*Vibrational Spectra of Methyl Ether. I. Assignment of the Spectra**

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In a series of aliphatic ethers, methyl ether has significance for the study of molecular spectra in this homologues because of its simplest structure.

A number of investigations on the vibrational spectra of the molecule have been reported. Herzberg[1] gave an assignment of the vibrational bands using the data published previously[2]. By Ryskina[3] and Siebert[4] the calculation of the normal vibration and assignments were given. Although assignments based on the more detailed measurements of infrared and Raman spectra have been given by Hadni[5] and by Taylor and Vidale[6], there still remains some arbitrariness in their results because they studied the spectra of only one isotopic compound. Therefore, it is desirable to measure the spectra of deuterated compounds in order to obtain more reliable results.

The results of the measurement of the infrared and Raman spectra of methyl ether ($(CH_3)_2O$) and of methyl ether-d_6 ($(CD_3)_2O$) and an assignment of the spectra, referring to that of dimethoxy methane and its deuterated compounds[8], are reported here.

Experimental

Samples. — Methyl ether was prepared from methanol and sulfuric acid. Crude gaseous ether was passed through a concentrated aqueous solution of sodium hydroxide and trapped first with ice-salt and finally with acetone-dry ice. Then it was purified by distillation over metallic sodium. Purification was repeated until no change in the infrared spectrum was observed. A sufficiently pure sample for infrared measurement was obtained, but a shoulder near 1050 cm^{-1} still remained in the Raman spectrum after the final purification. It was considered, therefore, that a very small amount of methanol remained in the sample.

Deuterated ether was prepared from deuterated methanol (CD_3OH or CD_3OD) and deuterated sulfuric acid in the same way as non-deuterated ether. The concentration of deuterium in the sample was analyzed by means of proton magnetic resonance and found to be about 99%.

Measurement of Spectra.—Raman spectra were obtained in the liquid state by a Cary 81 spectrophotometer (3500～250 cm^{-1}, 35～38°C). The degree of depolarization was measured with polarizers around the Raman tube. In the case of non-deuterated methyl ether, a Raman tube for a 5 ml. sample was used, and for the deuterated compound, 0.2 and 0.4 ml. Raman tubes were employed, so the measurement of weak bands was difficult in the latter case.

Infrared spectra (3500～280 cm^{-1}) were obtained by using the following spectrophotometers: Perkin-Elmer 12C (LiF prism), 112G (3500～2000 cm^{-1}), 21 and 321 (NaCl and CsBr prisms), and Nippon-Bunko DS 301 (NaCl prism, 1000～1200 cm^{-1}). Measurement was carried out in the gaseous state over the whole range of the spectrum and also, in the carbon tetrachloride solution, in the sodium chloride and lithiam fluoride prism regions. The obtained spectra are shown in Fig. 1.

Assignment and Discussion

The structure of methyl ether was determined from electron diffraction[10] and microwave spectroscopy[11] to be approximately C_{2v} symmetry. If the molecule belongs to point group C_{2v}, vibrational bands can be classified into four species: $\Gamma = 7A_1 + 4A_2 + 6B_1 + 4B_2$. The vibrations belonging to A_2 are infrared inactive. The envelope of infrared absorption bands of a gaseous substance is of the B type for species A_1, A type for B_1, and C type for B_2. Raman lines which belong to species A_1 are polarized. These characteristics are referred to in the assignment of the bands.

Since the number of observed bands is less than the number of normal vibrations, some overlapping of bands is expected. Therefore, it is not always possible to determine definitely the species of bands by observation of the envelope of infrared absorption bands or by the measurement of the degree of depolarization in the Raman spectra.

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* The present paper is an extension of a series of studies on aliphatic ethers[7], dimethoxy methanes, ethylidene dialkyl ethers and related compounds[8].

1) G. Herzberg, "Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, New York (1945), p. 353.

2) K. W. F. Koglrausch, *Z. phsik. Chem.*, **B30**, 305 (1935); R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, **5A**, 285 (1937); B. L. Crawford and L. Joyce, *J. Chem. Phys.*, **7**, 307 (1939); K. S. Pitzer, ibid., **10**, 605 (1942).

