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Vibrational Spectra and Rotational Isomerism of Alkyl Vinyl Ethers

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The rotational isomerism of methyl vinyl ether, ethyl vinyl ether, and *n*-butyl vinyl ether has been studied by means of the vibrational spectra and normal frequency calculations. The enthalpy difference between the *skew* and *cis* isomers in the liquid state of methyl vinyl ether has been determined to be 1440±160 cal/mol. Series of C–O torsional transitions in the *cis* well have been observed for methyl vinyl ether and methyl-d_3 vinyl ether in the region near 230 cm^{-1} and analyzed. It has been concluded for ethyl vinyl ether that the *cis-trans* form (CT) is stable in the solid state and that three forms, CT, SG′, and ST, coexist in the liquid and gaseous states. The spectra in the solid state of *n*-butyl vinyl ether are consistent with the calculated frequencies of the CTTT form.

In a preceding paper the analysis of the mid-infrared spectra in the various states with the support by the normal coordinate treatment was successful for the determination of the rotational isomerism about the C–C axis neighboring a C=C double bond.[1] It was concluded that the *cis* and *skew* conformations are stable for the C–C bond neighboring the *trans* C=C bond, and only the *skew* conformation is stable for the C–C bond neighboring the *cis* C=C bond. As an extension of the work, the rotational isomerism about the C–O bond neighboring a C=C double bond has been studied for methyl vinyl ether, ethyl vinyl ether, and *n*-butyl vinyl ether with the additional information of the Raman spectra. The enthalpy differences among the rotational isomers in the liquid state have also been determined.

In the case of methyl vinyl ether and methyl-d_3 vinyl ether, series of the C–O torsional transitions in the *cis* well have been observed and analyzed by the method described in a preceding paper.[2]

The details and the results are reported in the present paper.

Experimental

Methyl vinyl ether, ethyl vinyl ether, and *n*-butyl vinyl ether were obtained commercially. Methyl vinyl ether was used without further purification. Ethyl vinyl ether and *n*-butyl vinyl ether were purified by fractional distillations. Methyl-d_3 vinyl ether was prepared by the interchange reaction,

$$CD_3OD + ROCH{=}CH_2 \rightleftharpoons ROD + CD_3OCH{=}CH_2,$$

with $Hg(OAc)_2$ as the catalyst and *n*-butyl vinyl ether as the starting alkyl vinyl ether. The purity of the sample was checked by means of infrared spectroscopy.

The infrared spectra were recorded on a Hitachi EPI-L double beam grating spectrometer in the region 700—250 cm^{-1} and on a Hitachi FIS-1 vacuum double beam grating spectrometer in the region 300—60 cm^{-1}. The spectra in the gaseous state were obtained by using the 10-cm and 4.9-m cells with white polyethylene windows and those in the liquid state were taken with 0.025—0.01 mm cells of KBr, KRS-5, or polyethylene windows. The spectra in the solid state were observed at the temperature of liquid nitrogen. Sample deposited on a cooled window of KRS-5, silicon, or KBr was repeatedly annealed until no further spectral change was observed. A low-temperature cell and a Hitachi 205 double beam grating spectrometer at the Institute for Protein Research of Osaka University[3] were used for the measurement of the infrared spectra of methyl vinyl ether in the liquid state.

The Raman spectra were obtained on a JEOL JRS-400D spectrophotometer with the 5145 Å line of a Coherent Radiation CR-3 argon ion laser as the exciting line and on a Spex 1401 spectrophotometer equipped with an NEC He-Cd laser and an NEC He–Ne laser. The He–Cd laser line at 4416 Å and the He–Ne laser line at 6328 Å were used as exciting lines. The latter instrument was calibrated with neon gas emission lines and the observed Raman frequencies are believed accurate to 2 cm^{-1}. The Raman spectra at low temperatures were obtained with a simple glass Dewar-type low temperature cell. The temperature of the sample was controlled by the amount of liquid nitrogen or of Dry Ice added to the cell. The temperature was measured with a thermocouple directly inserted into the sample.

The mid-infrared spectra of the three compounds in the gaseous, liquid, and solid states are shown in Figs. 1—3. The far-infrared spectra of methyl vinyl ether and methyl-d_3 vinyl ether are shown in Fig. 4. The Raman spectra of the three compounds are shown in Figs. 5—7. The observed frequencies are listed in Table 1.

