InfraRed and Raman Spectra of Polyatomic Molecules. VIII. Dimethyl Ether

Bryce L. Crawford Jr. and Lois Joyce

Articles you may be interested in

Potential function (III).—The equations for (II) apply also for (IIId) and (IIIh), except that the constants K now have different meanings. K_1, K_2'', K_3' and K_4 are the same as above. Where there is a choice of sign in the following equations, the upper sign is for the first and the lower sign for the second of the two symmetry types whose symbols precede the equation.

(IIId):

$$A_{1g}, A_{2u}: K_2' = K_\beta \pm k_{\beta\beta} + ZK_\alpha$$
$$- 2(K_{\alpha\beta} \pm \tfrac{1}{2}k_{\beta\alpha} \pm k_{\beta\alpha}')\sqrt{Z}.$$

$$E_u, E_g: K_2 = K_\beta \pm \tfrac{1}{2}k_{\beta\beta}; K_5 = \tfrac{1}{2}Y(K_{\alpha\beta} \pm k_{\beta\alpha} \mp k_{\beta\alpha}').$$

(IIIh):

$$A_1', A_2'': K_2' = K_\beta \pm \tfrac{1}{2}k_{\beta\beta} + ZK_\alpha$$
$$- 2(K_{\alpha\beta} \pm k_{\beta\alpha})\sqrt{Z}.$$

$$E', E'': K_2 = K_\beta \pm \tfrac{1}{2}k_{\beta\beta}; K_5 = \tfrac{1}{2}Y(K_{\alpha\beta} \pm k_{\beta\alpha}).$$

Further details.—The symmetry coordinates used by Howard were also used in this work. The labor involved in the preliminary fitting of the potential function to the observed frequencies was greatly diminished by reducing the cubic equations to quadratics through neglect of the nondiagonal elements of the secular determinant in the row and column associated with the "hydrogen stretching" symmetry coordinate. The roots of the quadratics were usually within one percent of the corresponding roots of the cubic equations.

For finding the approximate solutions of complete cubic equations, the graphical method of Massau as simplified by d'Ocagne[31] was found very useful.

---

[31] M. d'Ocagne, *Traité de Nomographie* (Gauthier-Villars, Paris, 1921), p. 385.

Infra-Red and Raman Spectra of Polyatomic Molecules. VIII. Dimethyl Ether

Bryce L. Crawford, Jr.* and Lois Joyce†

Mallinckrodt Chemical Laboratory, Harvard University, Cambridge, Massachusetts

(Received February 20, 1939)

The infra-red spectrum of dimethyl ether has been studied from 2.5 to 22.5μ, and the available Raman data correlated with it. A tentative vibrational analysis is given.

IN CONNECTION with the research program on potentials restricting internal rotations of methyl groups, now in progress in this laboratory,[1] we have examined the infra-red spectrum of dimethyl ether between 2.5 and 22.5μ. We present here the infra-red data, together with an evaluation of the available Raman data and a tentative assignment of the vibrational frequencies.

EXPERIMENTAL

The material used was obtained from the Ohio Chemical Company; its purity was listed as 99.95 percent. It was used without further purification. The spectrometer has been previously described;[2] fluorite, rocksalt and KBr prisms were used in the appropriate regions. The absorption curve is given in Fig. 1; the frequencies of the absorption maxima are tabulated in Table I. The very weak shoulders found at 1102 and 2325 cm^{-1} are somewhat doubtful. The indications of the 1102 cm^{-1} shoulder are especially weak; however, these indications appear on every record of this region. A strong band not far below 450 cm^{-1} is shown quite clearly by the absorption curve. It is unfortunate that we were not able to go out to longer wave-lengths and find the center of this band.

The accuracy with which the frequencies were determined is indicated by the effective slit-widths given at appropriate points in Fig. 1.

---

* National Research Fellow in Chemistry.
† Present address, University of Illinois, Urbana, Illinois.
[1] B. L. Crawford, Jr., J. W. Linnett and W. H. Avery, J. Chem. Phys. 6, 682 (1938); G. B. Kistiakowsky, J. R. Lacher and W. W. Ransom, *ibid.* 6, 900 (1938); G. B. Kistiakowsky, J. R. Lacher and F. Stitt, *ibid.* 7, 289 (1939); F. Stitt, *ibid.* 7, 297 (1939).

