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Vibrational Spectra of Dimethylaminosulfonyl Chloride and Its *C*-Deuterated Derivative

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The infrared and Raman spectra of dimethylaminosulfonyl chloride and its *C*-deuterated derivative have been recorded in the liquid state. The fundamental frequencies have been assigned by referring to the band intensities, Raman depolarization ratios and isotopic frequency shifts. A normal coordinate analysis based on a planar C_s molecular model has been carried out by using a simple Urey-Bradley force field for stretching and bending coordinates and a valence force field for torsional coordinates. The calculated frequencies based on a refined set of force constants agree well with the observed ones.

Infrared and Raman spectra of dimethylaminosulfonyl chloride, $(CH_3)_2NSO_2Cl$, have been reported by Bürger *et al.*[1] and Schneider *et al.*[2] The latter authors have also carried out a normal coordinate analysis for the simplified 7 body model, C_2NSO_2Cl. There seems to remain, however, much ambiguity on assignments of several skeletal vibrations which are expected to couple with the methyl group modes. The present work has been undertaken to clarify this point by referring to the spectral change on deuterating the two methyl groups, and to compare the related force constants with those of other sulfonyl compounds. A normal coordinate analysis has been carried out for the complete molecular model including the motion of the hydrogen atoms. By using a refined set of 25 force constants, the observed frequencies of both the isotopic compounds have been reproduced satisfactorily.

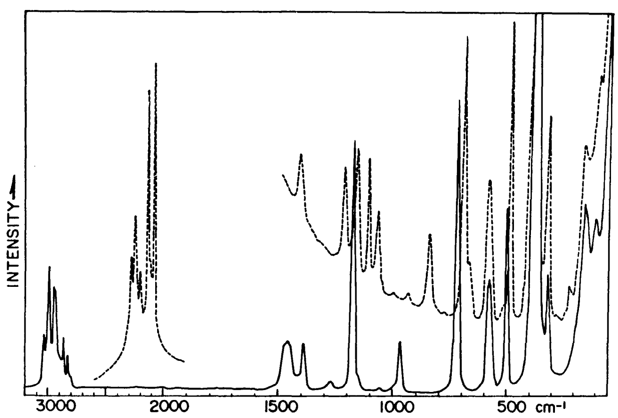

Fig. 2. Raman spectra of DMSCl (——) and DMSCl-d_6 (----).

Experimental

Materials. Dimethylaminosulfonyl chloride, DMSCl, was prepared by the reaction between sulfuryl chloride and dimethylamine hydrochloride (reagent grade).[3] Dimethyl-d_6-aminosulfonyl chloride, DMSCl-d_6, was synthesized by the same reaction with the use of dimethyl-d_6-amine hydrochloride (Merck AG., 98% deuterated), and distilled twice under reduced pressure (bp 83—85 °C at 25 mmHg). The isotopic purity of the product was estimated to be more than 98% by NMR spectra.

Measurements. The infrared spectra were measured in the liquid state on a JASCO DS 403G grating spectrophotometer. The absorption frequencies were calibrated by the standard absorptions of polystyrene, indene and water vapor. The Raman spectra were measured for the liquid samples sealed in 1 mm unheparinized haematocript tubes on a JEOL S-1 laser Raman spectrophotometer. The 488.0 nm line of a Coherent 52G Ar$^+$ laser was used as the excitation source.

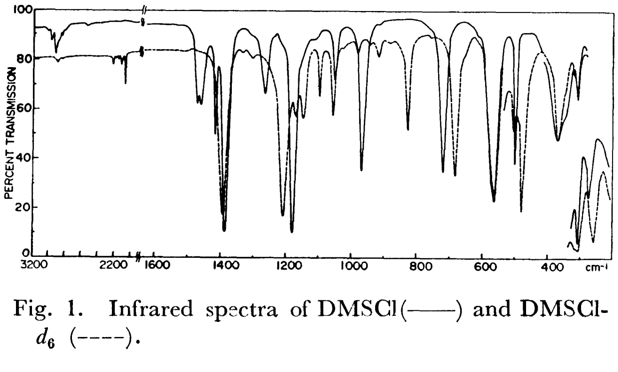

Fig. 1. Infrared spectra of DMSCl (——) and DMSCl-d_6 (----).

