The Infrared Spectrum of Dimethyl Sulfone

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In the preceding paper[1] normal vibrations and force constants of the methanesulfonate ion were determined empirically. In this paper the infrared spectrum of dimethyl sulfone was measured, the normal vibrations of this molecule were calculated using force constants of the methanesulfonate ion, and they were compared with the experimental values.

Calculation of Normal Vibrations

The calculation was done by means of Wilson's method[2] and treated as a five-body problem assuming the methyl radical to be one particle. As the intramolecular potential, Urey-Bradley field[3] was assumed as done in the case of the methanesulfonate ion[1]. By assuming all the valence angles of sulfur to be tetrahedral, the following elements of G and F materices were obtained[4].

Elements of G matrix for A_1 type vibrations

$$g_{11}=\frac{2}{3}\mu_{\mathrm{S}}+\mu_{\mathrm{Me}}$$

$$g_{12}=-\frac{2}{3}\mu_{\mathrm{S}}$$

$$g_{13}=\frac{2}{\sqrt{3}}(\sigma'-1)\mu_{\mathrm{S}}$$

$$g_{14}=-\frac{\sqrt{8}}{3}(\sigma'+1)\mu_{\mathrm{S}}$$

$$g_{22}=\frac{2}{3}\mu_{\mathrm{S}}+\mu_{\mathrm{O}}$$

$$g_{23}=-\frac{2}{\sqrt{3}}(\sigma'-1)\mu_{\mathrm{S}}$$

$$g_{24}=\frac{\sqrt{8}}{3}(\sigma'+1)\mu_{\mathrm{S}}$$

$$g_{33}=\frac{3}{2}(\sigma'^2\mu_{\mathrm{Me}}+\mu_{\mathrm{O}})+2(\sigma'-1)^2\mu_{\mathrm{S}}$$

$$g_{34}=-\frac{1}{\sqrt{6}}\{3(\sigma'^2\mu_{\mathrm{Me}}-\mu_{\mathrm{O}})+4\sigma'(\sigma'-1)\mu_{\mathrm{S}}\}$$

$$g_{44}=\sigma'^2\mu_{\mathrm{Me}}+\mu_{\mathrm{O}}+\frac{4}{3}(\sigma'+1)^2\mu_{\mathrm{S}}$$

Elements of F matrix for A_1 type vibrations

$$f_{11}=K_{\mathrm{SMe}}+2(s^2_{\mathrm{Me}}F_{\mathrm{Me}}+t^2_{\mathrm{MeO}}F'_{\mathrm{MeO}}$$
$$+s^2_{\mathrm{MeO}}F_{\mathrm{MeO}})$$

$$f_{12}=-2(t_{\mathrm{MeO}}t_{\mathrm{OMe}}F'_{\mathrm{MeO}}+s_{\mathrm{MeO}}s_{\mathrm{OMe}}F_{\mathrm{MeO}})$$

$$f_{13}=\sqrt{\frac{2}{3}}\{(t_{\mathrm{MeO}}s_{\mathrm{OMe}}F'_{\mathrm{MeO}}+t_{\mathrm{OMe}}s_{\mathrm{MeO}}F_{\mathrm{MeO}})$$
$$+\sigma t_{\mathrm{Me}}s_{\mathrm{Me}}(F'_{\mathrm{Me}}+F_{\mathrm{Me}})\}$$

$$f_{14}=\sigma t_{\mathrm{Me}}s_{\mathrm{Me}}(F'_{\mathrm{Me}}+F_{\mathrm{Me}})$$

$$f_{22}=K_{\mathrm{SO}}+2(t^2_{\mathrm{OMe}}F'_{\mathrm{MeO}}+s^2_{\mathrm{OMe}}F_{\mathrm{MeO}}+s^2_{\mathrm{O}}F_{\mathrm{O}})$$

$$f_{23}=\sqrt{\frac{2}{3}}(t_{\mathrm{OMe}}s_{\mathrm{MeO}}F'_{\mathrm{MeO}}+t_{\mathrm{MeO}}s_{\mathrm{OMe}}F_{\mathrm{MeO}})$$
$$-t_{\mathrm{O}}s_{\mathrm{O}}(F'_{\mathrm{O}}+F_{\mathrm{O}})\}$$

$$f_{24}=-t_{\mathrm{O}}s_{\mathrm{O}}(F'_{\mathrm{O}}+F_{\mathrm{O}})$$

$$f_{33}=\frac{1}{3}\{\sigma^2(H_{\mathrm{Me}}-s^2_{\mathrm{Me}}F'_{\mathrm{Me}}+t^2_{\mathrm{Me}}F_{\mathrm{Me}})$$
$$+(H_{\mathrm{O}}-s^2_{\mathrm{O}}F'_{\mathrm{O}}+t^2_{\mathrm{O}}F_{\mathrm{O}})\}$$

$$f_{34}=\frac{1}{\sqrt{6}}\{-\sigma^2(H_{\mathrm{Me}}-s^2_{\mathrm{Me}}F'_{\mathrm{Me}}+t^2_{\mathrm{Me}}F_{\mathrm{Me}})$$
$$+(H_{\mathrm{O}}-s^2_{\mathrm{O}}F'_{\mathrm{O}}+t^2_{\mathrm{O}}F_{\mathrm{O}})\}$$

$$f_{44}=\frac{1}{2}\{\sigma^2(H_{\mathrm{Me}}-s^2_{\mathrm{Me}}F'_{\mathrm{Me}}+t^2_{\mathrm{Me}}F_{\mathrm{Me}})$$
$$+(H_{\mathrm{O}}-s^2_{\mathrm{O}}F'_{\mathrm{O}}+t^2_{\mathrm{O}}F_{\mathrm{O}})\}+\frac{3}{\sqrt{8}}\kappa/r^2_{\mathrm{SO}}$$