Normal Vibration Calculations

For the purpose to correlate the observed vibration bands with the normal modes of the rotational isomers, the normal vibrations have been calculated by Program NCTB, which is a combination of GCCC, BGLZ, and LSMB,[4] and the HITAC 8800/8700 Computer of the

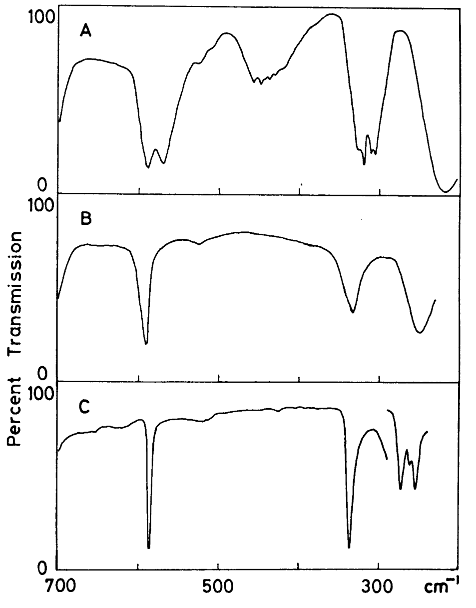

Fig. 1. Infrared spectra of methyl vinyl ether.
A: Gas, B: liquid, C: solid.

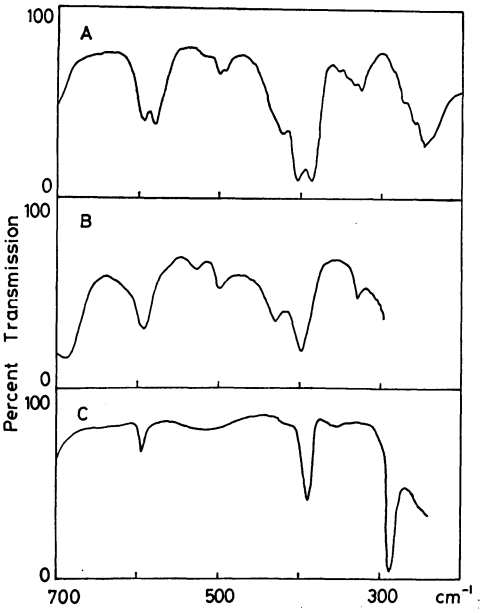

Fig. 2. Infrared spectra of ethyl vinyl ether.
A: Gas, B: liquid, C: solid.

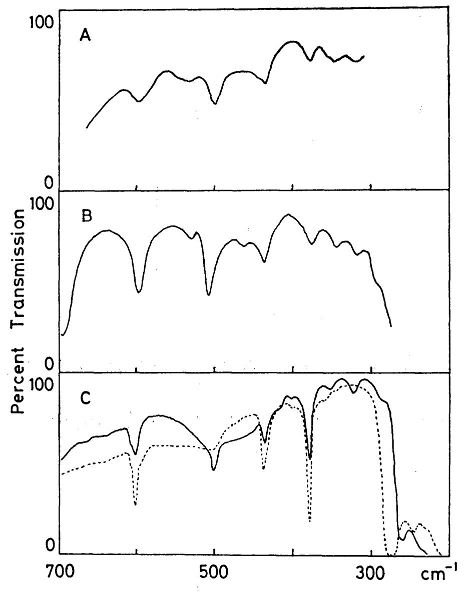

Fig. 3. Infrared spectra of *n*-butyl vinyl ether.
A: Gas, B: liquid, C: —— amorphous solid, ······ annealed solid.