The infrared spectra are shown in Fig. 1 and the Raman spectra in Fig. 2. The observed frequencies are listed in Table 1 together with approximate band intensities and assignments.

Vibrational Assignments

The fundamental frequencies of dimethylaminosulfonyl chloride were given rough assignments by Bürger *et al.*[1] and Schneider *et al.*[2] on the assumption that the vibrations of the methyl hydrogen atoms were virtually independent of the skeletal vibrations of the molecule. The spectral change on the *C*-deuteration of the methyl groups in this work revealed, however, that there are considerable vibrational couplings between the methyl groups and the other part of the molecule. The infrared bands at 1470 and 1459 cm^{-1} and the Raman band at 1456 cm^{-1} are assigned clearly to the CH_3 asymmetric deformation vibrations and the infrared band at 1416 cm^{-1} to the CH_3 symmetric deformation. On the *C*-deuteration, these bands disappear and the corresponding bands due to the CD_3 groups appear around 1150, 1100, and 1060 cm^{-1}. At the same time the strong infrared and Raman bands at 1177 cm^{-1} due certainly to the SO_2 symmetric stretching vibration shift to 1207 cm^{-1}. In the infrared spectrum no appreciable change in relative intensity is observed with these fre-

TABLE 1. OBSERVED FREQUENCIES AND ASSIGNMENTS

$(CH_3)_2NSO_2Cl$			$(CD_3)_2NSO_2Cl$		
IR[a)]	Raman[a, b)]	Assignments[c)]	IR[a)]	Raman[a, b)]	Assignments[c)]
2970 vw	2970 s , p 2950 s , p	$\nu_a CH_3(a',a'')$	2230 vw	2241 m, p	$\nu_a CD_3(a',a'')$
2860 vw	2860 m, p	$\nu_s CH_3(a',a'')$	2070 vw	2115 s , p 2075 s , p	$\nu_s CD_3(a',a'')$
1470 m	—	$\delta_a CH_3(a',a'')$	1395 vs	1400 m, dp	$\nu_a SO_2(a'')$
1459 m	1456 wb, p	$\delta_a CH_3(a',a'')$	1207 vs	1207 m, p	$\nu_s SO_2+\nu_s CNC(a')$
1416 m	—	$\delta_s CH_3(a',a'')$	1173 m	—	$\nu_a CNC+\delta_s CD_3(a'')$
1385 vs	1387 m, dp	$\nu_a SO_2(a'')$	1153 m	1155 m, p	$\nu_s SO_2+\delta_s CD_3 +\nu_s CNC(a')$
1264 m	1270 vw, p?	$\nu skel+\rho CH_3(a')$	1099 w	1102 m, p	$\delta_s CD_3+\nu SN(a')$
1177 vs	1177 s , p	$\nu_s SO_2(a')$ $\nu_a CNC+\rho CH_3(a'')$	1057 m	1065 m, p	$\delta_a CD_3(a',a'')$
1115 vw	—	$\rho CH_3(a')$	982 w	990 vw, dp	$\delta_a CD_3+\delta_s CD_3(a'')$
1049 m	1053 vw, ?	$\rho CH_3(a'')$	919 w	920 vw, p	$\rho CD_3(a')$
966 s	967 w, p	$\rho CH_3+\nu_s CNC(a')$ $\rho CH_3+\nu_a CNC(a'')$	827 m	835 vw, dp	$\rho CD_3(a'')$
			755 vw	760 vw, ?	$\rho CD_3+\nu skel(a')$ $\rho CD_3+\nu_a CNC(a'')$
716 s	718 vs, p	$\nu SN+\nu_s CNC(a')$	682 s	684 s , p	$\nu SN+\nu_s CNC(a')$
562 s	576 s , p	$\beta SO_2+\nu SCl(a')$	561 s	575 m, p	$\beta SO_2+\nu SCl(a')$
—	—	$\delta skel+\rho SO_2(a'')$	505 m	510 sh, ?	$\delta skel+\rho SO_2(a'')$
500 s	504 s , p	$\omega SO_2+\nu SCl(a')$	478 m	480 m, p	$\omega SO_2+\nu SCl(a')$
369 m	374 vs, p	$\nu SCl+\omega SO_2(a')$ $\delta skel(a')$	369 m	374 vs, p	$\nu SCl+\omega SO_2(a')$
			318 sh	—	$\delta skel(a')$
309 w	315 w, dp	$t SO_2(a'')$	309 w	315 w, dp	$t SO_2(a'')$
276 w	—	$\delta skel(a')$	257 w	—	$\delta skel(a')$
—	—	$\rho SO_2+t CNC(a'')$	—	218 vw, dp	$\rho SO_2+t CNC(a'')$
—	153 m, p	$\delta skel(a')$	—	150 m, p	$\delta skel(a')$
—	105 w, ?	$\tau SN(a'')$	—	95 w, ?	$\tau SN(a'')$

