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Normal Vibrations of Benzenesulfonate and Benzene-d_5-sulfonate Ions

Toyozo Uno, Akio Kuwae, Yutaka Saito, and Katsunosuke Machida
Faculty of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto 606

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Infrared and Raman spectra of sodium benzenesulfonate and its fully *C*-deuterated derivative have been recorded in the solid state and in the aqueous solution. The normal coordinate analysis has been made for $C_6H_5SO_3^-$ and $C_6D_5SO_3^-$ ions based on the C_{2v} symmetry. A valence force field was assumed and the force constants were refined by the least squares method. It was found that the diagonal force constants for the CH out-of-plane bending vibrations at the *ortho* and the *para* positions are greater than the corresponding constant for the *meta* position. This result reflects well the effect of the electron attractive substituent in monosubstituted benzene derivatives. The force constants obtained were transferred to *p*-toluenesulfonate ion successfully.

The infrared spectra of benzenesulfonic acid salts have been studied by a few investigators with limited interest in the asymmetric and the symmetric stretching frequencies of the SO_3^- group.[1-3] Exceptionally, Margoshes *et al.*[4,5] quoted a band at 750 cm^{-1} as a datum to illustrate a correlation between the out-of-plane CH deformation frequencies and the electronegativity and the mass of the substituent in a series of monosubstituted benzenes. No reports seem to have been published yet on the overall vibrational assignments for benzenesulfonate ion. In the present work, we have investigated the infrared and Raman spectra of sodium benzene- and benzene-d_5-sulfonates, assigning the fundamental frequencies in detail and carrying out the normal coordinate analysis for both the in-plane and the out-of-plane vibrations. Special attention has been drawn on the infrared band at 750 cm^{-1} due to the CH out-of-plane deformation vibration in which all the hydrogen atoms move in phase. This band appears normally in the region between 770 and 720 cm^{-1} for monosubstituted benzenes. As well known for the cases of nitrobenzene and benzoic acid derivatives, the in-phase CH out-of-plane deformation frequency is raised when the substituent becomes strongly electron attractive. Although the $-SO_3^-$ group is supposed to be an electron attractive substituent, benzenesulfonate ion shows this band in the middle of the normal range, 750 cm^{-1}. In this respect it is of interest to clarify the role of the mass and the electronegativity of the substituent in determining the CH out-of-plane deformation frequencies.

Experimental

Commercially available sodium benzenesulfonate and sodium *p*-toluenesulfonate were recrystallized from methanol. Sodium benzene-d_5-sulfonate was kindly supplied by Dr. Y. Tanaka of Okayama University. The infrared spectra were recorded on a Koken DS-301 spectrophotometer equipped with NaCl prisms (4000—650 cm^{-1}), on a Perkin Elmer Model 521 grating spectrophotometer (800—250 cm^{-1}) and on a Hitachi FIS-3 grating spectrophotometer (400—33 cm^{-1}). The measurements were made for the mulls with Nujol or hexachlorobutadiene over the whole range, and for the aqueous (H_2O and D_2O) solutions between 1700 and 650 cm^{-1}. The Raman spectra of the crystalline powder samples sealed in capillary tubes were measured on a JEOL S-1 laser Raman spectrophotometer. The slit width was 12 cm^{-1}. The Raman polarization measurement was made for the saturated aqueous solution. The 514.5 nm line of a Coherent 52 G Ar$^+$ laser was used as the excitation source. The infrared and the Raman specra of sodium benzene- and benzene-d_5-sulfonates are shown in Figs. 1 and 2. The observed fundamental frequencies are listed in Table 1 together with the assignments and the calculated frequencies.