Table 1. Observed frequencies of methyl vinyl ether, ethyl vinyl ether, and *n*-butyl vinyl ether in cm^{-1}

Gas		Liquid		Solid	
IR	R	IR	R	IR	R
Methyl vinyl ether					
702 *C*		707	707	720 714	722 718
585 *B*	590	591	591	595	591
	525	525	527		
464 *C*					
456 *C*					
451 *C*					
444 *C*					
435 *C*					
	413[a]				
328 *AB*	326	336	333	340	344
234 *C*	232	250	248	273	280
230 *C*				263	264
226 *C*				256	254
					119
					90
					84
					68
					39
					28
Ethyl vinyl ether					
700 *C*		704	708	710 704	719 710
594 *B*	598	595	600	598	605 599
523	525	530	533		
500 *B*	496	500	500		
425	435	437	436		
395 *B*	396	400	398	395	397
				280	280
247	238		245		248
			215		228 217
					136
					80
					68
					50
					40
					33
					27
					20
n-Butyl vinyl ether					
700		700	702	710	709
602		600	600	605 598	611
534		530	538		
498		505	497		
		455	459		
437		437	437	436	440
380		380	378	378	380
344		350	350		
			337		
		320	322		
			265		289
			246	278	276
				268	
					251
					162
					141
					133
					95
					72
					59
					42
					31
					26

a) Origin unknown.

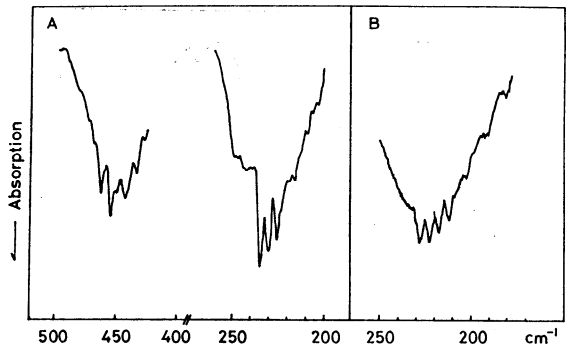

Fig. 4. Far-infrared spectra of gaseous methyl vinyl ether.
A: Methyl vinyl ether, B: methyl-d_3 vinyl ether.

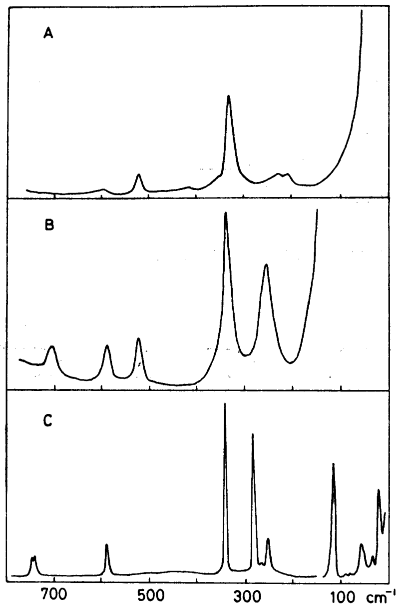

Fig. 5. Raman spectra of methyl vinyl ether.
A: Gas 500 mmHg, B: liquid, C: solid.

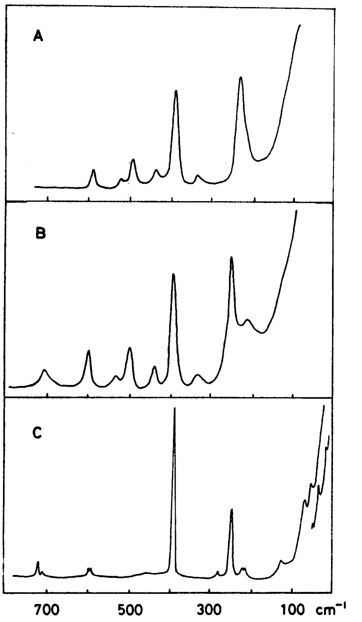

Fig. 6. Raman spectra of ethyl vinyl ether.
A: Gas 420 mmHg, B: liquid, C: solid.

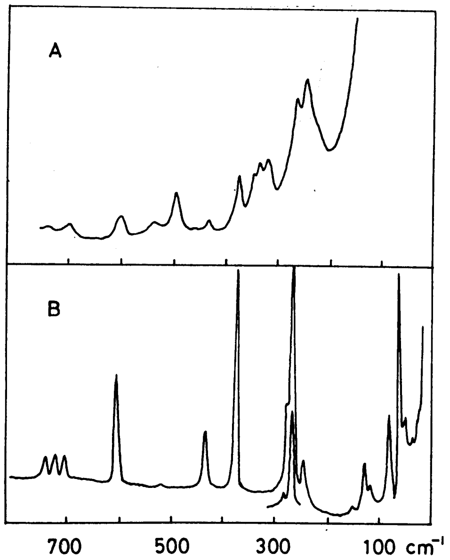

Fig. 7. Raman spectra of *n*-butyl vinyl ether.
A: Liquid, B: solid.