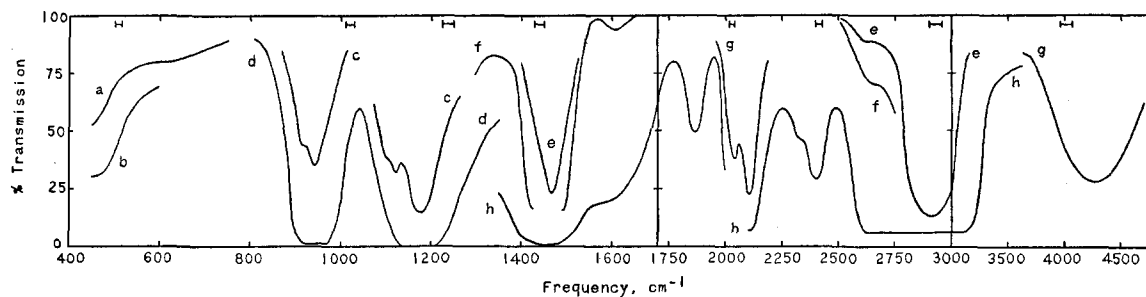[2] H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. 6, 197 (1938).

FIG. 1. Infra-red absorption of methyl ether. Path length, 30 cm. KBr prism: *a*, 208 mm pressure; *b*, 730 mm. Rock-salt prism: *c*, 15 mm; *d*, 208 mm. Fluorite prism: *e*, 34 mm; *f*, 117 mm; *g*, 254 mm; *h*, 760 mm. Effective slit-widths are shown near the top of the graph.

DISCUSSION

Previous work

The infra-red spectrum of dimethyl ether apparently has been studied previously only by Coblentz.[3] With due allowance for impurities contained in his sample (especially butane), his results for the stronger bands are in good agreement with ours.

The Raman spectrum has been studied several times.[4–8] The results of the investigations are tabulated in Table II. It will be seen that the agreement on the stronger lines is satisfactory. Of the weaker lines, we may accept that at 1100 cm^{-1} without question; the 1155 cm^{-1} line is also probably real. Two observers found a line near 300 cm^{-1}, but the discrepancy in the frequencies given is so serious that this line must be regarded as doubtful. We have rejected the lines at 160, 583 and 702 cm^{-1}, since each was found by a single observer only.

We may correlate the Raman and infra-red frequencies as shown in Table I. It is seen that each Raman frequency is also observed in the infra-red, in agreement with the selection rules (Table III and the following paragraph). The frequency shift is going from liquid to gas is roughly constant, about 20 cm^{-1}. A shift of this magnitude is quite reasonable in the case of a polar liquid such as methyl ether.

[3] W. W. Coblentz, *Investigations of Infrared Spectra* (Carnegie Institute of Washington, 1905), Part I.
[4] R. Ananthakrishnan, Proc. Ind. Acad. Sci. **A5**, 285 (1937).
[5] M. Vol'kenstein and Ya. K. Syrkin, Nature **139**, 288 (1937).
[6] S. C. Sirkar, Ind. J. Phys. **7**, 257 (1932).
[7] A. Dadieu and K. W. F. Kohlrausch, Monats. f. Chemie **57**, 225 (1931).
[8] K. W. F. Kohlrausch, Monats. f. Chemie **68**, 349 (1936).

Assignments

Although we shall not attempt a quantitative vibrational analysis at present, certain qualitative conclusions may be pointed out. The highest symmetry which the methyl ether molecule may have corresponds to the group C_{2v}; on this basis the normal coordinate representation, including two internal rotations, would have the structure $\Gamma = 7A_1 + 4A_2 + 4B_1 + 6B_2$. The various "group frequencies" which may be expected are apportioned among the symmetry classes as shown in Table III. The selection rules, which are not particularly helpful, are also given in this table.

TABLE I. *The vibrational spectra of methyl ether.*

INFRA-RED		RAMAN*	
FREQUENCY CM^{-1}	INTENSITY**	FREQUENCY CM^{-1}	INTENSITY POLARIZATION†
—	—	300	?, *P*
below 440	?	412	1, *P*
610	*w*	—	—
920	*m*		
940	*s*	920	5, *P*
1102	?		
1122	*m*	1100	0, ?
1180	*s*	1155	0, *D*
1466	*vs*	1450	4, *D*
1605	*w*	—	—
1862	*m*	—	—
2033	*m*	—	—
2101	*ms*	—	—
2325	?	—	—
2400	*mw*	—	—
2653	*w*	—	—
		2810	10, *P*
		2863	6, *P*
2915	*vs*	2916	5, *P*
		2951	4, *P*
		2986	6, *P*
4274	*m*	—	—