3) S. J. Ryskina, *J. Phys. Chem.* (*U.S.S.R.*), **22**, 21 (1948).

4) H. Siebert, *Z. anorg. u. allgem. Chem*, **271**, 65 (1953).

5) A. Hadni, *Compt. rend.*, **229**, 349 (1954).

6) R. C. Taylor and G. L. Vidale, *J. Chem. Phys.*, **26**, 122 (1957).

7) Y. Mashiko, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 470 (1958); **80**, 593 (1959).

8) K. Nukada, *Spectrochim. Acta*, to be published.

9) K. Nukada, This Bulletin, **35**, 3 (1962).

10) K. Kimura and M. Kubo, *J. Chem. Phys.*, **30**, 151 (1959).

11) P. H. Kasai and R. J. Myers, ibid., **30**, 1096 (1959).

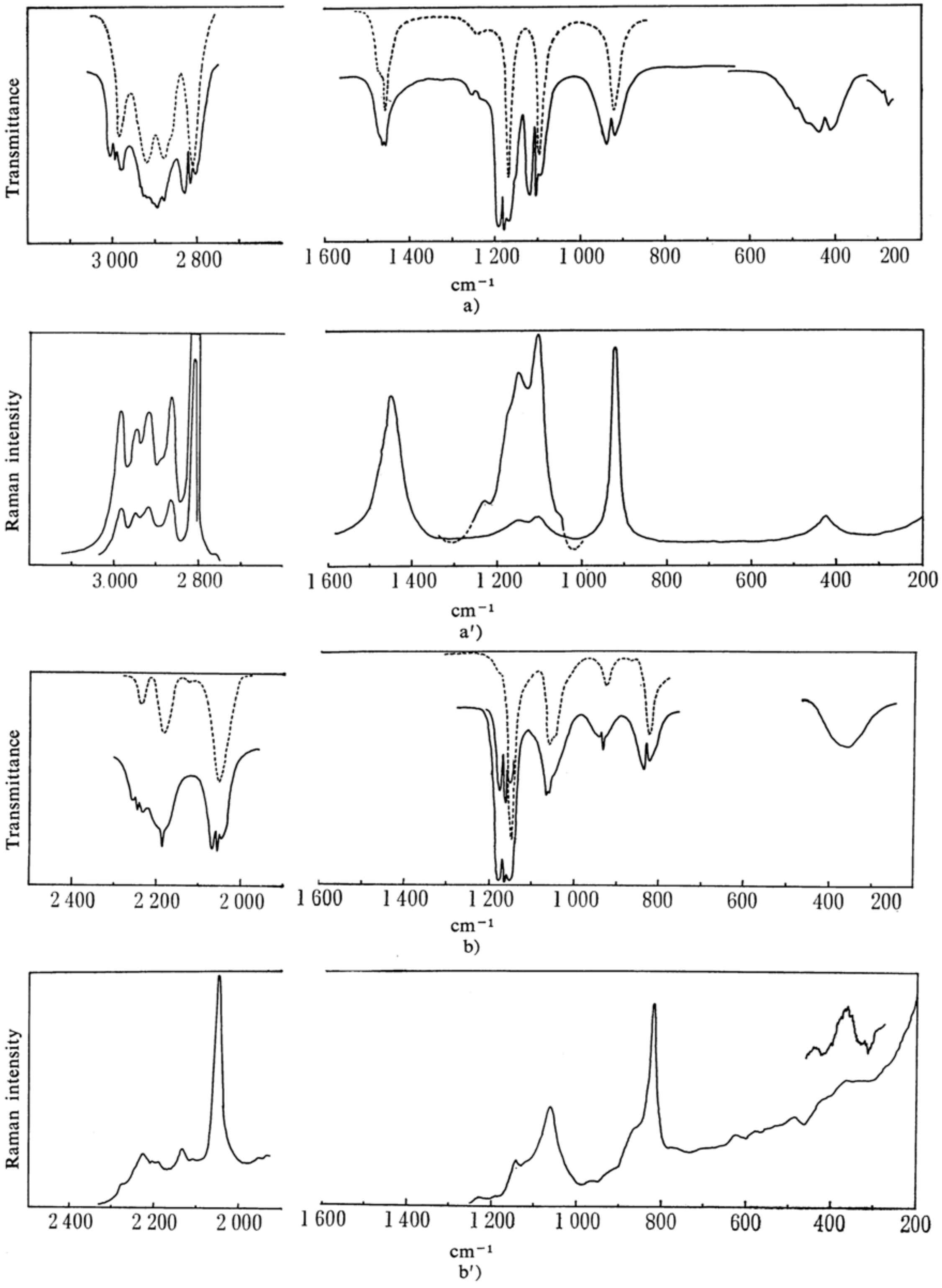

Fig. 1. Infrared and Raman spectra of CH_3OCH_3 and CD_3OCD_3.

a) Infrared spectra of CH_3OCH_3 } —— gas
b) Infrared spectra of CD_3OCD_3 } - - - CCl solution, concentration; undetermined
a') Raman spectrum of CH_3OCH_3 } pure liquid
b') Raman spectrum of CD_3OCD_3 }

TABLE I. ASSIGNMENT OF CH_3OCH_3 (IN cm^{-1})

		Herzberg[1]	Ryskina[3]	Siebert[4]	Hadni[5]	Taylor & Vidale[6]	Mashiko[7]
A_1	ν_1 C–H asym. str.	2986	2915	—	2900	2997 ?	2985
	ν_2 C–H sym. str.	2812	2810	—	2900	2821 ?	2845
	ν_3 CH_3 asym. def.	1466	1466	1450	1466	1457^{*3}	1464
	ν_4 CH_3 sym. def.	1466	—	1450	1466	1242	1451
	ν_5 CH_3 rocking	1180	1180	— ?	1135	1053	1142
	ν_6 C–O sym. str.	930^{*1}	940 ?	920	932	929	929
	ν_7 COC deformation	414	440	413	412	413	414
A_2	ν_8 C–H asym. str.	—	2915	—	2900	2889 ?	2865
	ν_9 CH_3 asym. def.	1466	1466	1450	1466	1457^{*3}	1451
	ν_{10} CH_3 rocking	1180	1102	— ?	918	1291, 1167, 1147 ?	1105