Computer Center of the University of Tokyo. The bond lengths and the bond angles of methyl vinyl ether determined by microwave spectroscopy[5] were used for the CH_2=CH–O–CH_2 part and 1.522 Å, 1.09 Å, and the tetrahedral angle were assumed for the other C–C bonds, C–H bonds, and the rest of the angles. The values of force constants were transferred from those of 1-alkenes,[1] except for those given in Table 2. The values given in this table were determined so as to give the best fit with the observed frequencies for the *cis* form of methyl vinyl ether. These values were transferred to ethyl vinyl ether with various conformations and the CTTT form of *n*-butyl vinyl ether. The torsion angles are taken to be 0°, 60°, 120°, and 180° for the *cis*, *gauche*, *skew*, and *trans* forms, respectively.

TABLE 2. FORCE CONSTANTS OF METHYL VINYL ETHER[a] (MUBFF)

K(C–O)	2.40 md/Å	*W*(=CH)	0.37md·Å
H(C=C–O)	0.487	*W*(=CH_2)	0.28
H(C–O–C)	0.26	*Y*(C=C)	0.518
F(C=C–O)	0.40	*Y*(=C–O)	0.147
F(C–O–C)	0.40	*Y*(O–CH_3)	0.11
R(*cis* C=C–O–C)	0.369	*WY*(=CH_2, C=C)	0.049
		WY(=CH, C=C)	0.145
		YY(=C–O, O–CH_3)	0.064

a) Only the values of modified force constants are listed in the table. Other force constants are transferred from those of olefins (see Table III of Ref. 1).

As in the case of 1-alkene molecules, the *cis* repulsion constant R were taken into account for the two carbon atoms of the =CH_2 and –O–C parts in the *cis* position. The inclusion of this constant explains the C–O–C bending and C=C–O bending vibrations simultaneously.

Results and Discussion

Methyl Vinyl Ether. Since the bands with frequencies less than 750 cm^{-1} are significantly related

TABLE 3. CALCULATED AND OBSERVED FREQUENCIES OF METHYL VINYL ETHER IN cm^{-1}

Calculated (Observed)					Assignment
0° (*cis*)		90°, 120° (*skew*)	180° (*trans*)		
ip	op		ip	op	
	700(707)	713, 712(707[a])		702	=CH wag.
586(591)		533, 515(526)	504		C=CO bend.
326(335)		347, 341(335[a])	280		COC bend.
	244(249[a])	248, 253(249[a])		281	CH_3 tor.
	227(249)	158, 154(—)		155	=C–O tor.

a) Overlapped.

to the molecular conformation, the frequencies observed in this region are summarized and compared with the calculated frequencies in Table 3. The infrared and electron diffraction studies by Owen and Sheppard[6] and Owen and Seip[7] show that this molecule has the two rotational isomers, the *cis* form and the *skew* form with the torsion angle 80—110°. This fact is in agreement with the result for the 1-butene molecule which has *cis* and *skew* for the stable conformations.[8] Accordingly, we assigned the observed bands to the vibrations of the *cis* and *skew* forms, by taking into account the possibility of a considerable deviation of the *skew* form torsion angle.

As shown in Table 3, the strong bands observed in the gaseous state at 702 cm^{-1} (*C* type), 585 cm^{-1} (*B* type), and 328 cm^{-1} (*A* and *B* hybrid) are assigned reasonably to the =CH– wagging, C=C–O in-plane, and C–O–C in-plane bending vibrations of the *cis* isomer, respectively. The two low frequency vibrations, methyl torsion and C–O torsion, are predicted to appear at 225 ± 20 cm^{-1} and 219 ± 20 cm^{-1} from the microwave study.[5] The fairly strong band at about 230 cm^{-1} is composed of three distinct equally separated sharp absorptions (Fig. 4). The corresponding band of the methyl deuterated compound is composed of a quartet and is observed lower than that of the undeuterated compound by 4 cm^{-1} (Fig. 4). We assign this band to =C–O– torsion, taking the small isotopic shift in frequency into account. The methyl torsion may be weak and overlapped with this band. The weak and broad band with some structure near 450 cm^{-1} is explained as the progression of =C–O– torsional transitions for $\Delta v=2$. The details about the potential of internal rotation will be discussed in the later part of this paper.

