Infrared and Raman Spectra of Diethoxymethane and Diethoxymethane-d_2

By Kenkichi NUKADA

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In previous papers, the author has reported the characteristic vibrations of infrared spectra of dialkoxymethanes[1] and ethylidene dialkyl ethers[2], and more recently the assignment of vibrational spectra of dimethoxymethane ($CH_3OCH_2OCH_3$) and its deuterated compounds[3].

In this paper, infrared and Raman spectra of diethoxymethane (DEM, $C_2H_5OCH_2OC_2H_5$) and diethoxy methane-d$_2$ (DEM-d$_2$, $C_2H_5OCD_2 \cdot OC_2H_5$) are presented and the assignment of spectra are given by referring to the above-mentioned results[1-3].

DEM has four internal rotational axes and there is a possibility of more than two rotational isomers existing in it. The author has examined the rotational isomerism of dialkoxymethanes and concluded that dimethoxymethane, the simplest homologue of DEM, takes one form in vapor and liquid phases near room temperature. He did not obtain such a definite conclusion in the case of DEM, but from the similarity of the change of infrared spectra among various phases between dimethoxymethane and DEM, he suggested that DEM also takes one and the same form in vapor and liquid phases (two ethoxyl groups rotate about 120° in an anticlockwise sense from the central OCO plane) near room temperature[4]. In this paper, the assignment is given with the assumption mentioned above.

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[1] K. Nukada, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 1112 (1959).

[2] K. Nukada, ibid., **80**, 976 (1959).

[3] K. Nukada, *Spectrochim. Acta*, to be published.

[4] K. Nukada, This Bulletin, to be published.

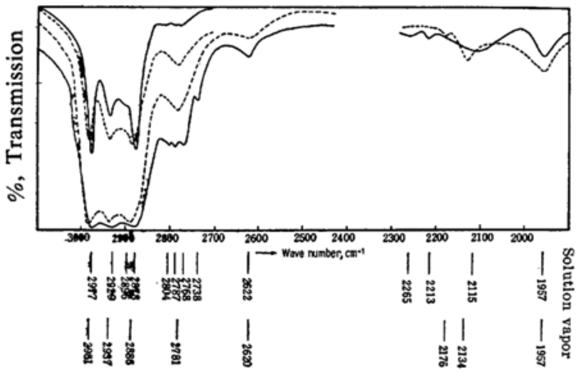

Fig. 1a. Infrared spectra of DEM (C–H and C–D stretching region).

Solid line, CCl_4 solution (25 and 5 vol. %, 0.15 mm.) Dashed line, vapor

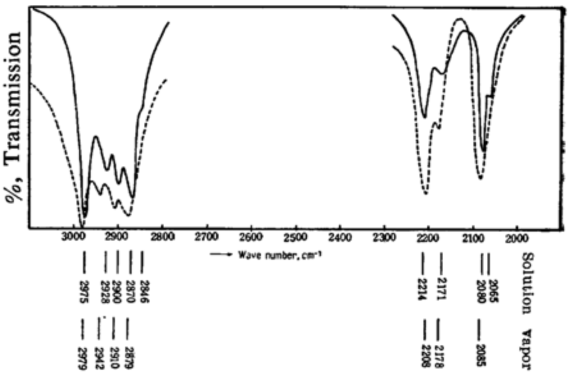

Fig. 1c. Infrared spectra of DEM-d$_2$ (C–H and C–D stretching region).

Solid line, CCl_4 solution, (10 vol.%, 0.15 mm.) Dashed line, vapor

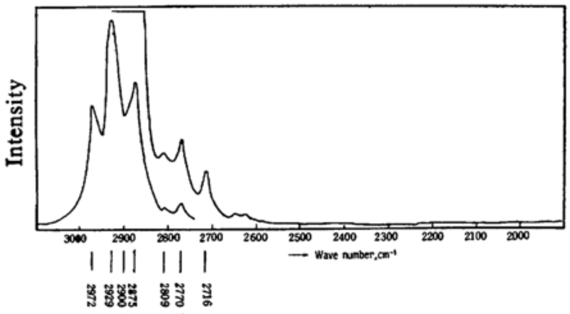

Fig. 1b. Raman spectra of DEM (C–H and C–D stretching region).

