The Normal Vibrations of Methanesulfonate Ion

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In the preceding paper[1] the infrared spectra of *n*-alkane-1-sulfonates were investigated and it was found that two S–O stretching vibrations and C–S stretching vibration were in the rock salt region.

In this paper the normal vibrations of the methanesulfonate ion were calculated, assuming the Urey-Bradley's field as the intra-molecular potential. This calculation was treated as a five-body problem, supposing the methyl radical to be one particle.

Calculation of Normal Vibration

Molecular Shape.—It was assumed that the methyl radical was one particle and the molecular shape of the methanesulfonate ion was similar to that of chloroform, i. e., this ion had the symmetry property of C_{3v}. This assumption is not reckless under the first order approximation[2].

Intra-molecular Potential. — As intra-molecular potential, the following Urey-Bradley's field[3] is assumed

$$V=\sum V_{r_i}+\sum_{i>j} V_{\alpha_{ij}}+\sum_{i>j} V_{q_{ij}}$$

where

$$V_{r_i}=K'_i r_i \varDelta r_i+\frac{1}{2}K_i(\varDelta r_i)^2$$

$$V_{\alpha_{ij}}=H'_{ij}r^2\varDelta\alpha_{ij}+\frac{1}{2}H_{ij}(r_{ij}\varDelta\alpha_{ij})^2$$

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[1] K. Fujimori, This Bulletin, in press.

[2] A. Simon and H. Kriegsmann, *Chem. Ber.*, **89**, 1718 (1956).

[3] H. C. Urey, C. A. Bradley, *Phys. Rev.*, **38**, 1969 (1931).

$$V_{q_{ij}}=F'_{ij}q_{ij}\Delta q_{ij}+\frac{1}{2}F_{ij}(\Delta q_{ij})^2$$

and

K_i and K'_i: stretching force constants
H_{ij} and H'_{ij}: bending force constants
F_{ij} and F'_{ij}: repulsive force constants
r_i: distance between the central atom and the i-th atom
q_{ij}: distance between non-bonded atoms
r^2_{ij}: equals r_ir_j
α_{ij}: valence angle.

***G* and *F* Matrixes.**—The G and F marixes of this molecule were made by Wilson's method[4] and were factored by symmetry property of C_{3v}[5]. The following elements were obtained.

a) *A_1 type vibration (totally symmetric vibration)*.—i) Elements of G matrix

$$g_{11}=\mu_{\mathrm{S}}+\mu_{\mathrm{R}} \qquad g_{22}=-\frac{1}{3}\mu_{\mathrm{S}}+\mu_{\mathrm{O}}$$

$$g_{12}=-\frac{1}{\sqrt{3}}\mu_{\mathrm{S}} \qquad g_{23}=\frac{4}{3}\mu_{\mathrm{S}}$$

$$g_{13}=-\frac{4}{\sqrt{3}}\mu_{\mathrm{S}} \qquad g_{33}=\frac{16}{3}\mu_{\mathrm{S}}+2\mu_{\mathrm{O}}$$

ii) Elements of F matrix

$$f_{11}=K_{\mathrm{S-R}}+3t^2_{\mathrm{R-O}}F'_{\mathrm{R-O}}+3s^2_{\mathrm{R-O}}F_{\mathrm{R-O}}$$

$$f_{12}=\sqrt{3}\,(-t_{\mathrm{O-R}}t_{\mathrm{R-O}}F'_{\mathrm{R-O}}+s_{\mathrm{R-O}}s_{\mathrm{O-R}}F_{\mathrm{R-O}})$$

$$f_{13}=\frac{\sqrt{3}}{2}(t_{\mathrm{R-O}}s_{\mathrm{O-R}}F'_{\mathrm{R-O}}+t_{\mathrm{O-R}}s_{\mathrm{R-O}}F_{\mathrm{R-O}})$$

$$f_{22}=K_{\mathrm{S-O}}+t^2_{\mathrm{O-R}}F'_{\mathrm{R-O}}+s^2_{\mathrm{O-R}}F_{\mathrm{R-O}}$$
$$+4s^2_{\mathrm{O-O}}F_{\mathrm{O-O}}$$

$$f_{23}=\frac{1}{\sqrt{2}}\{(t_{\mathrm{O-R}}s_{\mathrm{R-O}}F'_{\mathrm{R-O}}+t_{\mathrm{R-O}}s_{\mathrm{O-R}}F_{\mathrm{R-O}})\sigma$$
$$-2t_{\mathrm{O-O}}s_{\mathrm{O-O}}(F'_{\mathrm{O-O}}+F_{\mathrm{O-O}})\}$$