Elements of G and F matrices for A_2 type vibration

$$g=\frac{3}{2}\sigma'^2\mu_{\mathrm{Me}}+\frac{3}{2}\mu_{\mathrm{O}}+\frac{1}{3}(5\sigma'^2+2\sigma'+5)\mu_{\mathrm{S}}$$

$$f=\sigma(H_{\mathrm{MeO}}-s_{\mathrm{MeO}}s_{\mathrm{OMe}}F'_{\mathrm{MeO}}+t_{\mathrm{MeO}}t_{\mathrm{OMe}}F_{\mathrm{MeO}})$$
$$-\frac{1}{\sqrt{8}}\kappa/r^2_{\mathrm{SO}}$$

Elements of G matrix for B_1 type vibrations

$$g_{11}=\frac{4}{3}\mu_{\mathrm{S}}+\mu_{\mathrm{Me}}$$

$$g_{12}=-\frac{2}{3}(\sigma'+3)\mu_{\mathrm{S}}$$

$$g_{22}=\frac{1}{2}\sigma'^2\mu_{\mathrm{Me}}+\frac{3}{2}\mu_{\mathrm{O}}+\frac{1}{3}(\sigma'+3)^2\mu_{\mathrm{S}}$$

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[2] E. B. Wilson, *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).

[3] H. C. Urey and C. A. Bradley, *Phys. Rev.*, **38**, 1946 (1931).

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Elements of F matrix for B_1 type vibrations

$$f_{11}=K_{\mathrm{SMe}}+2(t^2{}_{\mathrm{Me}}F'{}_{\mathrm{Me}}+t^2{}_{\mathrm{MeO}}F'{}_{\mathrm{MeO}}+s^2{}_{\mathrm{MeO}}F_{\mathrm{MeO}})$$

$$f_{12}=\sqrt{2}\,(t_{\mathrm{MeO}}s_{\mathrm{OMe}}F'{}_{\mathrm{MeO}}+t_{\mathrm{OMe}}s_{\mathrm{MeO}}F_{\mathrm{MeO}})$$

$$f_{22}=\sigma(H_{\mathrm{MeO}}-s_{\mathrm{OMe}}s_{\mathrm{MeO}}F'{}_{\mathrm{MeO}}+t_{\mathrm{MeO}}t_{\mathrm{OMe}}F_{\mathrm{MeO}})+\frac{3}{\sqrt{8}}\kappa/r^2{}_{\mathrm{SO}}$$

Elements of G matrix for B_2 type vibrations

$$g_{11}=\frac{4}{3}\mu_{\mathrm{S}}+\mu_{\mathrm{O}}$$

$$g_{12}=-\frac{2}{3}(3\sigma'+1)\mu_{\mathrm{S}}$$

$$g_{22}=\frac{3}{2}\sigma'^2\mu_{\mathrm{Me}}+\frac{1}{2}\mu_{\mathrm{O}}+\frac{1}{3}(3\sigma'+1)^2\mu_{\mathrm{S}}$$

Elements of F matrix for B_2 type vibrations

$$f_{11}=K_{\mathrm{SO}}+2(t^2{}_{\mathrm{OMe}}F'{}_{\mathrm{MeO}}+s^2{}_{\mathrm{OMe}}F_{\mathrm{MeO}}+t^2{}_{\mathrm{O}}F'{}_{\mathrm{O}})$$

$$f_{12}=\sqrt{2}\,\sigma(t_{\mathrm{OMe}}s_{\mathrm{MeO}}F'{}_{\mathrm{MeO}}+t_{\mathrm{MeO}}s_{\mathrm{OMe}}F_{\mathrm{MeO}})$$

$$f_{22}=\sigma(H_{\mathrm{MeO}}-s_{\mathrm{OMe}}s_{\mathrm{MeO}}F'{}_{\mathrm{MeO}}+t_{\mathrm{MeO}}t_{\mathrm{OMe}}F_{\mathrm{MeO}})+\frac{3}{\sqrt{8}}\kappa/r^2{}_{\mathrm{SO}}$$

where, K is the stretching force constant, H is the bending force constant and F and F' are repulsive force constants. And μ is the reciprocal of the atomic weight of sulfur, oxygen or the methyl radical.