Pure liquid

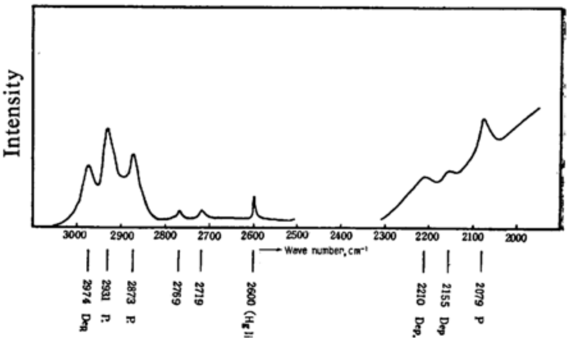

Fig. 1d. Raman spectra of DEM-d$_2$ (C–H and C–D stretching region).

Pure liquid

Experimental

DEM and DEM-d$_2$ were prepared from ethanol and formaldehyde, and from ethanol and formaldehyde-d$_2$, respectivity. The detailed description of the prepatation will be reported elsewhere[5].

Infrared spectra were obtained by means of a Perkin Elmer 12C spectrophotometer equipped with a lithium fluoride prism and a 21 spectrophotometer equipped with a sodium chloride or a cesium bromide prism.

Raman spectra were obtained by means of a Cary 81 spectrophotometer. In the case of DEM-d$_2$, a capillary tube, the capacity of which is 0.2 cc. was used. The degree of depolarization was measured by wrapping two kinds of polaroids around a Raman tube.

The spectra thus obtained are illustrated in Figs. 1—3.

Results and Discussion

C–H and C–D Stretching Vibrations. — The features of the Raman spectra of DEM and DEM-d$_2$ are quite similar in the 3000 cm^{-1} region. They have two strongly polarized bands at 2929~2931 cm^{-1} and at 2873~2875 cm^{-1}, and one depolarized band at 2972~2974 cm^{-1}. The features of the infrared spectra are, on the other hand, slightly different from each other. Thus, the intensity ratios of the bands at 2928~2929 cm^{-1} to those at 2896~2900 cm^{-1} are different in these two compounds.

The strongest infrared bands at 2977~2975 cm^{-1} in DEM and DEM-d$_2$ (the corresponding Raman bands being strongly depolarized) are assigned to the asymmetrical methyl stretching of the ethoxyl group[2].

The strong infrared bands at 2870~2878 cm^{-1}, having corresponding strongly polarized Raman bands, in DEM and DEM-d$_2$ are assigned to the symmetrical methyl stretching[1].

In dimethoxymethane-d$_6$ ($CD_3OCH_2OCD_3$), bands at 2932 and 2887 cm^{-1} are assigned respectively to the asymmetrical and the symmetrical methylene stretchings of OCH_2O group[3]. The corresponding CD_2 stretchings

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[5] K. Nukada, *Reports Gov. Chem. Ind. Research Inst. Tokyo*, to be published.

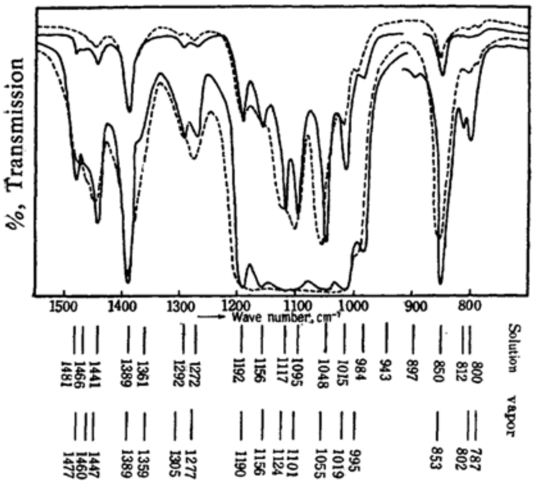

Fig. 2a. Infrared spectra of DEM (finger print region).

Solid line, CCl_4 and CS_2 solution (0.15 mm., 20 and 3 vol.%), dashed line, vapor

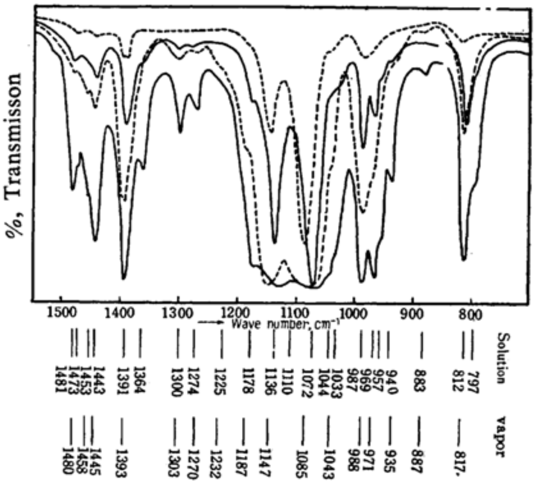

Fig. 2c. Infrared spectra of DEM-d_2 (finger print region).

