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Raman Spectrum of the Complex of Nitrobenzene with Aluminum Chloride

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Synopsis. Raman spectrum of the complex of nitrobenzene with aluminum chloride in a nitrobenzene solution was measured. The shift frequencies and the degree of depolarization of Raman bands of the nitrobenzene in the complex are different from those of nitrobenzene. The differences were discussed based on the prior assignment of Raman bands of nitrobenzene.

Aluminum complex of nitrobenzene is well-known as the acceptor in many charge transfer complexes. Although infrared spectra were reported recently,[1] laser Raman spectral data are not available. In the present study, a laser excited Raman spectrum of the complex of nitrobenzene with aluminum chloride was measured in order to get information of the structure of the complex primarily based on the degree of depolarization.

Experimental

Raman spectrum of the nitrobenzene saturated with anhydrous aluminum chloride at room temperature was measured using 0.1 ml Raman cell. The spectrum was recorded on a Japan Spectroscopic Co., Ltd. Model R-800T Raman Spectrophotometer, being excited with a Spectra Physics argon ion laser (model 165) using 514.5 nm line (300 mW). The Raman shift frequencies, the intensities, and the degree of depolarization are shown in Table 1.

Results and Discussion

The observed Raman bands are classified into two groups. One consists of the Raman bands of the complex, whose shift frequencies are almost the same as those of nitrobenzene and are overlapped by nitrobenzene bands, while the other consists of those marked with C in Table 1. The Raman bands of the latter group except for those having the shift frequencies, 1470 and 1182 cm^{-1}, are due to the nitro group. All the Raman bands of both groups have the values of degree of depolarization smaller than 0.75, showing that the complex has neither symmetry axes nor symmetry planes. Especially, the degree of depolarization ($\rho=0.67<0.75$) of the Raman band (shift frequency, 180 cm^{-1}), which corresponds to an out-of-plane bending vibration (b_1 symmetry species), suggests that the plane including the benzene ring and the nitro group no longer exists in the complex or the plane is no longer symmetry plane, even if it existed. Remarkable changes of the shift frequencies of the nitro group in the complex formation show the coordination of aluminum atom to oxygen atom. The shift frequency, 398 cm^{-1}, of the Raman band of aluminum chloride in the complex is different from those of corresponding bands (a_1 symmetry species; 350 cm^{-1} for acetonitrile solutions;[3] 371 cm^{-1} for the vapor state[4]), but is almost the same as that of monomeric aluminum chloride in argon matrix.[5] Therefore, the almost planar structure similar to that of aluminum chloride in argon matrix,[5] persists even in the complex.

Table 1. Observed shift frequencies (in cm^{-1}), intensities (I) and degree of deaolarization (ρ) of the Raman bands of the nitrobenzene saturated with aluminum chloride at room temperature

Shift frequency	I	ρ		Corresponding bands of the components of the complex[2,5]
1595	17	0.49		$C_6H_5NO_2$ a_1(CC str.)
1546	12	0.35	C	
1533	sh	?		$C_6H_5NO_2$ b_2(NO_2 asym. str.)
1485	2	≈0.40		$C_6H_5NO_2$ a_1(CC str.)
1470	5	0.35	C	
1351	100	0.17		$C_6H_5NO_2$ a_1(NO_2 asym. str.)
1270	14	0.48	C	
1182	4	0.55	C	
1166	sh	?		$C_6H_5NO_2$ b_2(CH bend.)
1110	18	0.16		$C_6H_5NO_2$ a_1
1024	12	0.11		$C_6H_5NO_2$ a_1(CH bend.)
1007	57	0.07		$C_6H_5NO_2$ a_1(ring)
856	27	0.08		$C_6H_5NO_2$ a_1(NO_2 bend.)
850	sh	?	C	
797	1	?		$C_6H_5NO_2$ b_1(CH bend.)
713	<1	?		$C_6H_5NO_2$ b_1(NO_2 wag.)
685	2	0.18		$C_6H_5NO_2$ a_1
615	7	0.60		$C_6H_5NO_2$ b_2(CCC bend.)
610	sh	?		$AlCl_3$ E′
530	<1	?		$C_6H_5NO_2$ b_2(NO_2 rock.)
465	1	≈0	C	
398	9	0.08		$C_6H_5NO_2$ a_1, $AlCl_3$ a_1
250	2	0.50		$C_6H_5NO_2$ b_2
180	4	0.67		$C_6H_5NO_2$ b_1
175	sh	?		$AlCl_3$ E′

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