The following notations are also used:

$$s_{ij}=(r_i-r_j\cos\alpha_{ij})/q_{ij},$$

$$s_{.i}=(r_i-r_j\cos\alpha_i)/q_{ij},\quad t_{ij}=r_j\sin\alpha_{ij}/q_{ij},$$

$$t_{ji}=r_i\sin\alpha_{ij}/q_{ij},\quad \sigma=r_{\mathrm{SMe}}/r_{\mathrm{SO}},\quad \sigma'=1/\sigma,$$

κ (intramolecular tension)

$$=-(K'{}_ir_{ij}{}^2+H'{}_{ij}r_{ij}q_{ij}\sqrt{t_{ij}t_{ji}}),$$

where r denotes S–O or S–Me bond length, q_{ij} denotes distance between non-bonded atoms, α_{ij} denotes valence angle and $r^2{}_{ij}=r_ir_j$.

For the S–O and S–Me bond length, the following values were assumed. S–O= 1.43 Å, S–Me=1.80 Å⁵⁾.

Force constants were transferred from methanesulfonate ion¹⁾, diethyl sulfide⁶⁾, tetramethyl silane⁷⁾ and sulfur dioxide⁸⁾. Their values are given in Table I.

TABLE I. FORCE CONSTANTS

F. C.	10^5 dyn./cm.	Ref.	F. C.	10^5 dyn./cm.	Ref.
K_{SMe}	3.05	1)	$F'{}_{\mathrm{Me}}$	−0.020	7)
K_{SO}	9.86	8)	F_{O}	0.64	1)
H_{Me}	0.157	6)	$F'{}_{\mathrm{O}}$	−0.064	1)
H_{O}	0.552	1)	F_{MeO}	0.35	1)
H_{MeO}	0.250	1)	$F'{}_{\mathrm{MeO}}$	−0.035	1)
F_{Me}	0.200	7)	κ	0.328*	1)

* Unit is 10^{-11} dyn./cm.

Results and Discussion

The calculated normal vibrations are given in Table II. The infrared spectrum of dimethyl sulfone in a solid state is shown in Fig. 1. The absorption frequencies are compared with the observed values and their assignments are made as shown in Table III.

TABLE II. CALCULATED NORMAL VIBRATIONS (in cm^{-1})

Type	Wave number	Assignment
A_1	741	S-Me stretching
	314	$\mathrm{S(Me)_2}$ bending
	1252	S-O stretching
	521	$\mathrm{SO_2}$ bending
A_2	408	twisting
B_1	795	S-Me stretching
	472	$\mathrm{S(Me)_2}$ rocking $\mathrm{SO_2}$ wagging
B_2	1345	S-O stretching
	428	$\mathrm{S(Me)_2}$ wagging $\mathrm{SO_2}$ rocking

TABLE III. ABSORPTIONS AND ASSIGNMENTS (in cm^{-1})

Wave number	Assignment	Calcd.
3024 (m) 2962 (w)	C-H stretching	
1430 (m) 1412 (m)	$\mathrm{CH_3}$ degenerated bending	
1337 (s)	$\mathrm{CH_3}$ symmetric bending	
1315 (s) 1290 (s)	S-O stretching	1345
1130 (s)	S-O stretching	1252
938 (s)	Me rocking	
761 (s)	S-Me stretching	795
695 (m)	S-Me stretching	741

C–H stretching frequencies have higher wave numbers than those of hydrocarbons because of strong electronegativity of $-\mathrm{SO_2}-$ group. This phenomenon was also found in the case of lower sulfonates⁹⁾. Methyl rocking vibration at 938 cm^{-1} has lower wave number than that of methanesulfonate ion. The reason may be attributed to the coupling with S–O stretching vibration.

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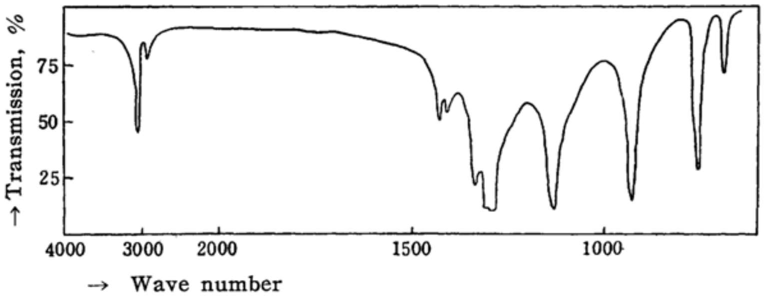

Fig. 1. Infrared spectrum of dimethyl sulfone.

The deviation between the observed and calculated frequencies may be attributed to the high value of S–O stretching force constant and the low value of O–O repulsive force constants.

Experimental

The infrared spectrum was obtained by a Perkin-Elmer Model 21 double-beam infrared spectrophotometer using NaCl prism. The KBr disk method was employed to obtain the spectrum in solid state.

Dimethyl sulfone was prepared by oxidation of dimethyl sulfoxide with hydrogen peroxide in acetic acid solution[10]. After the reaction mixture was treated with acetaldehyde and the solvent was removed, dimethyl sulfone was recrystallized from ethanol. The melting point of this compound is 108.5°C and the referenced value is 109°C[11].

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