Solid line, CCl_4 and CS_2 solution, (0.15 mm., 20 and 3 vol.%), dashed line, vapor

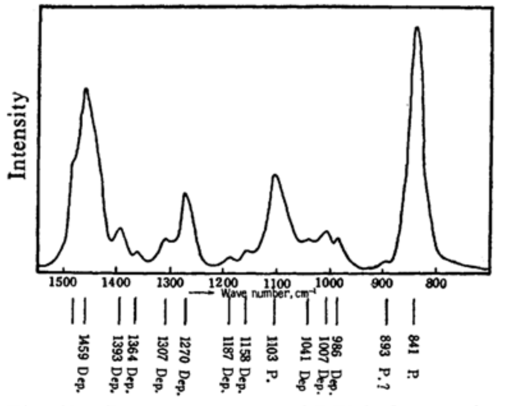

Fig. 2b. Raman spectrum of DEM (finger print region).

Pure liquid

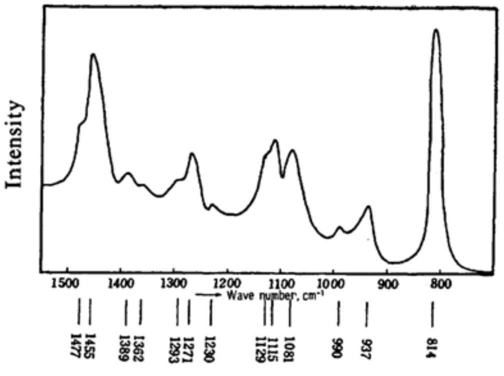

Fig. 2d. Raman Spectrum of DEM-d_2 (finger print region).

Pure liquid

are found in dimethoxymethane-d_2 ($CH_3OCD_2 \cdot OCH_3$) to be at 2188 (strongly depolarized in Raman) and at 2080 cm^{-1} (strongly polarized in Raman), respectively. In DEM-d_2, two strong infrared bands appear at 2214 (the corresponding Raman band being strongly depolarized) and at 2080 cm^{-1} (the corresponding Raman band being strongly polarized); hence they are assigned to the asymmetrical and the symmetrical CD_2 stretchings of the OCD_2O group, respectivery, on the analogy of the above mentioned results. The asymmetrical and symmetrical methylene stretchings of the OCH_2O group in DEM are then expected to appear near 2930 and 2890 cm^{-1}, respectively. The relative intensity of the infrared band at 2928∼2929 cm^{-1} becomes lower in DEM-d_2 as compared with the one in DEM, while that at 2870∼2878 cm^{-1} does not chow an appreciable change between DEM and DEM-d_2. Then it is certain that the asymmetrical methylene stretching of the OCH_2O group exists at 2930 cm^{-1} in DEM, and that it is probably overlapped by the other type of vibration. The overlapping band is presumably the asymmetrical methylene stretching of ethoxy group[2]. The bands at 2870∼2878 cm^{-1} in DEM and DEM-d_2 are assigned to the symmetrical methylene stretching of the ethoxyl group, overlapped by the symmetrical methylene stretching of the OCH_2O group, as described above, and also by the symmetrical methyl stretching of the ethoxyl group. Since the intensity of these bands does not alter appreciably between DEM DEM-d_2, the absorbance of the symmetrical methylene stretching

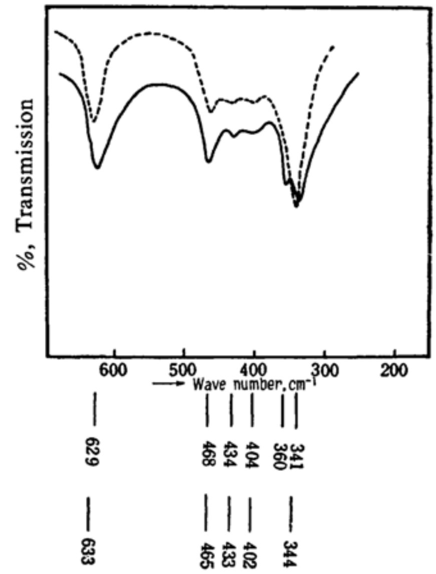

Fig. 3a. Infrared spectra of DEM (skeletal deformation region).