	ν_{11} CH_3 torsion	160 ?	—	—	160	—	170^{*4}
B_1	ν_{12} C–H asym. str.	2916	2915	—	2900	2889 ?	2980
	ν_{13} C–H sym. str.	2916	2863	—	2900	2889 ?	2900
	ν_{14} CH_3 asym. def.	1466	1466	1450	1466	1457^{*3}	1464
	ν_{15} CH_3 sym. def.	1466	—	1450	1466	1457^{*3}	1451
	ν_{16} CH_3 rocking	1180	1122	1155	1177	1291, 1167, 1147 ?	1115
	ν_{17} C–O antisym. str.	1112^{*2}	1102	1102	1103	1122	1169
B_2	ν_{18} C–H asym. str.	2916	2915	—	2900	2889 ?	2845
	ν_{19} CH_3 asym. def.	1466	1466	1450	1466	1457^{*3}	1464
	ν_{20} CH_3 rocking	1180	1102	— ?	940	1291, 1167, 1147 ?	1098
	ν_{21} CH_3 torsion	300 ?	—	—	270	—	265^{*4}

^{*1} and ^{*2} The averaged value between two observed frequencies

^{*3} The averaged value among three observed frequencies

^{*4} Y. Mashiko and K. S. Pitzer, *J. Phys. Chem.*, **62**, 367 (1958).

Before making the assignment of vibrational spectra of the molecule, the authors would like to examine the results of other authors as shown in Table I. In the assignment given by Herzberg[1], a point in question is that he assigned a band at 1180 cm^{-1} to the methyl rocking vibrations belonging to four species. Coincidence of the wave numbers of the four bands would be impossible because two of them (A_1, B_1) are the in-plane methyl rocking, and others (A_2, B_2) are the out-of-plane methyl rocking, vibrations. Moreover, since the band at 1179 cm^{-1} measured in the present experiment has a clear envelope of the A or C type, it is difficult to consider it as the overlapping of four bands.