a) vs, very strong; s, strong; m, medium; w, weak; vw, very weak; b, broad; sh, shoulder. b) p, polarized; dp, depolarized. c) v, stretching; β, bending; δ, deformation; ρ, rocking; ω, wagging; t, twisting; τ, torsion.

quency shifts, while in the Raman spectrum the intensity of the 1177 cm^{-1} band of DMSCl seems to be partitioned among the 1207, 1155, and 1102 cm^{-1} bands of DMSCl-d_6. This result suggests that the SO_2 symmetric stretching vibration of DMSCl-d_6 couples strongly with the CD_3 deformation vibrations. On the contrary, the SO_2 asymmetric stretching band around 1390 cm^{-1} undergoes only a slight isotope shift in both the infrared and Raman spectra. The infrared band at 1264 cm^{-1} assigned previously to the CH_3 rocking vibration[1,2)] proved to disappear on the *C*-deuteration. According to the calculated normal modes, the contribution of the skeletal stretching vibrations to this band is also important. The infrared bands at 1115, 1049, and 966 cm^{-1} vanishing on the *C*-deuteration were assigned to the CH_3 rocking vibrations and were classified into the a′ and the a″ species by referring to the depolarization ratios of the corresponding Raman bands and the results of a preliminary calculation. The 1049 and the 966 cm^{-1} bands were assigned to the skeletal stretching vibrations by the previous authors.[1,2)] Similarly, the infrared bands at 919, 827, and 755 cm^{-1} of DMSCl-d_6 newly appearing on the *C*-deuteration were assigned to the CD_3 rocking vibrations. The infrared band at 716 cm^{-1} of DMSCl shifts to 682 cm^{-1} on the *C*-deuteration and can be assigned to the S–N stretching vibration in agreement with the assignment of Bürger *et al.*[1)] According to the calculated normal modes, the S–N stretching vibration contributes also to the infrared bands at 1264, 1177 and 966 cm^{-1} of DMSCl and at 1207, 1153, 1099, and 755 cm^{-1} of DMSCl-d_6.

The polarized Raman band at 374 cm^{-1} is extremely strong and remains unshifted on the *C*-deuteration. This band is assigned certainly to the S–Cl stretching vibration from analogy with the spectra of CH_3SO_2Cl and CD_3SO_2Cl.[4)] The previous authors assigned this band to the C–N–C deformation vibration,[1,2)] but such a strong band is missing in the Raman spectrum of $(CH_3)_2NSO_2NH_2$.[5)] On the *C*-deuteration of DMSCl, the infrared bands at 562 and 309 cm^{-1} remain unshifted but those at 500 and 276 cm^{-1} shift to lower frequencies by about 20 cm^{-1}. By referring to the Raman depolarization ratios and the assignments of the related compounds,[4,6–9)] the 562, 500, and 309 cm^{-1} bands were assigned to the SO_2 bending, wagging and twisting vibrations, respectively, and the 276 cm^{-1} band to the skeletal deforamtion vibration. The present as-