The band observed at about 525 cm^{-1} in the Raman spectra in the gaseous and liquid states is missing in the spectrum in the solid state. This band is the only band assigned to the *skew* form. This fact is justified by the large enthalpy difference to be described below.

The situation about the key band sensitive to the conformation of this molecule is different from that of 1-alkenes. For the latter case the *cis* conformation gives a band near 550 cm^{-1} which is assigned to one of the CH out-of-plane vibrations of the vinyl group and the *skew* conformation gives a band near 640 cm^{-1}, the frequency shift being caused by the coupling between this vibration and the skeletal deformation vibration. In the case of methyl vinyl ether, this vibration has a higher frequency near 700 cm^{-1} and the coupling with the skeletal deformation is small in the *skew* conformation. The C=C–O bending vibration, on the other hand, seems to be the key band to the conformation. The calculated frequency for the C=C–O bending mode varies from 586 cm^{-1} to 504 cm^{-1} as the torsion angle changes from 0° (*cis*) to 180° (*trans*).

The barrier to internal rotation of the C–O axis has been studied in one-dimensional approximation by the use of three $\Delta v=1$ and four $\Delta v=2$ torsional transitions of methyl vinyl ether and four $\Delta v=1$ transitions of methyl-d_3 vinyl ether. The method described in the preceding paper[2] was used for the analysis. $F(\alpha)$'s were calculated numerically by Pitzer's method[9] and expanded in Fourier cosine series. $F(\alpha)_{cis}$ was calculated with the structural parameters determined for the *cis* form by microwave spectroscopy.[5] $F(\alpha)_{skew}$ was calculated with the same structural parameters as those for $F(\alpha)_{cis}$ except the value of the angle C–O–C, 112°, determined by the electron diffraction analysis.[7] Then, $F(\alpha)_{\text{hybrid}}$ was determined so that it may be continuous as going from the *cis* form to the *skew* form. $F(\alpha)$ determined in this way corresponds to the situation that the angle C–O–C varies as the OCH_3 group rotates around the C–O axis. $F(\alpha)_{cis}$ and $F(\alpha)_{\text{hybrid}}$ were used in the calculation. The values of parameters of $F(\alpha)_{cis}$ and $F(\alpha)_{\text{hybrid}}$ are as follows:

$$\begin{aligned}F(\alpha)_{cis} &= \underset{(2.4960)}{2.8807} + \underset{(0.4485)}{0.6620}\cos\alpha + \underset{(0.2191)}{0.2940}\cos 2\alpha\\ &\quad + \underset{(0.0545)}{0.0826}\cos 3\alpha + \underset{(0.0167)}{0.0260}\cos 4\alpha + \underset{(0.0047)}{0.0079}\cos 5\alpha\\ &\quad + \underset{(0.0014)}{0.0024}\cos 6\alpha\end{aligned}$$

$$\begin{aligned}F(\alpha)_{\text{hybrid}} &= \underset{(2.4246)}{2.7724} + \underset{(0.4008)}{0.5905}\cos\alpha + \underset{(0.2187)}{0.2840}\cos 2\alpha\\ &\quad + \underset{(0.0533)}{0.0786}\cos 3\alpha + \underset{(0.0172)}{0.0255}\cos 4\alpha + \underset{(0.0048)}{0.0078}\cos 5\alpha\\ &\quad + \underset{(0.0015)}{0.0024}\cos 6\alpha\end{aligned}$$

where the values in parentheses are for the deuterated species.

At first, several set values of V_1, V_2, and V_3 were estimated from the $1\leftarrow0$ and $2\leftarrow1$ transitions, 234 cm^{-1} and 230 cm^{-1}, and the enthalpy differences, 1150 ± 250 cal/mol (402 ± 87 cm^{-1})[6] and the energy levels were calculated. After preliminary calculations the value of V_2 was fixed at 628.4 cm^{-1}. The least squares adjustment was performed for the following four cases:

Case A: $F(\alpha)_{cis}$ and the data of methyl vinyl ether are used.