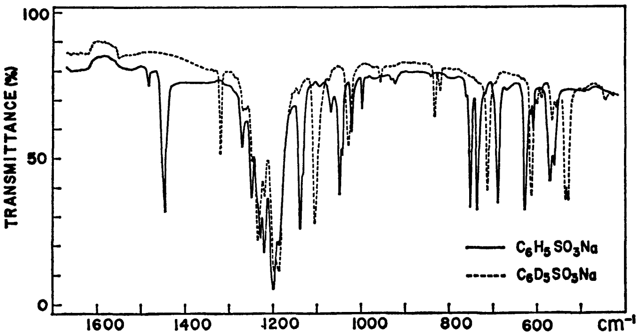

Fig. 1. Infrared spectra of sodium benzenesulfonate and sodium benzene-d_5-sulfonate.

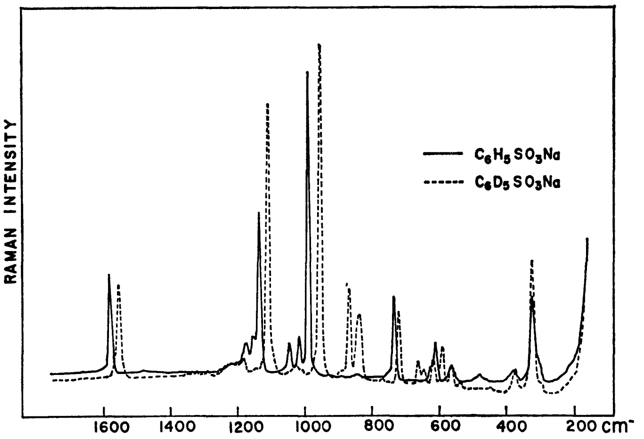

Fig. 2. Raman spectra of sodium benzenesulfonate and sodium benzene-d_5-sulfonate.

Assignments

For sodium benzene-d_5-sulfonate, one of the b_2 CD in-plane deformation frequencies expected around 850 cm^{-1} could not be found in either the infrared or the Raman spectrum. All the other fundamentals due to the ring in-plane vibrations of benzene- and benzene-d_5-sulfonate ions were easily assigned by referring to the available data for toluene,[6] chlorobenzene[7,8] and their ring deuterated compounds.[6,8,9]

TABLE 1. OBSERVED AND CALCULATED FUNDAMENTAL FREQUENCIES (cm^{-1})

Species	Sodium benzenesulfonate				Sodium benzene-d_5-sulfonate			
	Obsd		Calcd	Assignment	Obsd		Calcd	Assignment
	IR	Raman			IR	Raman		
a_1		1584$^{a)}$	1588	νCC+βCH	1552 w	1555$^{a)}$	1549	νCC+δring
	1487 w	1489 vw	1492	βCH+νCC			1353	νCC+βCD
		1177 w	1190	βCH+νCC	1107 s	1110 s p	1117	νCS+ν_sSO$_3$+νCC
	1137 s	1136 s p	1137	νCS+νCC+ν_sSO$_3$	1030 m	1022 w p	1031	ν_sSO$_3$+νCC+δring
	1049 s	1048 w p	1048	ν_sSO$_3$+νCC	957 w	953 s p	950	δring+νCC
	1020 m	1022 w p	1024	νCC+δring		866 m p	854	βCD
	995 w	991 s p	998	δring+νCC	834 m$^{a)}$	837 m p	825	βCD+νCC
	735 s	735 m p	736	νCS+δring	711 s	718 m p	709	νCS+δring
	560 s	567 w	568	δ_sSO$_3$+δring	566 w	562 w	563	δ_sSO$_3$+δring
	330 m	322 m p	329	δ_sSO$_3$+δring+νCS	323 m	322 m p	322	δ_sSO$_3$+δring+νCS
b_2		1584 m dp	1588	νCC	1552 w	1555 m dp	1546	νCC
	1447 s	1448 vw	1450	βCH+νCC	1320 m		1316	νCC+βCD
	1310 vw		1323	βCH			1283	νCC
			1286	νCC	1193 vs$^{a)}$		1193	ν_aSO$_3$
	1194 vs$^{a)}$		1193	ν_aSO$_3$		1048 vw	1033	βCD
	1157 sh	1158 w	1161	βCH			835	βCD
	1069 w		1076	νCC+βCH	822 w		813	βCD
	628 s	624 sh	621	δring	611 s$^{a)}$	616 w	611	δ_aSO$_3$
	614 w	610 w dp	611	δ_aSO$_3$	589 w	590 w dp	599	δring
	383 w	376 w dp	383	ρSO$_3$+δCS	378 w$^{a)}$	372 w dp	378	ρSO$_3$
	218 m		219	δCS	207 m		207	δCS
b_1	1194 vs		1194	ν_aSO$_3$	1193 vs		1194	ν_aSO$_3$
	985 vw		984	γCH	834 m		837	γCD+tor
	921 w		919	γCH+tor	761 vw		765	γCD+tor
	750 s		748	tor+γCH+γCS	611 s	616 w	613	δ_aSO$_3$+tor
	688 s		687	tor+γCH	599 sh		604	δ_aSO$_3$+tor+γCD
	609 m		609	δ_aSO$_3$	531 s	536 vw	530	γCD+tor
	478 w	478 w	469	tor+ρSO$_3$+γCS	433 m		442	ρSO$_3$+tor+γCS
	383 w		385	tor+ρSO$_3$	378 w	372 w dp	361	tor+γCS+ρSO$_3$
	133 m		139	γCS	125 w		132	γCS
a_2	965 vw		962	γCH		772 vw	772	γCD+tor
	840$^{b)}$		853	γCH	655 vw		663	γCD
	407 sh		417	tor+γCH	371 sh		367	tor+γCD