TABLE 2. PRODUCT AND MODIFIED SUM RULES

	Product rule ratios[a)]		Modified sum rule[c)]
	Obsd[b)]	Calcd	
a′	19.693	20.634	1.5534×10^7 (cm^{-1})^2
a″	19.760	19.828	1.5492×10^7 (cm^{-1})^2

a) $\Pi(\nu_i \mathrm{DMSCl}/\nu_i{}' \mathrm{DMSCl}\text{-}d_6)$. b) The calculated frequencies were used in place of the unobserved frequencies. c) $\Sigma(\nu_i \mathrm{DMSCl})^2-\Sigma(\nu_i{}' \mathrm{DMSCl}\text{-}d_6)^2$.

TABLE 3. FORCE CONSTANTS (in mdyn/Å)

K(SO)	9.723_1	K(SN)	3.010_3	K(SCl)	1.439_9	K(CN)	2.580_3	K(CH)	4.573[a]
H(OSO)	1.099_3	H(OSN)	0.115_6	H(OSCl)	0.141_0	H(NSCl)	0.213[a]	H(SNC)	0.243_1
H(CNC)	0.091_2	H(NCH)	0.357_4	H(HCH)	0.457_9	F(OSO)	-0.581_4	F(OSN)	1.657_4
F(OSCl)	0.402[a]	F(NSCl)	0.200[a]	F(SNC)	0.685_1	F(CNC)	0.703[a]	F(NCH)	0.372_8
F(HCH)	-0.037_0	κ(S)[b]	0.022[a]	κ(C)[b]	-0.048_8	τ(SN)[c]	0.279_4	τ(CN)[c]	0.090[a]

a) Assumed. b) in mdyn Å. c) Torsional constant in mdyn Å/rad^2.

signments of the SO_2 deformation vibration are considerably different from those of the previous authors.[1,2] An infrared band at 505 cm^{-1} and a Raman band at 218 cm^{-1} of DMSCl-d_6 newly appearing on the *C*-deuteration are assignable to the a″ skeletal deformation and the SO_2 rocking vibrations, respectively. The corresponding bands of DMSCl seem to be overlapped by the neighboring bands at the higher frequency side. The weak Raman band at 105 cm^{-1} of DMSCl is assigned to the S–N torsional vibration since the observed shift to 95 cm^{-1} on the *C*-deuteration is too small for the CH_3 torsion. No bands assignable to the CH_3 or the CD_3 torsional vibrations were observed.

Normal Coordinate Analysis

Following Schneider *et al.*,[2] we assumed that dimethylaminosulfonyl chloride takes the C_s structure in which each SO bond is at the trans position of a CH_3–N bond. In this model, the normal modes of DMSCl are classified as 18a′+15a″. The structure parameters used in the calculation are shown in Fig. 3. The bond lengths and the valence angles related to the C_2NS skeleton were taken from tetramethylsulfuric diamide[10] and those related to the SO_2 group from sulfuryl chloride.[11] The tetrahedral angle was assumed for the methyl group. The local symmetry coordinates were constructed in the usual form[12] and the redundant coordinate associated with the $-SO_2-$ group was eliminated numerically on diagonalizing the G matrices. The torsional coordinates were those defined by Miyazawa and Fukushima.[13]

A simple Urey-Bradley force field including 25 force constants was employed for the stretching and the bending coordinates and a valence force field for the torsional coordinates. Initially, the force constants for the $(CH_3)_2N$– group were transferred from methylamine,[14] those for the $-SO_2Cl$ group from sulfuryl chloride[7] and those around the S–N bond from sulfuric diamide.[9] The torsional force constants τ(C–N) and τ(S–N) were assumed to be equal to the constants for the C–C and the C–S torsional coordinates of dialkyl disulfide,[15] respectively. On refining the force constants, the observed frequencies were taken mostly from the infrared