Ryskina[3] assigned a band at 1122 cm^{-1} to the methyl rocking vibration of species B_1, but we consider it to be a branch of the band at 1102 cm^{-1}. In her assignment, the band at 1102 cm^{-1} was assigned to the overlapping of three bands, the species of which was A_2, B_1 and B_2, but this assignment is also questionable for a reason similar to that mentioned above.

Siebert[4] studied the molecular vibration of methyl sulfide ($(CH_3)_2S$) and of methyl selenide ($(CH_3)_2Se$) as well as of methyl ether, but the bands which he assigned were so few that the present authors will not refer to his results.

Hadni[5] considered that there were three fundamental bands at 940, 932 and 918 cm^{-1}. In the present experiment, however, the asymmetric feature of the R branch of the infrared band is not so marked enough to be the basis of such a conclusion, and, in addition, the infrared spectrum in solution shows a single band at 920 cm^{-1}. Therefore, the bands observed at 940 and 916 cm^{-1} should be considered as branches of a B-type band.

The Raman spectra of the molecule in both gaseous and liquid states were measured by Taylor and Vidale[6]. New bands were observed at 1291 (gas) 1242 (gas and liquid), 1167 (liquid) and 1053 cm^{-1} (gas and liquid). Among these, 1291 cm^{-1} had not been observed by other authors. As suggested by the following fact, this band is due to contaminated carbon dioxide. In the synthesis of the sample, carbon dioxide from dry ice used for the trap or from the reacting mixture could be absorbed in ether to some extent. In fact, the same band was observed in the prepared sample in the present experiment if no care was taken to remove it.

The band at 1053 cm^{-1}, which was also observed in the present Raman measurement as a very weak shoulder, might originate from the strongest band of methanol being included as a trace.

C–H and C–D Stretching Vibrations.—Of the observed bands two bands at 2996 and 2817 cm^{-1}

are characteristic bands of aliphatic methoxyl groups[8,9]. These two bands are assigned respectively to overlapping asymmetric and symmetric stretchings of species A_1 and B_1. The fact that both of them show A or C-type band envelopes instead of the B-type for A_1 species may suggest these overlappings. The band at 2952 cm^{-1} observed only in the Raman measurement is assigned to the asymmetric stretching vibration of the infrared inactive species A_2. Of two bands at 2925 and 2887 cm^{-1} which have strong infrared intensities, the one at 2925 cm^{-1} is assumed to be a B_2 band because to the B_2 species belongs an asymmetric C–H stretching vibration whose frequency should not lie far from the A_1 and B_1 asymmetric stretching vibrations. Detailed discussions of the C–H stretching vibrations of methyl ether have not been given in previous papers, but the assignment given here does not contradict that of homologue which have methoxy groups[8,9]. The strong Raman band at 2869 cm^{-1} and the infrared band at 2887 cm^{-1} are to be assigned to an overtone or combination tone of methyl deformation vibrations.

Deuterated methyl ether shows clearer envelopes of absorption bands in the C–D stretching region than non-deuterated ether does in the C–H stretching region. This can be explained because the ratio of rotational constants B/A increases as the molecule changes from methyl ether to methyl ether-d_6. The bands at 2248 and 2054 cm^{-1} are of the A type, and the band at 2184 cm^{-1} is of the C type. As in the case of C–H stretching vibrations, the band with the highest frequency (2248 cm^{-1}) is assigned to the overlapping asymmetric stretchings and that with the lowest (2054 cm^{-1}), to the overlapping symmetric stretching vibrations of species A_1 and B_1. Then the C-type band at 2184 cm^{-1} (strong in infrared and weak in Raman) is assigned to the vibration of species B_2. The Raman band at 2202 cm^{-1} is assigned to the asymmetric stretching vibration of species A_2. Though the Raman bands at 2285, 2137 and 2100 cm^{-1} also have no corresponding infrared bands, by referring to the assignment of non-deuterated methyl ether it is reasonable to assume that a band nearer to that of species B_2 is to be assigned to species A_2. The strongly polarized band at 2137 cm^{-1} which has a medium intensity is possibly an overtone or combination band of CD_3 deformation vibrations.