a) Overlapped frequencies. b) Frequency estimated from combination band.

TABLE 2. ANALYSIS OF SUMMATION BANDS

Obsd	Calcd	Obsd	Calcd
1963	$1970=985(b_1)+985(b_1)$	1763	$1761=840(a_2)+921(b_1)$
1955	$1950=965(a_2)+985(b_1)$	1745	$1735=750(b_1)+985(b_1)$
1900	$1906=921(b_1)+985(b_1)$	1716	$1715=750(b_1)+965(b_2)$
1889	$1886=921(b_1)+965(a_2)$	1682	$1680=840(a_2)+840(a_2)$
1805	$1805=840(a_2)+965(a_2)$	1670	$1671=750(b_1)+921(b_1)$
1775$^{a)}$	$1771=1157(b_2)+614(b_2)$		

a) Combination band of in-plane fundamentals.

The infrared bands observed at 1194 and 1049 cm^{-1} for the crystal of sodium benzenesulfonate are assigned to the asymmetric and the symmetric SO$_3^-$ stretching vibrations, respectively.[1)] The former band is broad and splits complicatedly, but in the aqueous solution this splitting disappears and only a single broad absorption is observed in the same frequency region. The symmetric stretching band is sharp and shifts to 1033 cm^{-1} on going to the aqueous solution. Sodium benzene-d_5-sulfonate shows the corresponding infrared bands at 1193 and 1030 cm^{-1}. In analogy with the case of benzenesulfonyl chloride[10)] the C–S stretching vibration is thought to couple with a ring vibration, contributing to the infrared bands at 1137 and 735 cm^{-1} of sodium benzenesulfonate and those at 1107 and 711 cm^{-1} of sodium benzene-d_5-sulfonate.

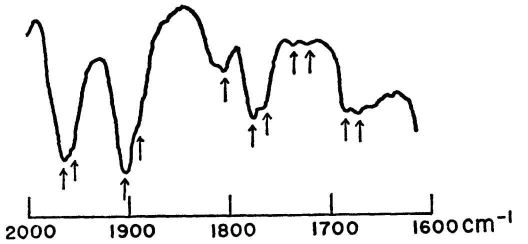

Fig. 3. Infrared summation bands in the region between 1600 and 2000 cm^{-1}. The arrows show the observed absorptions.