$$f_{33}=\frac{1}{2}\{(H_{\mathrm{R-S-O}}-s_{\mathrm{R-O}}s_{\mathrm{O-R}}F'_{\mathrm{R-O}}$$
$$+t_{\mathrm{R-O}}t_{\mathrm{O-R}}F_{\mathrm{R-O}})\sigma$$
$$+(H_{\mathrm{O-S-O}}-s^2_{\mathrm{O-O}}F'_{\mathrm{O-O}}+t^2_{\mathrm{O-O}}F_{\mathrm{O-O}})\}$$
$$+\frac{3}{\sqrt{8}}\kappa/r^2_{\mathrm{S-O}}$$

b) *E type vibration (doubly degenerated vibration)*.—i) Elements of G matrix

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

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

$$g_{13}=\frac{4\sqrt{2}}{3}\mu_{\mathrm{S}}$$

$$g_{22}=\mu_{\mathrm{O}}+\left(\frac{1}{\sigma}\right)^2\mu_{\mathrm{R}}+\frac{1}{6}\left(\frac{3}{\sigma}+1\right)^2\mu_{\mathrm{S}}$$

$$g_{23}=-\frac{2}{3}\left(\frac{3}{\sigma}+1\right)\mu_{\mathrm{S}}+\frac{1}{2}\mu_{\mathrm{O}}$$

$$g_{33}=\frac{8}{3}\mu_{\mathrm{S}}+\frac{5}{2}\mu_{\mathrm{O}}$$

ii) Elements of F matrix

$$f_{11}=K_{\mathrm{S-O}}+t^2_{\mathrm{O-R}}F'_{\mathrm{R-O}}+s^2_{\mathrm{O-R}}F_{\mathrm{R-O}}$$
$$+3^2t_{\mathrm{O-O}}F'_{\mathrm{O-O}}+s^2_{\mathrm{O-O}}F_{\mathrm{O-O}}$$

$$f_{12}=(t_{\mathrm{O-R}}s_{\mathrm{R-O}}F'_{\mathrm{R-O}}+t_{\mathrm{R-O}}s_{\mathrm{O-R}}F_{\mathrm{R-O}})\sigma$$

$$f_{13}=-t_{\mathrm{O-O}}s_{\mathrm{O-O}}(F'_{\mathrm{O-O}}+F_{\mathrm{O-O}})$$

$$f_{22}=(H_{\mathrm{O-S-R}}-s_{\mathrm{R-O}}s_{\mathrm{O-R}}F'_{\mathrm{R-O}}$$
$$+t_{\mathrm{R-O}}t_{\mathrm{O-R}}F_{\mathrm{R-O}})\sigma+\left(\frac{1}{\sqrt{8}}\right)\kappa/r^2_{\mathrm{S-O}}$$

$$f_{23}=-\frac{\sqrt{2}}{2}\kappa/r^2_{\mathrm{S-O}}$$

$$f_{33}=(H_{\mathrm{O-S-O}}-s^2_{\mathrm{O-O}}F'_{\mathrm{O-O}}+t^2_{\mathrm{O-O}}F_{\mathrm{O-O}})$$
$$+\frac{1}{\sqrt{8}}\kappa/r^2_{\mathrm{S-O}}$$

where the following notations are used;

κ(intra-molecular tension)

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

$$\sigma=r_{\mathrm{R-S}}/r_{\mathrm{S-O}}, \qquad s_{ij}=(r_i-r_j\cos\alpha_{ij})/q_{ij}$$

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

and $t_{ji}=r_i\sin\alpha_{ij}/q_{ij}$

and μ_{S}, μ_{O} and μ_{R} are reciprocals of atomic weights for sulfur, oxygen and the methyl radical, respectively.

Constants Used in Calculation.—*a*) *Nuclear distances.*—

S–O : 1.50 A[6]
S–R : 1.80 A*

b) *Valence angles.*—Valence angles for O–S–O and R–S–O are assumed to equal the tetrahedral one, that is 109°28′.

c) *Force constants.*—$K_{\mathrm{S-O}}$, $H_{\mathrm{O-S-O}}$ and $F_{\mathrm{O-O}}$ are taken from those for sulfate ion[8], and $K_{\mathrm{R-S}}$ is taken from $H_{\mathrm{Me-S}}$ of dimethyl sulfide[9]. $H_{\mathrm{R-S-O}}$ is taken from the mean of $H_{\mathrm{O-S-O}}$ for sulfate ion and $H_{\mathrm{CH_2-S-CH_2}}$ for diethyl sulfide[9]. $F_{\mathrm{R-O}}$ is taken from the mean of $F_{\mathrm{O-O}}$ for sulfate ion and $F_{\mathrm{Me-Me}}$ for tetramethyl silane[8]. $\kappa_{\mathrm{MeSO^-_3}}$ is taken

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

5) T. Shimanouchi, *Bulletine Inst. Phys. Chem. Research Tokyo* (*Riken Iho*), **21**, 825 (1942).