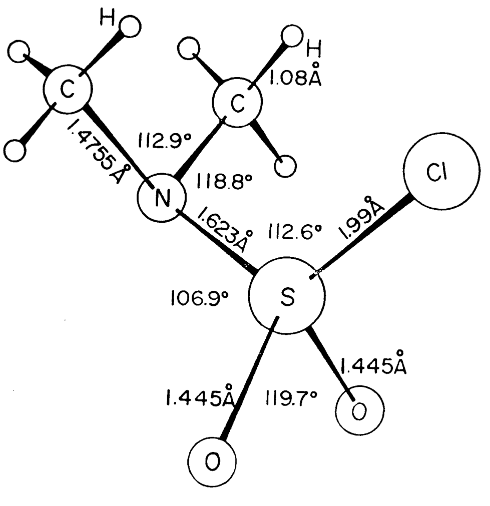

Fig. 3. Molecular structure and structural parameters.

TABLE 4. FUNDAMENTAL FREQUENCIES OF DMSCl AND DMSCl-d_6

	DMSCl		DMSCl-d_6	
	Obsd	Calcd	Obsd	Calcd
a′	2970	2981	2230	2222
	2970	2979	2230	2215
	2860	2849	2070	2053
	1470	1476	1207	1228
	1459	1471	1153	1159
	1416	1440	1099	1107
	1264	1238	1057	1053
	1177	1166	1057	1029
	1115	1109	919	888
	966	960	755	792
	716	725	682	665
	562	563	561	559
	500	505	478	490
	369	369	369	364
	369	365	318	335
	276	290	257	267
	—	196	—	140
	153[a]	117	150[a]	108
a″	2970	2980	2230	2217
	2970	2979	2230	2215
	2860	2848	2070	2050
	1470	1467	1395	1391
	1459	1462	1173	1175
	1416	1430	1057	1055
	1385	1390	1057	1041
	1177	1163	982	1019
	1049	1057	827	813
	966	992	755	793
	—	512	505	483
	309	305	309	302
	—	252	218[a]	235
	—	200	—	144
	105[a]	105	95[a]	94

a) Raman frequency.

data. These frequencies satisfied the isotopic product rule[16] and the modified sum rule[17] fairly well as shown in Table 2. The force constants were refined first by referring to the Jacobian matrix elements, and then by the method of least squares. The final set of the force constants is listed in Table 3, and the calculated frequencies are compared with the observed ones in Table 4.

In support of the empirical assignments given in the preceding section, the observed shifts of the skeletal frequencies below 750 cm^{-1} on the *C*-deuteration were reproduced well by the calculation. The stretching constant $K(SN)$ is appreciably smaller than the corresponding constants of $NH_2SO_2NH_2$[9] and $CH_3SO_2NH_2$,[6] probably because the electron drawing effect of the chlorine atom tends to reduce the S–N bond order. The constant $K(SCl)$ is also smaller than that of $ClSO_2Cl$[7] but is comparable with that of CH_3SO_2Cl.[4] The value of $K(SO)$ is close to the average of those of $NH_2SO_2NH_2$[9] and $ClSO_2Cl$,[7] reflecting well the intermediate structure, NSO_2Cl, of DMSCl. Regarding $K(SO)$, it may be also pointed out that $CH_3SO_2NH_2$,[6] $CH_3SO_2CH_3$[8] and $NH_2SO_2NH_2$[9] are all alike while DMSCl resembles CH_3SO_2Cl.[4] Thus, the effect of the NR_2($R=H$ or CH_3) group on the S–O bond order is similar to that of the CH_3 group, and in this respect the SO_2 group differs markedly from the C=O group as pointed out by Bellamy and Williams.[18]

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