Solid line, pure liquid (0.2 mm.), dashed line vapor

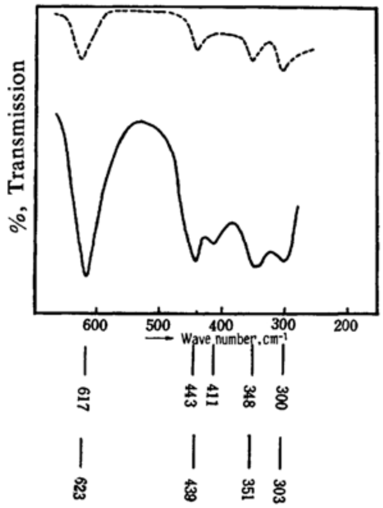

Fig. 3c. Infrared spectra of DEM-d_2 (skeletal deformation region).

Pure liquid (0.2 mm.)

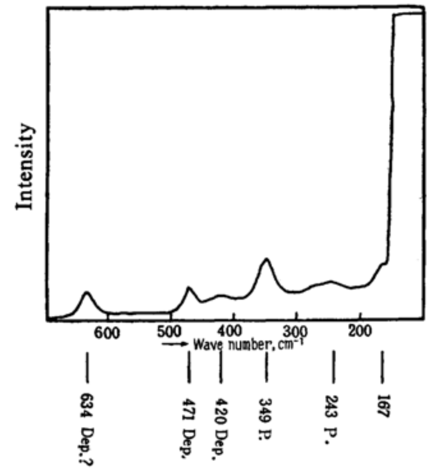

Fig. 3b. Raman spectrum of DEM (skeletal deformation region).

Pure liquid

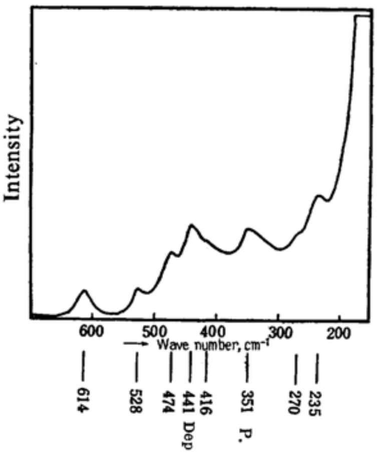

Fig. 3d. Raman spectrum of DEM-d_2 (skeletal deformation region).

Pure liquid

of the OCH_2O group is concluded to be small.

The possibility of the Fermi resonance occurring between two types of methylene groups may be small, because the interaction between them is believed to be negligible.

The remaining weak bands may be overtone and/or combination.

Skeletal Stretching and C–H and C–D Deformation Vibrations. — The appearance of the spectra of DEM and DEM-d_2 is quite similar in the range between 1480 and 1270 cm^{-1} both in infrared and Raman. Therefore, the absorbance of the ethoxyl group is more predominant than that of the OCH_2O group in this frequency region.

Medium infrared and Raman bands appear at 1477∼1481 cm^{-1} both in DEM and DEM-d_2. In ethylidene diethyl ether ($C_2H_5OCH(CH_3)\cdot OC_2H_5$), ethylidene methyl ethyl ether ($CH_3OCH(CH_3)OC_2H_5$), 2, 2-diethoxypropane ($C_2H_5OC(CH_3)_2OC_2H_5$)⁶⁾, triethyl orthoformate ($HC(OC_2H_5)_3$) and in triethyl orthopropionate

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6) K. Nukada, ibid., to be published.