Case B: $F(\alpha)_{cis}$ and the data of methyl-d_3 vinyl ether are used.

Case C: $F(\alpha)_{cis}$ and the data of methyl vinyl ether and methyl-d_3 vinyl ether are used.

Case D: $F(\alpha)_{\text{hybrid}}$ and the data of methyl vinyl ether and methyl-d_3 vinyl ether are used.

The results are given in Table 4. The agreement between the observed and the calculated is satisfactory for both Case A and Case B, but the obtained potential parameters are different for these two cases. In Case C, the calculated frequencies of the normal species are higher than the observed and those of the deuterated

TABLE 4. OBSERVED AND CALCULATED C–O TORSIONAL TRANSITIONS[a] IN cm^{-1}

Transition (*cis*)	ν_{obsd}	ν_{calcd} Case A	Case B	Case C	Case D
Methyl vinyl ether					
1←0	234	233.3		240.8	238.6
2←1	230	229.8		235.4	233.1
3←2	226	225.1		229.1	226.8
2←0	464	463.2		476.2	471.7
3←1	456	454.9		464.5	459.8
4←2	444	444.4		451.1	446.5
5←3	435	431.6		435.9	431.7
Methyl-d_3 vinyl ether					
1←0	227		226.4	218.7	218.0
2←1	222		222.1	214.6	213.7
3←2	217		217.1	209.7	208.7
4←3	212		211.5	204.3	203.3

a) Potential parameters and dispersions are as follows in the order of Cases A, B, C, and D; V_1, -19.6 (8.1), -27.0(11.7), -3.4(14.8), and -3.8(13.5); V_2, 628.4 fixed; V_3, 1765.8 (62.8), 1908.2 (119.6), 1775.6(85.2), and 1810.1(83.1); V_6, -119.7(25.8), -91.0(48.6), -90.0(39.9), and -83.8(38.1).

species are lower than the observed. This inconvenience cannot be overcome even in Case D, where different structures are assumed for the different internal rotation angles. All these are explained by the difference of vibrational couplings in the normal and the deuterated species. In the normal species, the C–O torsion may couple with the methyl torsion, which is estimated at about 240 cm^{-1} by microwave study.[5] On the other hand, the methyl torsion shifts to lower frequency region on methyl deuteration and the coupling between C–O torsion and methyl-d_3 torsion becomes small; thus the one dimensional model approximation may work better for the deuterated species. This interpretation is verified by the normal coordinate analysis. The potential energy distribution shows that the methyl torsion and C–O torsion couple in the ratio of one to two in the normal species and in the ratio of one to six in the deuterated species. It is concluded that the set of potential parameters obtained with the data of methyl-d_3 vinyl ether is the most probable of the four cases. The values of the parameters for Case B are as follows: $V_1=-27.0$, $V_2=628.4$, $V_3=1908.0$, and $V_6=-91.0$ cm^{-1} (See also the footnote of Table 4). The *skew* transitions are calculated at about 160 cm^{-1}, but no distinct band has yet been observed.

The observed frequency, 234 cm^{-1}, of C–O torsion of methyl vinyl ether is much higher than that of methyl ethyl ether,[3] 113 cm^{-1}. This may be explained by the conjugation between the vinyl group and the lone pair electron of the oxygen atom.

Ethyl Vinyl Ether. The observed frequencies are compared with the calculated in Table 5. Owen and Sheppard analyzed the rotational fine structure of the band at 813 cm^{-1} and suggested that the stable conformer is the planar "sickle shaped" form (the *cis-trans* form).[10] From the comparison of the infrared spectra of gaseous, liquid, and solid states (Fig. 2), it is clear that the dominant isomer in the gaseous state is also dominant in the liquid state and remains in the solid state. The weak bands at 523, 500, 425, and 330 cm^{-1} in the spectrum of the gaseous state are also observed in the spectrum of the liquid state and are assigned to the less stable forms. The intensity dependence on temperature was examined for the Raman bands at 600, 533, 500, 436, and 398 cm^{-1} as will be given below. The results indicate that the bands at 600 and 398 cm^{-1} belong to the most stable isomer (the CT form) and the two bands at 500 and 436 cm^{-1} and the band at 533 cm^{-1} are due to the other two less stable isomers. In other words, three rotational isomers coexist in the liquid and gaseous states of ethyl vinyl ether. The obtained enthalpy differences of the two less stable isomers to the CT form are of the same order as the enthalpy difference of the *skew* isomer to the *cis* isomer of methyl vinyl ether. This fact suggests that the two isomers take the *skew* conformation around the C–O axis.