Methyl Deformation Vibrations. — In the region of methyl deformation vibrations, infrared and Raman bands are observed only around 1460 cm^{-1}. The infrared spectrum of gaseous ether shows two sharp absorptions at 1464 and 1456 cm^{-1} which can not be considered as branches of a band both bacause the separation of 8 cm^{-1} between them is too small and because the appearance of the doublet does not seem to be that of any type of band envelopes. Furthermore, the infrared spectrum in solution still shows three bands at 1470, 1464 and 1454 cm^{-1}. Therefore, it is suitable to regard them as the superposition of some bands.

Taylor and Vidale[6] assigned the band at 1242 cm^{-1} to a methyl symmetric deformation. This might seem possible because the band is always observed in this region in molecules having a methoxyl group or groups[8,9]. This assignment, however, is denied by the following facts. The first objection stems from the relationship between the vibrational frequencies of methyl symmetric deformation and methyl rocking given by Wilmshurst[12]. Applying it to the observed frequencies, if the frequency of methyl symmetric deformation is assumed to be 1244 cm^{-1}, that of the rocking vibration should be obtained about 900 cm^{-1} or lower where no bands are observed actually; however, both methyl deformation and rocking vibrations prove to appear in the higher frequency region. The second objection stems from the fact that, as Sheppard[13] mentioned, in CH_3X type molecules with various kinds of atoms or group X, the methyl symmetric deformation of methoxyl groups appeared at about 1460 cm^{-1}.

Nukada observed methyl deformation vibrations of dimethoxy methane and dimethoxy methane-d_2 ($CH_3OCD_2OCH_3$) only near 1460 cm^{-1} and not below. From the relative intensity of the infrared and Raman spectra and the degree of polarization, he assigned the bands at 1460 and 1455 cm^{-1} to the symmetric and asymmetric deformations respectively[8]. Considering these, it seems reasonable to assume that all the methyl deformations of methyl ether lie in the range of 1470~1450 cm^{-1}, though at present it is impossible to assign the observed bands to six normal vibrations individually.

CD_3 deformation vibrations are expected to appear around the region of $\nu_{\delta CH_3}/\sqrt{2}$ cm^{-1} or higher. Corresponding to those of non-deuterated ether, infrared bands of a similar complicated shape and a strong Raman band are observed at 1062 and 1056 cm^{-1} and at 1062 cm^{-1} respectively. The assignment is made, as in the case of methyl ether, by treating the six bands together.

Skeletal Vibrations.—There are three skeletal vibrations: a C–O symmetric stretching

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[12] J. K. Wilmshurst, ibid., **26**, 426 (1957).

[13] N. Sheppard, *Trans. Faraday Soc.*, **51**, 1465 (1955).

TABLE II. OBSERVED BANDS OF CH_3OCH_3 AND CD_3OCD_3 (IN cm^{-1})

Infrared				Raman	
Gas		Type of the band	Solution	Liquid	Degree of depolarization
a) CH_3OCH_3					
2996	3008 2996 s 2980	A or C	2985 s	2989 s	?
				2952 s	?
2925	2935 2925 s 2918	?	2918 s	2922 s	?
2887	2893 2887 s 2876	?	2880 s	2893 sh	D
			2864 sh	2869 s	P
2817	2831 2817 s 2803	A or C	2813 s	2815 vs	SP
			1470 w		
	1464 m		1464 w	1452 s	D
	1456 m		1454 m		
1244	1255 1235 w	B	1240 w		
				1227 w	D
1179	1192 1179 vs 1170	C or A	1167 vs	1170 sh	
	(1153 vw)			1150 m	D
1102	1116 1102 vs 1090	A or C	1094 vs	1104 m	D
928	938 918 s	B	920 s	922 s	SP
470	484 457 sh	B			
418	425 412 m	B		428 m	P
b) CD_3OCD_3					
			2280 w	2285 w	P
2248	2258 2248 s 2235	A	2239 s	2230 m	D
				2202 w	
2184	2193 2184 s 2173	C	2182 s	2185 w	
			2138 vvw	2137 m	SP
			2126 vw		
			2109 vvw	~2100 w	
2054	2067 2054 s 2042	A	2051 s	2053 vs	SP
1162	1173 1162 vs 1149	A	1146 vs	1142 m	?
	1062 m		1058 m	1062 s	D
	1056 m		1048 m		
	1033 sh				