6) A. Simon and H. Kriegsmann, *Z. Phys. Chem.*, **209**, 369 (1955).

* Summation of Pauling's covalent radii of single carbon and sulfur[7].

7) L. Pauling, "The Nature of the Chemical Bond", Cornell Univ. Press, Ithaca, N. Y. (1940), p. 164.

8) T. Shimanouchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **74**, 226 (1953).

9) M. Hayashi, ibid., **77**, 1962 (1956).

from the mean of $\kappa_{SO_4^{2-}}$ and $\kappa_{Si(CH_3)_4}$[8]. F' is assumed to be $-1/10$ F[8]. In Table I values of these force constants are given.

TABLE I. FORCE CONSTANTS

F. C.	(dyn./cm.)×10⁵	F. C.	(dyn./cm.)×10⁵
K_{S-O}	6.01	F'_{O-O}	−0.076
K_{S-R}	3.01	F_{O-R}	0.397
H_{O-S-O}	0.43	F'_{O-R}	−0.0397
H_{O-S-R}	0.294	κ	0.328*
F_{O-O}	0.76		

* Unit is (dyn./cm.)×10^{-11}.

Results, Assignment and Comparison with Observed Data

As the results of calculation, the following values were obtained:

$$\nu_1 = 788\,\text{cm}^{-1} \quad \nu_2 = 1002\,\text{cm}^{-1} \quad \nu_3 = 538\,\text{cm}^{-1}$$
$$\nu_4 = 1081\,\text{cm}^{-1} \quad \nu_5 = 537\,\text{cm}^{-1} \quad \nu_6 = 367\,\text{cm}^{-1}$$

Of these vibrations ν_1, ν_2 and ν_3 are totally symmetric and ν_4, ν_5 and ν_6 are doubly degenerated.

These values are compared with the results of Raman spectra of potassium methanesulfonate in aqueous solution studied by Simon and Kriegsmann[6]. Relatively strong lines which could not be considered as C–H stretching and C–H deformation vibrations, are as follows: 348 cm⁻¹(5b), 533 cm⁻¹(2), 560 cm⁻¹(4), 789 cm⁻¹(8), 1054 cm⁻¹ (10) and 1184 cm⁻¹ (2b). (Number in brackets are intensities of Raman lines.)

They attributed the lines at 789, 1054 and 1184 cm⁻¹ to ν_1 (C–S stretching vibration), ν_2 (S–O stretching totally symmetric vibration) and S–O stretching antisymmetric vibration, respectively.

By comparing the author's calculation with observed infrared spectra[1], the assignments can be made as indicated in Table II.

The agreement between the calculated and the observed frequencies is satisfactory except for S–O stretching vibration. The reason will be attributed to the fact that the S–O stretching force constant is taken from that of sulfate ion.

TABLE II. COMPARISON OF CALCULATED AND OBSERVED VALUES (in cm⁻¹)

Assignment	Raman	I. R.	Calcd. I	Calcd. II
C–S Stretching	789	789	788	789
S–O Stretching	1054	1060	1002	1055
Deformation	533		538	536
S–O Stretching	1184	1192	1080	1182
R–S–O Deformation	560		537	557
O–S–O Deformation	348		367	349

The force constants were corrected as indicated in Table III, using the trial and error method combined with the method of least squares[10]. If the calculation of normal vibration is done again using these corrected force constants, the agreement between the calculated and observed values becomes much more satisfactory. The calculated values are indicated in Table II as "Calcd. II".

TABLE III. CORRECTED FORCE CONSTANTS

F. C.	(dyn./cm.)×10⁵	F. C.	(dyn./cm.)×10⁵
K_{S-O}	7.31	F'_{O-O}	−0.065
K_{S-R}	3.05	F_{O-R}	0.34
H_{O-S-O}	0.552	F'_{O-R}	−0.034
H_{O-S-R}	0.26	κ	0.328*
F_{O-O}	0.65		

* Unit is (dyn./cm.)×10^{-11}.

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[10] D. E. Mann, T. Shimanouchi, J. H. Meal and L. Fano, *J. Chem. Phys.*, 27, 43 (1957).