TABLE 5. CALCULATED AND OBSERVED FREQUENCIES OF ETHYL VINYL ETHER IN cm^{-1}

Calculated (Observed) CT	CG	SG′	SG	ST	Assignment
654(706)	654	712(—)	692	690(—)	=CH wag.
588(598)	614	510(500)	559	526(532)	C=CO bend.
389(399)	421	441(437)	417	394(399)[a]	OCC bend.
	315	308(330)	305		COC bend., CH_3 tor.
267(—)				267(—)	CH_3 tor.
235(245)				259(—)	COC bend.
	221	231(215)	232		CH_3 tor., COC bend.
138(—)	126	145(—)	111	136(—)	=C–O tor.
109(—)	97	65(—)	82	71(—)	-O–C tor.

a) Overlapped.

The above discussion is supported by the results of the normal frequency calculations. The key bands to the conformation are the C=C–O bending vibration and the C–O–C bending vibration in the case of ethyl vinyl ether. It is noticed that the *cis* and *skew* forms around the =C–O– axis give frequencies of about 600 and 500 cm^{-1} and the *trans* and *gauche* forms around the –O–C– axis give frequencies of about 400 and 430 cm^{-1}, respectively. The observed frequencies in the solid state correspond well to the calculated frequencies of the CT form. Among the observed frequencies in the liquid state, 500 and 436 cm^{-1} correspond to the calculated frequencies, 510 and 441 cm^{-1}, of the SG′ form (the stretched form). The band at 533 cm^{-1} is assigned to the ST form, the calculated frequency being 526 cm^{-1}. The CG form may be eliminated from the discussion on conformation because of its steric instability.

n-*Butyl Vinyl Ether.* The observed frequencies and the calculated frequencies for the CTTT form are given in Table 6. The complex features of the spectra in the gaseous and liquid states indicate the coexistence of rotational isomers. The situation of the rotational isomerism around the C–C axis next to the O–C axis seems to be rather peculiar. The small repulsive interaction between the oxygen atom and the CH_2

Table 6. Calculated and observed frequencies of n-butyl vinyl ether in cm^{-1}

Calculated (Observed) CTTT form ip	Calculated (Observed) CTTT form op	Assignment[a]
	654 (701)	=CH wag.
599 (600)		C=CO bend.
426 (437)		$C_2C_3C_4$ def., OC_1C_2 def.
334 (379)		$C_1C_2C_3$ def., OC_1C_2 def.
	261 (265)	CH_3 tor.
256 (246)		$C_2C_3C_4$ def., COC_1 bend.
	172 (—)	=C–O tor.
	148 (—)	-O–C tor.
124 (—)		$C_1C_2C_3$ def., OC_1C_2 def.
	96 (—)	=C–O tor., C_1–C_2 tor.
	70 (—)	-O–C tor., C_2–C_3 tor.

a) The alkyl carbon atoms are numbered as $-O-C_1-C_2-C_3-C_4$.

group in the $O-CH_2-CH_2-CH_2$ part of n-butyl vinyl ether makes the *gauche* form more stable than that in the case of the ordinary n-hydrocarbons. The complex features of the spectra may partly be due to this situation. The spectra in the solid state, however, are rather simple and have similar patterns to those of methyl vinyl ether and ethyl vinyl ether in the region 600—300 cm^{-1}, with an additional band at 440 cm^{-1}. The bands at 611 and 380 cm^{-1} correspond to those at 591 and 344 cm^{-1} of methyl vinyl ether and those at 603 and 395 cm^{-1} of ethyl vinyl ether, respectively. This fact suggests that the stable isomer in the solid state is the *cis* conformer around the =C–O– axis and the *trans* conformer around the –O–C– axis. An extra band at 440 cm^{-1} may be assigned to the CCC deformation of the extended form of the n-butyl group. The corresponding vibration of trans n-butane is observed at 425 cm^{-1} in the solid state.[11]

The observed frequencies of the solid state are well explained by the calculated frequencies of the CTTT form. The calculated frequency at 426 cm^{-1} corresponds to the observed frequency at 440 cm^{-1} in the solid state.