Except for the strong infrared band at 750 cm^{-1}, the assignments of the CH out-of-plane deformation frequencies were accomplished with the aid of an analysis of the summation bands in the region between 2000 and 1600 cm^{-1}.[11] (see Fig. 3) The agreements between the sums of the fundamentals and the observed summation frequencies are good as shown in Table 2. Among these summation bands, the band near 1800 cm^{-1} due to the combination of the two a_2 vibrations is the least sensitive to the change of the substituent, since the a_2 vibrations do not involve the motion of the substituent when it is approximated to be a point mass. One of the a_2 fundamentals of benzenesulfonate ion is observed at 965 cm^{-1} in the infrared spectrum probably because the molecular symmetry is lowered in the crystal. The remaining a_2 fundamental is easily estimated from the summation frequency 1805 cm^{-1}. The assignments of the b_1 out-of-plane ring deformation frequencies were made by analogy with toluene[6] and chlorobenzene[7,9,12], and by referring to the result of the normal coordinate calculation with the starting set of force constants.

After the ring vibrational frequencies were identified, the infrared and the Raman bands left unassigned below 700 cm^{-1} were attributed to the symmetric and the asymmetric deformation vibrations and the rocking vibrations of the SO_3^- group by referring to the corresponding frequencies of methanesulfonate ion.[13] The presently assigned SO_3^- group frequencies are reasonable in comparison with those for *p*-aminobenzenesulfonate ion.[14]

Normal Coordinate Analysis

The structure determination by the X-ray analssis has not yet been made for sodium benzenesulfonate. Accordingly, the structure of benzenesulfonate ion was estimated in this work from analogy with the results of the X-ray analysis for magnesium and zinc salts.[15] The benzene ring was assumed to be a regular hexagon being coplanar with one of the S–O bonds. The six angles around the sulfur atom were taken to be tetrahedral. We adopted the molecular symmetry C_{2v} for benzenesulfonate ion by eliminating the interaction terms between the ring and the substituent from the force field.[16] The torsional motion around the C–S bond was excluded from the calculation. Figure 4 shows the structure parameters and the internal coordinate system.

The force field was assumed to be of the valence type and the initial values of force constants for the ring part were taken from toluene.[6] For the sulfonate part, the initial constants were set equal to the F matrix elements obtained from the Urey-Bradley force constants for methanesulfonate ion.[13] In the region above 500 cm^{-1}, the transferred force constants reproduced fairly well the fundamental frequencies already assigned, and the remaining frequencies could be selected so as to reproduce the calculated values as closely as possible under the restriction from the Raman polarization and the isotope effects. Preliminary calculations showed, however, that the agreement between the observed and the calculated frequencies below 500 cm^{-1} could not be improved within the framework of the transferred force field, so that we introduced the interaction constants $F_{\Phi-\rho SO_3}$ and $F_{M-\rho SO_3'}$ with initial values zero. These constants are defined by the terms in the potential function

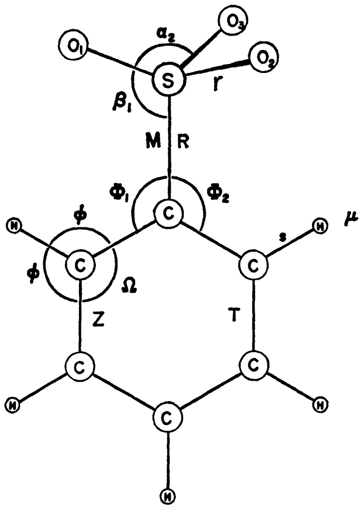

Fig. 4. The structure and the internal coordinates used in the calculation. Bond lengths(in Å): CH, 1.084; CC, 1.397; CS, 1.82; SO, 1.39.

$$V = \cdots\cdots + F_{\Phi-\rho SO_3} S_\Phi S_{\rho SO_3} + F_{M-\rho SO_3'} S_M S_{\rho SO_3'} + \cdots\cdots,$$

where the coordinates S_Φ, $S_{\rho SO_3}$, S_M and $S_{\rho SO_3'}$ are given by

$$S_\Phi = (\Phi_2 - \Phi_1)/\sqrt{2}$$

$$S_{\rho SO_3} = (2\beta_1 - \beta_2 - \beta_3)/\sqrt{6}$$

$$S_M = M$$

and

$$S_{\rho SO_3'} = (\beta_2 - \beta_3)/\sqrt{2},$$

respectively.