TABLE I. VIBRATIONAL FREQUENCIES OF DIETHOXYMETHANE AND DIETHOXYMETHANE-d$_2$*

DEM			DEM-d$_2$			Assignment
IR		Raman	IR		Raman	
Vapor	Liq.		Vapor	Liq.		
2981(s)	2977(s)	2972(s) Dep.	2979(s)	2975(s)	2974(s) Dep.	asym. CH$_3$ stretching
2937(m)	2929(m)	2929(s) S. P.	2942(m)	2928(m)	2931(s) S. P.	asym. CH$_2$ stretching (OCH$_2$O, EtO)
	2896(w)		2910(m)	2900(m)		combination or overtone
2886(m)	2878(s)	2875(s) S. P.	2879(s)	2870(s)	2873(s) S. P.	{sym. CH$_3$ stretching {sym. CH$_2$ stretching (OCH$_2$O, EtO)
			2208(s)	2214(s)	2210(w) Dep.	asym. CD$_2$ stretching
			2178(m)	2171(m)	2155(w) Dep.	CD$_2$, combination or overtone
			2085(s)	2080(s)	2079(m) S. P.	sym. CD$_2$ stretching
			2063(sh)	2065(sh)		CD$_2$, combination or overtone
1477(vw)	1481(m)	1481(m, sh)	1480(vw)	1481(m) 1473(vw)	1477(m, sh)	CH$_2$ scissoring (OCH$_2$O, EtO)
1460(vw)	1466(vw)	1459(s) S. Dep.	1458(vw)	1453(vw)	1455(s) S. Dep.	asym. CH$_3$ deformation
1447(w)	1441(vw)		1445(w)	1443(m)		EtO, combination or overtone (COCOC)
1389(m)	1389(m)	1393(m) Dep.	1393(m)	1391(m)	1389(m)	{sym. CH$_3$ deformation {CH$_2$ wagging (OCH$_2$O)
1359(vw)	1361(vw)	1364(w) Dep.		1364(vw)	1362(w)	CH$_2$ wagging (EtO)
1305(w)	1292(w)	1307(w) Dep.	1303(vw)	1300(w)	1293(w)	CH$_2$ rocking (EtO)
1277(w)	1272(w)	1270(s) Dep.	1270(vw)	1274(w)	1272(s) Dep.	CH$_2$ twisting (EtO)
			1232(vw)	1255(w)	1230(w) P. ?	CD$_2$ scissoring or twisting+COCOC stretching
1190(m)	1192(m)	1187(w) Dep.				CH$_2$ twisting or wagging (OCH$_2$O)
1156(w)	1156(m)	1158(w) Dep.				CH$_2$ rocking (OCH$_2$O)
1124(m)	1117(s)		1147(s)	1136(s)	1129(w)	asym. COCOC streching
				1110(vvw)	1115(s) P.	CD$_2$ scissoring or twisting
1101(s)	1095(s)	1103(s) P.	1085(s)	1072(s)	1081(s)	sym. COCOC stretching
1055(s)	1048(s)	1041(w) Dep.	988(m)	987(s)	990(m)	asym. COCOC stretching
1019(m)	1015(s)	1007(m) Dep.	935(vw)	940(w)	937(m) Dep.	sym. CC stretching
995(w)	984(w)	986(w) Dep.	971(w)	969(m)		asym. CC stretching
853(m)	850(m)	841(s) S. P.	817(w)	812(s)	814(s) S. P.	sym. COCOC stretching
	943(vw)					
	897(vw)	893(w) P. ?	887(vw)	883(vw)		
802(vw)	812(vw)					
787(vw)	800(vw)			797(vw)		
633(s)	629(s)	634(m) Dep. ?	623(s)	617(s)	614(m)	asym. COCOC deformation
					528(w)	
					474(w)	
465(m)	468(s)	471(m) Dep.	439(s)	443(s)	441(m) Dep.	sym. COCOC deformation
433(w)	434(m)	420(w) Dep.		411(m)	416(w)	
402(w)	404(m)					
	360(w)					
344(s)	341(s)	349(m) S. P.	351(s)	348(s)	351(m) P.	sym. COCOC deformation
			303(m)	300(m)		
					270(vw)	
		243(w) S. P.			235(w)	sym. OCC deformation
		167(w)				

* P. and Dep. mean "polarized" and "depolarized", and S. means "strongly".

($C_2H_5C(OC_2H_5)_3$)[7], a weak or medium infrared band is observed in this region. But in diisopropoxymethane (($(CH_3)_2CHOCH_2OCH\cdot(CH_3)_2$)[8], ethylidene dimethyl ether ($CH_3\cdot OCH(CH_3)OCH_3$), trimethyl orthoformate ($HC(OCH_3)_3$), trimethyl orthoacetate ($CH_3C\cdot(OCH_3)_3$) and in trimethyl ortho-*n*-valerate ($CH_3(CH_2)_3C(OCH_3)_3$)[7], no band exists in this region. Hence the bands at 1477~1481 cm^{-1} are assigned to the methylene vibration of the ethoxyl group, certainly the scissoring vibration. The methylene scissoring of the OCH_2O group can also exist at this frequency[3], but the absorbance of the latter may probably smaller than that of the former and it is hard to observe it.