TABLE II. (Continued)

Infrared		Solution	Raman	
Gas	Type of the band		Liquid	Degree of depolarization
931 { 939 931 m 920	C	926 m		
		(895)		
872 sh		(864)	865 sh	D
		(847)		
		(836)		
827 { 834 820 s	B	824 s	821 vs	P
362 m			365 w	P

TABLE III. ASSIGNMENT OF CH_3OCH_3 AND CD_3OCD_3

		CH_3OCH_3	CD_3OCD_3	Vibrational modes of CH_3OCH_3 (CD_3OCD_3)
A_1	ν_1	2996	2248	C-H (C-D) asym. str.
	ν_2	2817	2054	C-H (C-D) sym. str.
	ν_3	1470～1456	1062～1056	CH_3 (CD_3) deformation
	ν_4	1470～1456	1062～1056	
	ν_5	1244	1033	CH_3 (CD_3) rocking
	ν_6	928	827	C-O sym. str.
	ν_7	418	362	COC deformation
A_2	ν_8	2952	2202	C-H (C-D) asym. str.
	ν_9	1470～1456	1062～1056	CH_3 (CD_3) deformation
	ν_{10}	1150	—	CH_3 (CD_3) rocking
	ν_{11}			Torsion
B_1	ν_{12}	2996	2248	C-H (C-D) asym. str.
	ν_{13}	2817	2054	C-H (C-D) sym. str.
	ν_{14}	1470～1456	1162	CH_3 deformation, (C-O antisym. str.)
	ν_{15}	1470～1456	1062～1056	CH_3 (CD_3) deformation
	ν_{16}	1227	1062～1056	CH_3 rocking, (CD_3 deformation)
	ν_{17}	1102	872	C-O antisym. str., (CD_3 rocking)
B_2	ν_{18}	2925	2184	C-H (C-D) asym. str.
	ν_{19}	1470～1456	1062～1056	CH_3 (CD_3) deformation
	ν_{20}	1179	931	CH_3 (CD_3) rocking
	ν_{21}			Torsion

(species A_1), a C–O antisymmetric stretching (B_1), and a COC deformation (A_1).

As can be seen in Table I, the bands at 920 and 420 cm^{-1} have been assigned to the skeletal vibrations of species A_1 by all authors. In the present experiment, strong B-type infrared bands and polarized Raman bands are observed at 928 at 418 cm^{-1} and and are assigned to A_1 bands.

The band of methyl ether-d_6 at 827 cm^{-1} has characteristics corresponding to those of a band at 928 cm^{-1} of methyl ether, so it is assigned to the C–O symmetric stretching vibration. Similarly, the Raman band observed at 365 cm^{-1} is assigned to the COC deformation vibration the measurement of the degree of depolarization, although the corresponding infrared band at 362 cm^{-1} does not show the shape of the B type but a broad singlet structure.

To the assignment of the C–O antisymmetric stretching vibration some consideration should be given. For this vibration an A type infrared band and a depolarized Raman band ether band are to be expected. Methyl ether-d_6 has the very strong A-type infrared band at 1162 cm^{-1} (in the liquid phase the frequency shifts to 1146 cm^{-1}) and no further similar bands in the region, and it also has a Raman band of medium intensity at 1142 cm^{-1}, so the band can be assigned to the C–O antisymmetric stretching vibration.