TABLE II. *Raman data for methyl ether.**

A†	V AND S	S	D AND K	K
160(½)P	—	—	—	—
300(0)P	—	333(0)	—	—
412(1)P	408	416(0)	—	416(0)
—	—	—	—	(583(0?))
—	—	—	—	(702(00?))
916(b)P	921	921(2)	924(2)	920(5)
1105 ?	1095	1102(0)	—	1095(½)
1155(½)D	—	—	(1150(1))	—
1445(6)D	1448(2)	1454(1)	1451(1)	1450(3)
2810(10)P	2813(10)	2814(7)	2814(5)	2813(10)
2863(6)P	2868(3)	2869(3)	(2862(2))	2862(6)
2916(5)P	2908(3)	2921(3)	2914(2)	2917(5)
2951(4)P	2947(2)	2952(3)	2953(2)	2949(3)
2986(6)P	2988(6)	2989(3)	2990(2)	2986(6)

* Frequencies in cm^{-1}; relative intensities as given by each author
† A = Ananthakrishnan, reference 4; V and S = Vol'kenstein and Syrkin, reference 5; S = Sirkar, reference 6; D and K = Dadieu and Kohlrausch, reference 7; K = Kohlrausch, reference 8.

The frequencies of the ν_H and $\delta_{H,\perp}$ types are well known and quite constant in different molecules. The $\delta_{H,\parallel}$ frequency is more variable, ranging from 1250 to 1480 cm^{-1} in the methyl halides; in methyl ether we should expect it to lie somewhat below 1450 cm^{-1}, due to $\delta_{H,\perp} - \delta_{H,\parallel}$ interactions in the A_1 and B_2 classes. The estimate of 1100–1200 cm^{-1} for the CH_3 rocking frequency τ_M is derived from comparison with the methyl halide frequencies. The $C-O$ frequencies $\nu_M(\pi)$ and $\nu_M(\sigma)$ should lie near the 1030 cm^{-1} frequency of methyl alcohol; the third "water-type" frequency, δ_M, is more uncertain.

With these considerations in mind, the tentative assignment of fundamental frequencies

TABLE IV. *Tentative assignments for fundamental frequencies of methyl ether.*

TYPE	NUMBER OF VIBRATIONS	FREQUENCY
ν_H	6	2900
$\delta_{H,\perp}$	4	1466
$\delta_{H,\parallel}$	2	1466?
τ_M	4	1180
$\nu_M(\sigma)$	1	1122
$\nu_M(\pi)$	1	940
δ_M	1	(412)*
γ	2	?

* Liquid-phase frequency.

shown in Table IV seems most probable. Gas-phase (infra-red) frequencies have been used in this table, except for the 412-cm^{-1} Raman frequency, which lies too low to be observed in the infra-red. The assignments of $\nu_M(\sigma)$, $\nu_M(\pi)$ and δ_M agree with those given by Kohlrausch[8] and by Bonner.[9]

The considerations summarized in Table III would lead one to expect at least two frequencies near 1450 cm^{-1}, since the $\delta_{H,\perp}$ and $\delta_{H,\parallel}$ vibrations fall in the same symmetry classes in two cases (A_1 and B_2), and should split apart by classical resonance even if they would otherwise fall together. The infra-red spectrum shows quite clearly, however, a single sharp band in this region (1466 cm^{-1}). The assignment of the $\delta_{H,\parallel}$ frequency is accordingly rather puzzling. The possibility of this frequency being too weak to be detected must of course be taken into account.

[9] L. G. Bonner, J. Chem. Phys. **5**, 293 (1937).

TABLE III. *Types of vibration in methyl ether.*

DESIGNATION*	SYMMETRY**				TOTAL NUMBER	TYPE	APPROXIMATE FREQUENCY TO BE EXPECTED CM⁻¹
	$A_1 (\pi, s)$	$A_2 (\sigma, a)$	$B_1 (\pi, a)$	$B_2 (\sigma, s)$			
γ	0	1	1	0	2	"Internal rotation"	?
ν_H	2	1	1	2	6	$C-H$ stretching	2900
$\delta_{H,\perp}$	1	1	1	1	4	$C-H$ bending	1450
$\delta_{H,\parallel}$	1	0	0	1	2	$C-H$ bending	~1400
τ_M	1	1	1	1	4	CH_3 rocking	~1100–1200
ν_M	1	0	0	1	2	$C-O$ stretching	~1000
δ_M	1	0	0	0	1	$C-O-C$ deformation	low
Totals	7	4	4	6	21		
Raman-active†	+	+	+	+			
Infra-red-active†	+	—	+	+			

* ∥, ⊥ = parallel and perpendicular, respectively, to the $C-O$ axis of the methyl group involved.
** π, σ = symmetric and antisymmetric, respectively, to plane bisecting the $C-O-C$ angle. s, a = symmetric and antisymmetric, respectively, to plane of the C and O atoms.
† +, — = active and inactive, respectively.