All compounds containing oxygen atoms which the author has studied[1-4,6-8] have weak infrared and strong and depolarized Raman bands around 1460 cm^{-1} except for dimethoxymethane and dimethoxymethane-d$_8$ ($CD_3\cdot OCD_2OCD_3$). The last two compounds contain no methyl group, thus the bands in this region should be due to the methyl group. Therefore the bands at 1455~1466 cm^{-1} (very weak in infrared and strong and depolarized in Raman) in DEM and DEM-d$_2$ are assigned to the asymmetrical methyl deformation of the ethoxyl group.

The origin of infrared bands at 1440~1443 cm^{-1} both in DEM and DEM-d$_2$ is not clear, but they must be due to the vibration of the ethoxyl group, or the combination or overtone of skeletal vibrations.

The medium infrared and polarized Raman bands at 1389~1393 cm^{-1} both in DEM and DEM-d$_2$ are assigned to the symmetrical methyl deformation of the ethoxyl group. From the result on dimethoxymethane and its deuterated compounds[3] the methylene wagging of the OCH_2O group could exist in this region. So in DEM, these two bands may probably overlap.

The very weak infrared and weak Raman bands at 1359~1362 cm^{-1} in DEM and DEM-d$_2$ are assigned to the methylene wagging of the ethoxyl group.

The features of doublet at 1292~1307 cm^{-1} and 1270~1274 cm^{-1} do not alter strongly between DEM and DEM-d$_2$, thus these bands are also due to the ethoxyl group. Of these, the former bands are assigned to the methylene rocking and the latter to the methylene twisting, because the Raman intensity of the latter is greater than that of the former and it is expected that the twisting vibration, the species of which is A, should give a stronger band.

In conclusion, it becomes clear that bands due to the ethoxy group are at 1477~1481, 1455~1466, 1441~1443, 1389~1393, 1361~1364, 1292~1307 and at 1270~1274 cm^{-1} (all the values are those of liquid phase). The skeletal vibrations may not appear in such a high frequency region.

The weak Raman band at 1230 cm^{-1} (having a corresponding very weak infrared band) in DEM-d$_2$ may be due to CD_2 vibration coupled with the COCOC skeletal vibration. Since the Raman band is polarized, it is assigned to the CD_2 scissoring or twisting, being coupled with an A type skeletal stretching, to some extent.

The medium bands at 1187~1192 cm^{-1} both in infrared and Raman in DEM disappear in DEM-d$_2$ (in which a very weak infrared band appears at 1178 cm^{-1}, though the origin of this band may be different as the intensity is too low). Hence these bands are due to the methylene vibration of the OCH_2O group, probably the twisting or wagging.

The bands at 1156~1158 cm^{-1} in DEM both in infrared and Raman disappear in DEM-d$_2$. In dimethoxymethane and dimethoxymethane-d$_6$, weak infrared bands at this freqencey are assigned to the methylene rocking of the OCH_2O group[3]. According to these results, these bands are assigned to the methylene rocking of the OCH_2O group.

From the study on dimethoxymethane and its deuterated compounds, the skeletal COCOC stretching should exist between 1150~800 cm^{-1} [3]. In DEM and DEM-d$_2$, the additional skeletal stretchings due to CC bonds could exist in this region. But the absorbance of the latter ones may be smaller than that of the former, hence the features of the spectra of DEM and DEM-d$_2$ are actually similar to those fo dimethoxymethane at this frequency region.

The infrared bands at 1117 and at 1136 cm^{-1} in DEM and DEM-d$_2$ are the next strongest bands in the liquid phase, and the corresponding Raman bands are very weak. In dimethoxymethane and its deuterated compounds, the strong infrared bands around 1140 cm^{-1}, the corresponding Raman bands of which are extremely weak, are assigned to the asymmetrical skeletal stretching[3]. These bands are then assigned to one of the asymmetrical COCOC stretchings.

The Raman band at 1115 cm^{-1} in DEM-d$_2$ is due to the OCD_2O methylene vibration. As it is strongly polarized, it may be assigned to the scissoring or twisting being coupled with the symmetrical skeletal stretching to some extent.

The strong infrared band at 1095 cm^{-1} in

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[7] K. Nukada, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 1028 (1960).

[8] K. Nukada, This Bulletin, to be published.