In the case of methyl ether, one of the two strong infrared bands at 1179 and 1102 cm^{-1} (A or C type) has to be assigned to the C–O antisymmetric stretching vibration of species B_1. Formerly Mashiko[7] observed two pairs of

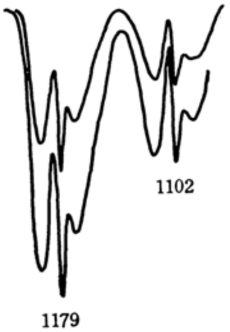

Fig. 2. Infrared spectrum of CH_3OCH_3 (gas) spectral slit width ; 1 cm^{-1}.

bands, at 1169 and 1142 cm^{-1} and at 1105 and 1098 cm^{-1}, which had the appearance of B type, but in the present measurement, they proved to be triplet bands having P, Q and R branches. As the matter of fact, only two remarkable bands are observed in this region in the infrared spectrum in solution. The two infrared bands in a geseous state show a similar shape, so it is difficult to decide which one is the antisymmetric skeletal stretching vibration. The infrared spectrum in a gaseous state, measured under various pressures with a constant spectral slit width (1 cm^{-1}, Nippon Bunko DS-301), is shown in Fig. 2. Since the intensity ratios of the Q branch to the P and R branches at 1179 cm^{-1} are larger than those at 1102 cm^{-1}, the two bands could be of different species. If one band is assigned to a C–O antisymmetric stretching vibration, the other should be a methyl rocking vibration of species B_2 because of its strong intensity and shape in the infrared spectrum. As will be shown in a following paper[14], from the calculation of normal vibrations it has been concluded that the band at 1102 cm^{-1} is the C–O stretching vibration and that the one at 1179 cm^{-1} is the methyl rocking vibration.

Methyl Out-of-plane Rocking Vibrations. — Of the two methyl out-of-plane rocking vibrations, one belongs to species A_2 and the other to B_2. As stated above, the infrared band at 1179 cm^{-1} is assigned to the rocking vibration of methyl ether belonging to species B_2 (the corresponding Raman band may be a weak shoulder near 1170 cm^{-1}). In the case of methyl ether-d_6, the band at 931 cm^{-1} surely corresponds to this vibration, which shows a C-type band shape. The corresponding Raman band could not be observed distinctly.

It should be possible to determine the assignment of the methyl rocking vibration of species A_2 from only the Raman spectrum if the molecule belongs to symmetry C_{2v}. Thus, the Raman band at 1150 cm^{-1} is assigned to this vibration, and the fact that the frequency 1150 cm^{-1} is not so far from 1179 cm^{-1} of the B_2 rocking vibration supports the assignment. In deuterated ether, no suitable band could be detected, perhaps because the band is masked by other strong bands or because it has too weak an intensity to be observed in the specta.

Methyl In-plane Rocking Vibrations. — To species A_1 and B_1 belongs one rocking vibration each. In methyl ether, the B-type band is observed at 1244 cm^{-1}, and, from the preceding interpretation, this could not be a methyl deformation vibration. Moreover, the fact that in a molecule including methoxy groups a band was always observed near 1230 cm^{-1}[8,9] suggests that the band is, though weak, a fundamental. This band is therefore assigned to the A_1 methyl rocking vibration.

The depolarized Raman band is observed at 1227 cm^{-1}. In the paper of Tailor and Vidale, the Raman band observed by them at 1242 cm^{-1} was strongly polarized, but the present authors determined the band at 1227 cm^{-1} to be certainly depolarized. Therefore, it is unreasonable to regard the Raman band as corresponding to the infrared band at 1244 cm^{-1}. Therefore, it is assigned to the B_1 methyl rocking vibration.

In methyl ether-d_6, no infrared band with the band shape typical of methyl ether is observed. A shoulder at 1033 cm^{-1} is assigned to the A_1 methyl rocking vibration, and the weak band at 872 cm^{-1} in the Raman and infrared spectrum is assigned to the B_1 band. Applying the product rule to these frequencies, we get the following results which support the assignments.

	A_1	B_1
Theor.	0.1880	0.2150
Calcd.	0.1810	0.2117

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[14] Y. Kanazawa et al., to be published.