We attributed zero weights to the CH stretching frequencies and accordingly fixed the CH stretching constant K_s to the transferred value. The simultaneous least squares refinement of all the other force constants was found to result in divergence. Accordingly, the iteration was performed alternately for the force constants related to the substituent and for those related to the benzene ring, until the sum of the squared residuals became stationary. In this process, any force constants showing large dispersions were fixed automatically, and for this reason most of the off-diagonal substituent constants were left highly indeterminate. Fortunately,

TABLE 3. VALENCE FORCE CONSTANTS OF BENZENESULFONATE ION

	Type	Unit[a]	Value	Type	Unit	Value
(in-plane)	K_s[b]	1	5.0664	K_T	1	6.4266
	K_R	1	5.3908	H_ϕ	3	0.5161
	H_Φ	3	0.8943	H_Ω	3	0.9920
	F_{T^o}	1	0.7305	F_{T^m}	1	−0.3911
	F_{T^p}	1	0.3959	$F_{T\phi}$	2	0.1076
	$F_{T\Phi}$	2	0.0763	$F_{T\Omega}$	2	0.1187
	F_{TR}	1	0.4831	$F_{R\Phi}$	2	1.1137
	F_{ϕ^o}	3	0.0048	F_{ϕ^m}	3	−0.0074
	F_{ϕ^p}	3	0.0031			
(out-of-plane)	H_{μ^o}	3	0.4620[c]	H_{μ^m}	3	0.4166
	H_{μ^p}	3	0.4925	H_M	3	0.4524
	H_z	3	0.3440	f_{μ^o}	3	−0.0592
	f_{μ^m}	3	−0.0186	f_{μ^p}	3	−0.0093
	f_{z^o}	3	−0.0166	$f_{\mu z^o}$	3	−0.1708
	$f_{\mu z^m}$	3	−0.0061			
(SO_3 part)	K_r	1	8.1777	H_α	3	2.2993
	H_β	3	1.1144	F_{rR}	1	0.1559
	F_{rr}	1	0.3503	$F_{r\alpha}$	2	0.2799
	$F_{R\beta}$	2	0.2134	$F_{r\beta}$	2	0.2000
	$F_{\alpha\alpha}$	3	0.2004	$F_{\alpha\beta}$	3	0.0309
	$F_{\beta\beta}$	3	−0.6562	$F_{\Phi-\rho SO_3}$	3	−0.4487
	$F_{M-\rho SO_3'}$	3	0.3263			

a) 1. in mdyn/Å, 2. in mdyn/rad, 3. in mdyn Å/rad^2. b) The subscripts denote the coordinates involved. c) Standard errors for H_{μ^o}, H_{μ^m} and H_{μ^p} are 0.0243, 0.0292 and 0.0281 (mdyn Å/rad^2), respectively.

the ring frequencies were hardly affected by these constants, and the force constants for the ring part were believed to converge to the best values. The diagonal constants for the CH out-of-plane deformation coordinates at the *meta* and the *para* positions of the substituent, H_{μ^m} and H_{μ^p}, respectively, were constrained to the same value in the calculation for toluene by Lau and Snyder[6], but they were treated as the independent parameters in the present work. The final set of force constants are listed in Table 3.