DEM corresponds to the band at 1072 cm^{-1} in DEM-d_2. As the corresponding Raman bands are strong and strongly polarized (in DEM), these bands are assigned to one of the symmetrical COCOC stretchings.

The strong infrared band appears at 1048 cm^{-1} in DEM, but no corresponding band exists in DEM-d_2 near that frequency. In DEM-d_2, the remaining band, the intensity of which is rather high, is the band at 987 cm^{-1}. Furthermore the intensity of the corresponding Raman bands is not so high in both cases, thus it is reasonable to correlate the two bands as the same type of skeletal vibration. The remaining modes are one symmetrical and one asymmetrical vibration, but as described in detail later the symmetrical one should appear at 800~850 cm^{-1} both in DEM and DEM-d_2. Accordingly these bands are assigned to the asymmetrical COCOC stretching.

The bands at 1015 and 984 cm^{-1} in DEM and those at 940 and 969 cm^{-1} in DEM-d_2, may be due to CC stretchings. The former ones are assigned to the symmetrical mode and the latter to the asymmetrical one, respectively, since the intensity of the corresponding Raman bands of the former is higher than that of the latter.

The strongest and strongly polarized Raman bands exist at 841 and 814 cm^{-1} in DEM and DEM-d_2, respectively. In dimethoxymethane, its deuterated compounds3), methoxyethoxymethane and in diisopropoxymethane9), there appear the strongest and strongly polarized Raman bands, being assigned to the symmetrical skeletal stretching, between 900 and 800 cm^{-1}. Thus these bands are also definitely assigned to the symmetrical COCOC stretching. Just as in the case of dimethoxymethane and its deuterated compounds3), the corresponding infrared bands are not so strong, and in the vapor phase its intensity becomes lower than that of the liquid phase. As already mentioned in the study of dimethoxymethane, the mode of this vibration is such that two terminal ethoxyl groups vibrate symmetrically and the central OCO group does not move much.

Skeletal Deformation Vibrations. — It is expected that five skeletal angle deformations appear over 200 cm^{-1} and six torsional vibrations below 250 cm^{-1}. At the present, no infrared band below 280 cm^{-1} is obtained because of the experimental limitation and Raman band below 200 cm^{-1} is hardly observable since the strong exiting line disturbs the observation of weak Raman band. All the skeletal deformations could then be observed either in infrared or in Raman, while the torsional vibrations are hardly observable.

There are three pairs of strong Raman bands in DEM and DEM-d_2, namely at 634 and 614, 471 and 441, and 349 and 351 cm^{-1}. In dimethoxymethane, its deuterated compounds3) and in methoxyethoxymethane4), there appear such pairs of Raman bands. The appearance of infrared spectra is also quite similar between DEM and DEM-d_2, that is, three pairs of strong infrared bands appear at the same frequency regions. Hence they are certainly due to the skeletal deformations

Of these, the bands at 349~351 cm^{-1} are strongly polarized in Raman, so they are assigned to the symmetrical COCOC deformation. As in the case of dimethoxymethane and its deuterated compounds, these are the vibrations all skeletal angles of which move in the same phase.

The degree of depolarization of the remaining two bands is not clear, but on the analogy of dimethoxymethane the bands at 614~634 cm^{-1} in DEM and DEM-d_2 are assigned to the asymmetrical deformation and the last bands at 441~470 cm^{-1} to the other symmetrical one, two COC angles and the OCO angle of which vibrate in the opposite phases.

As the Raman bands at 235~243 cm^{-1} in DEM and DEM-d_2 are strongly polarized, they are assigned to the symmetrical OCC deformation. The assignment of the asymmetrical one is not clear.

The remaining weak bands may be overtone and/or combination of torsional vibrations.

Summary

Infrared spectra between 3000 and 280 cm^{-1} (vapor and liquid phases) and Raman spectra (liquid phase) of diethoxymethane ($C_2H_5 \cdot OCH_2OC_2H_5$) and of diethoxymethane-d_2 ($C_2H_5OCD_2OC_2H_5$) were observed and the assignment of the spectra is presented with the assumption that these molecules take one form both in the vapor and liquid phases. In the assignment, that of the homologues such as dimethoxymethane, its deuterated compounds, methoxyethoxymethane and diisopropoxymethane, are taken into consideration.

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Government Chemical Industrial
Research Institute of Tokyo
Shibuya-ku, Tokyo

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[9] K. Nukada, ibid., to be published.