The five Raman lines near 2900 cm⁻¹ are undoubtedly to be assigned to the ν_H frequencies, together with the overtones of the δ_H frequencies, which will resonate with the 2900 cm⁻¹ fundamentals. The single infra-red band found at 2915 cm⁻¹ is probably an unresolved complex of several frequencies; the resolution of our instrument is quite low in this region.

With regard to the frequency of the torsional oscillations, γ, there is the interesting possibility that the Raman line at 300 cm⁻¹, if real, corresponds to this motion. Reliable information on this point, however, must await the complete vibrational analysis and accurate thermal data.

In concluding, we should like to express to Professor E. B. Wilson, Jr., our appreciation of the use of his laboratory, and of many helpful discussions during this work.

The Prediction of Rate Constants from Equilibrium Data for Reactions in D₂O-H₂O Mixtures

FRANK BRESCIA
College of the City of New York, New York, New York
(Received February 15, 1939)

The concentrations of hydrogen and deuterium ions at different fractions of D in the solvent are calculated from the simultaneous solution of the equations $C_{H^+} \cdot C_{HDO} / C_{D^+} \cdot C_{H_2O} = 3.76$ and $C_{H^+} + C_{D^+} =$ concentration of strong acid. Similarly, the concentrations of hydroxyl and deuteroxyl ions are calculated from the equations $C_{OD^-} \cdot C_{H_2O} / C_{OH^-} \cdot C_{HDO} = 0.225$ and $C_{OH^-} + C_{OD^-} =$ concentration of alkali. It is then possible to predict reaction rates for specific hydrogen ion and specific hydroxyl ion catalyzed reactions, in mixtures of $H_2O - D_2O$, on the assumption that the rate is proportional to the fraction of D^+ in the first case and to the fraction of OD^- in the second.

IT IS possible to predict the rate constant for specific hydrogen ion and hydroxyl ion catalyzed reactions in mixtures of deuterium and protium oxides from equilibrium data.

From the equilibrium equation[1]

$$K_1 = \frac{C_{H^+} \cdot C_{HDO}}{C_{D^+} \cdot C_{H_2O}} = 3.76 \qquad (1)$$

and from the equation

$$C_{D^+} + C_{H^+} = \text{Concentration of Strong Acid} \qquad (2)$$

TABLE I. *Concentration of H⁺, D⁺, OH⁻ and OD⁻ at different fractions of D in the solvent.*

F_D^*	C_{H^+}	C_{D^+}	C_{OH^-}	C_{OD^-}
0.00	1.00	0.00	1.00	0.00
26.40	0.848	0.152	0.868	0.132
55.60	.627	.373	.665	.335
78.49	.376	.624	.417	.583
92.51	.152	.848	.175	.825
100.00	.00	1.00	.00	1.00

* $F_D = \Delta S(100)/0.1079 =$ Fraction of deuterium in the solvent.

[1] F. Brescia, J. Am. Chem. Soc. **60**, 2811 (1938).

in any $D_2O - H_2O$ mixture, the value of C_{H^+} and C_{D^+} can be calculated for different fractions of D in the solvent. The water concentrations, C_{HDO} and C_{H_2O}, are calculated from the equilibrium process[2] $H_2O + D_2O = 2HDO$ for which $K = 3.27$. A summary of the C_{H^+} and C_{D^+} values when the concentration of HCl is one molar is given in Table I.

The rate constant, k, at different fractions of D may then be calculated from these values of C_{H^+} and C_{D^+}, and from the values of the specific rate constant in ordinary water, k_{H^+}, and in $F_D = 100$ solvent, k_{D^+}, on the simple assumption that

$$k = k_{H^+} C_{H^+} + k_{D^+} C_{D^+}. \qquad (3)$$

This procedure was carried out for the reactions: the hydrolysis of acetal,[3] the hydrolysis of methyl acetate,[4] and the hydrolysis of ethyl

[2] B. Topley and H. Eyring, J. Chem. Phys. **2**, 217 (1934).
[3] W. J. C. Orr and J. A. V. Butler, J. Chem. Soc. (London) **1937**, 330.
[4] W. E. Nelson and J. A. V. Butler, J. Chem. Soc. (London) **1938**, 957.