the wavenumbers shift up to a greater extent; for durene, the bending vibration lowers its wavenumber. In the case of higher methyl-substituted benzenes, the non-uniform affection of mode 1 caused by vibrational coupling is continued. The frequency of mode 1 in the spectra of complexed 1,2,3,5-tetramethylbenzene does not demonstrate any shift while in the remaining spectra (1,2,3,4-tetrapentamethylbenzene and hexamethylbenzene) shifts appear for around 5 cm^{-1} .

The frequency shifts of mode 1 induced by complexation are significantly different to those which are generated by electronic excitation. Representative for all investigated molecules, mode 1 appears at 923 cm⁻¹ in the state ${}^{1}B_{2u}$ of benzene (electronic ground state: 992 cm⁻¹). This indicates that the electronic interaction of aromatic donator molecules with electronic acceptors does not simply correspond to electronic excitation.

Tangential stretching modes. In contrast to the weak affection of mode 1, the charge reduction in the

complexed aromatic hydrocarbons causes stronger and uniform frequency shifts of the tangential stretching vibrations 8a/b to lower wavenumbers. These shifts become more pronounced with increasing methyl substitution and are parallel to the increasing electron donator activity of higher methyl-substituted derivatives. Since specific shifts generated by distinct substitution patterns do not appear in the series of investigated complex spectra, the amount of vibrational interactions can hardly be obtained.

Therefore, the influence of charge reduction on pure tangential C=C stretching vibrations is only considered for complexed benzene in accordance with the discussion concerning the radial mode 1.

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