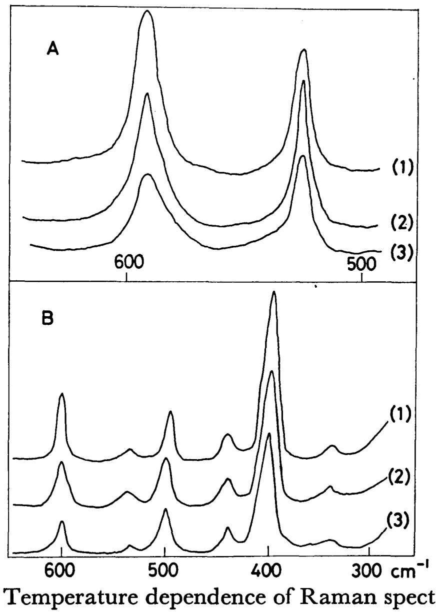

Fig. 8. Temperature dependence of Raman spectra.
A: Methyl vinyl ether, (1) 198 K (2) 215 K (3) 233 K.
B: Ethyl vinyl ether, (1) 206 K (2) 238 K (3) 297 K.

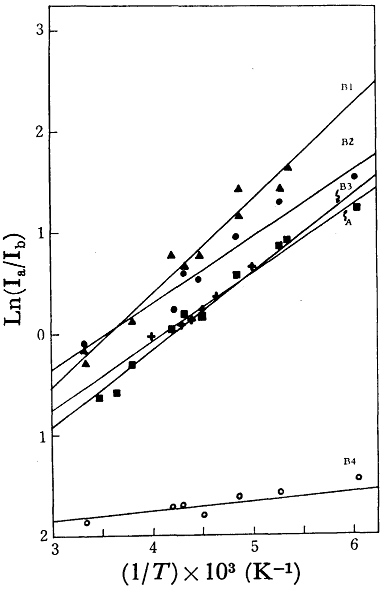

Fig. 9. Plots of Raman intensity *vs.* temperature.
A: +, methyl vinyl ether; a: 591 cm^{-1}, b: 527 cm^{-1}.
B: Ethyl vinyl ether; B1. ▲, a: 600 cm^{-1}, b: 533 cm^{-1}.
B2: ●, a: 600 cm^{-1}, b: 436 cm^{-1}. B3. ■, a: 600 cm^{-1},
b: 500 cm^{-1}. B4: ○, a: 600 cm^{-1}, b: 398 cm^{-1}.

Enthalpy Differences in the Liquid State. The Raman spectra of methyl vinyl ether and ethyl vinyl ether at different temperatures are shown in Fig. 8 and $\ln(I_a/I_b)$ plots *vs* $1/T$ are shown in Fig. 9, where I_a and I_b are the intensities of the Raman bands, a and b, belonging to the two rotational isomers.

For methyl vinyl ether, the enthalpy difference between the two isomers, the *skew* and *cis* forms, is obtained as 1440±160 cal/mol from the intensity dependence of the two bands at 527 and 591 cm^{-1} on temperature (Fig. 8A and plot A of Fig. 9). This value is consistent with the values 1150 and 1200 cal/mol obtained for the gaseous state by infrared[6] and electron diffraction[7] methods within the experimental errors.

In the case of ethyl vinyl ether, the intensity dependence on temperature has been examined for the Raman bands at 600, 533, 500, 436, and 398 cm^{-1} and the enthalpy differences obtained for the band pairs, 533 and 600 cm^{-1}, 436 and 600 cm^{-1}, 500 and 600 cm^{-1}, and 398 and 600 cm^{-1} are 1840±130, 1330±130, 1520±60, and 240±60 cal/mol, respectively (Fig. 8B and plots, B1, B2, B3, and B4 of Fig. 9). The enthalpy difference, 240±60 cal/mol, obtained for the bands at 398 and 600 cm^{-1} does not necessarily indicate that these bands are of different origins. It is possible that the band at 398 cm^{-1} is overlapped by the band due to the ST form (See Table 5).

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