Discussion

The mixing between the CH out-of-plane deformation and the ring torsional vibrations of benzenesulfonate ion is appreciable in the a_2 and the b_1 species. The infrared bands at 750 and 688 cm^{-1} characteristic of monosubstituted benzenes are contributed almost equally from the CH out-of-plane deformation and the torsional vibrations. The C–S out-of-plane deformation vibration also contributes to the 750 cm^{-1} band, explaining the fact that this frequency is sensitive to the mass of the substituent.[5] For the deuterated compound, the b_1 SO_3^- asymmetric deformation vibration couples with the torsional vibrations in the fundamentals at 611 and 599 cm^{-1}. The infrared band of the undeuterated compound at 478 cm^{-1} corresponds to the X-sensitive band at 508 cm^{-1} of nitrobenzene[17] and also to the 460 cm^{-1} band of benzenesulfonyl chloride.[10] According to the present calculation, this band is due to a coupled mode of the SO_3^- out-of-plane rocking, the C–S out-of-plane deformation and the ring torsional vibrations.

In the presently obtained force field of benzenesulfonate ion, the CH out-of-plane deformation constants for the *ortho* and the *para* hydrogen atoms are appreciably greater than that for the *meta* hydrogen atoms. The electronic theory due to Margoshes *et al.* states that the increase of the local π-electron density on the ring carbon facilitates the rehybridization from sp_2 to sp_3 orbitals on the out-of-plane deformation of the CH bond.[4] The present result is consistent with the prediction of this theory for the *meta*-orienting substituent. A similar conclusion was already obtained by Kakiuchi *et al.* in their simplified treatment of the CH out-of-plane deformation vibrations of some monosubstituted benzenes.[18,19] Usually, the characteristic infrared band due to the in-phase CH out-of-plane deformation vibration of monosubstituted benzene derivatives shifts to the high-frequency side when the substituent becomes more electron-attractive. Margoshes *et al.* also pointed out that, in the case of mono-atomic substituent X, a negative correlation exists between the frequency of this band and the reduced mass of the bond C–X.[5] For benzenesulfonate ion, the electron drawing character of the substituent tends to raise this frequency, while the large mass of the sulfur atom tends to lower it, and these effects cancell each other. In order to estimate the mass effect we tried a calculation in which the mass of sulfur is replaced by that of carbon and the bond length C–S by that of C–C in toluene, leaving the force constants unchanged. This calculation gave rise to an increase of the in-phase CH out-of-plane deformation frequency by about 10 cm^{-1}, to which the diminutions in the mass and the bond length were found to con-

Table 4. Observed and calculated frequencies of *p*-toluenesulfonate ion (CH$_3$ and SO$_3$ vibrations are omitted) (cm^{-1})

	ν_{obsd}	ν_{calcd} Initial	ν_{calcd} Final[a]
b$_1$ species	952	957	949
	813	818	897
	694	766	713
	622	609	609
	482	540	501
	406	412	409
	232	250	246
a$_2$ species	973	962	979
	846	852	848
	373	412	362

a) In the final calculation, $H_{\mu^o}=0.4881$, $H_{\mu^m}=0.4085$ and $H_z=0.2947$ mdyne Å/rad^2.

tribute equally.

In order to check the transferability of the force constants among related compounds, the normal coordinate calculation for *p*-toluenesulfonate ion was performed in the same way as that for benzenesulfonate ion. The force constants for the methyl group were transferred from toluene[6] and the others from the final set for benzenesulfonate ion. By using these constants, the observed frequencies of sodium *p*-toluenesulfonate were reproduced well except for two infrared frequencies 694 and 482 cm^{-1} to which the torsional vibrations contribute mainly. With the purpose to attain a better fit between the observed and the calculated frequencies, the force constants related to the CH out-of-plane deformation and the torsional vibrations were refined by the least squares method. After several cycles of refinements, the torsional constant H_z converged to an intermediate value between those of toluene and benzenesulfonate ion, and fairly good fit was obtained without large changes of the CH out-of-plane deformation constants. The results are shown in Table 4. The large differences in the torsional constants among differently substituted benzene derivatives indicate that the easiness of the torsional motion is highly sensitive to the ring-electron density, which in turn is related closely to the number and the kind of the substituents. For the other force constants, we may conclude that the transferability between benzenesulfonate and *p*-toluenesulfonate ions is fairly good.

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