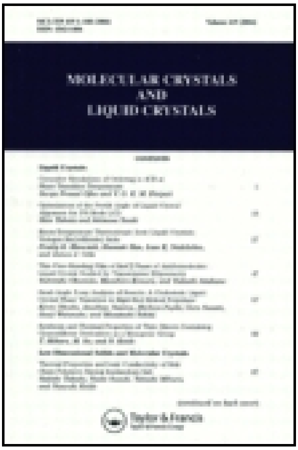

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Low Frequency Vibrational Spectra, Barriers to Methyl Rotations and Lattice Modes of Diethylether

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Low Frequency Vibrational Spectra, Barriers to Methyl Rotations and Lattice Modes of Diethylether

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The vibrational spectra of gaseous and crystalline $CH_3CH_2OCH_2CH_3$ and $CD_3CD_2OCH_2CH_3$ have been investigated below 500 cm^{-1}. Assignments of the low frequency fundamentals of the *trans-trans* and *trans-gauche* conformers are presented. Several torsional series were observed for the methyl groups in the far infrared spectra of the gaseous compounds. These series were analyzed using both coupled and uncoupled top treatments. No potential coupling was found; however, kinetic coupling of the two tops is evident. The low frequency spectra of the two crystalline phases were recorded. That of the stable modification was interpreted in terms of the non-centric space group $P2_12_12_1 \equiv D_2^4$. In the metastable phase, there are two molecules per unit cell each of which occupy equivalent sites of C_2, C_s or C_1 symmetry. Several lattice modes have been observed in the Raman spectra of each crystalline phase and tentative assignments are proposed.

INTRODUCTION

Internal rotation in molecules with two C_{3v} rotors, such as methyl groups, has been shown to yield rich far infrared spectra with many features originating from the torsional transitions.[1-8] The Raman spectra of these molecules are usually quite valuable for the information contained in the double-quantum jumps of the torsional transitions. With the extensive treatment of the semi-rigid model for a series of two-top molecules by Groner and Durig,[6] the torsional analysis of the low frequency spectrum of these molecules has become possible. The extent of the coupling of the two tops as the number of

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† Taken in part from the thesis of J. S. Church, which will be submitted to the Department of Chemistry in partial fulfillment of the Ph.D. degree.

atoms separating the two tops increases has become of interest, since the coupling radically changes the potential function of the torsional motion from that of a single C_{3v} rotor.

Recently we have investigated the low frequency spectra of dimethylether,[6] ethylmethylether[8] and methylvinylether.[7] It was found that in dimethyl- and ethylmethylether, where the tops are separated by one and two atoms, respectively, the torsional motions are strongly coupled.[6,8] With the success of the torsional analysis of the low frequency spectra of these molecules, the extent of coupling for two tops separated by three atoms seemed to be the next logical problem in our series of investigations, and thus, the analysis of the low frequency vibrational spectra of diethylether was undertaken.

Diethylether can have four possible conformers: *trans-trans, trans-gauche* and two *gauche-gauche* (C_s and C_2). The infrared and Raman spectra of diethylether have been extensively studied by several authors[9-11] and they have reported that at least two rotational isomers existed in the gaseous and liquid states, one of which was presumably the *trans-trans* conformer. Hayashi and Kuwada[12] have recorded the microwave spectra of six isotropic species of diethylether and have assigned the major lines to the *trans-trans* conformer. They also noted the existence of many weaker lines in all the spectral regions studied that could not be assigned to the *trans-trans* conformer. These lines were so complicated that their analysis was abandoned except for stating that they were probably due to a second conformer.

From more recent vibrational analyses it has been concluded[13,14] that the second conformer is the *trans-gauche* isomer and the energy difference between these two conformers, ΔH, is approximately 1.37 ± 0.10 kcal/mole.[14] In the crystalline state diethylether exists in the *trans-trans* conformation only. Perchard *et al.*[14] have reported the existence of two crystalline phases, one stable and the other metastable. The metastable phase occurs in the narrow temperature range from the triple point (149.86K) to 156.92K.[15] Below this temperature diethylether exists as a stable modification. Shimanouchi *et al.*[16] have recently carried out normal coordinate calculations for all of the possible conformers of diethylether, including many isotopically substituted species. The value of these calculations is somewhat in doubt, especially for the characterization of the low frequency modes, since the previous vibrational studies are far short of being complete in this spectral region.

It was hoped that the data obtained from this investigation would help to characterize low frequency modes of diethylether. It was also hoped that the potential function for the asymmetric CH_2-0 torsion could be determined and that the lattice modes for the two crystalline phases could be assigned. The results of our low frequency vibrational studies are reported herein.

EXPERIMENTAL

Diethylether-d_0 was prepared by the Williamson method from sodium ethoxide and ethyl iodide. The $NaOCH_2CH_3$ was obtained by adding metallic sodium to ethanol. The $CH_3CH_2OCD_2CD_3$ was also prepared by the Williamson method using CD_3CD_2I that was purchased from Merck, Sharp and Dohme. Both compounds were purified on a low temperature sublimation column and dried over sodium hydride.

The far infrared spectra between 450 and 80 cm^{-1} were recorded on a Digilab Model FTS-15B Fourier transform interferometer equipped with a 6.25 μ Mylar beamsplitter, high pressure Hg arc lamp source and TGS detector. The spectra of the gases were recorded by holding the samples at

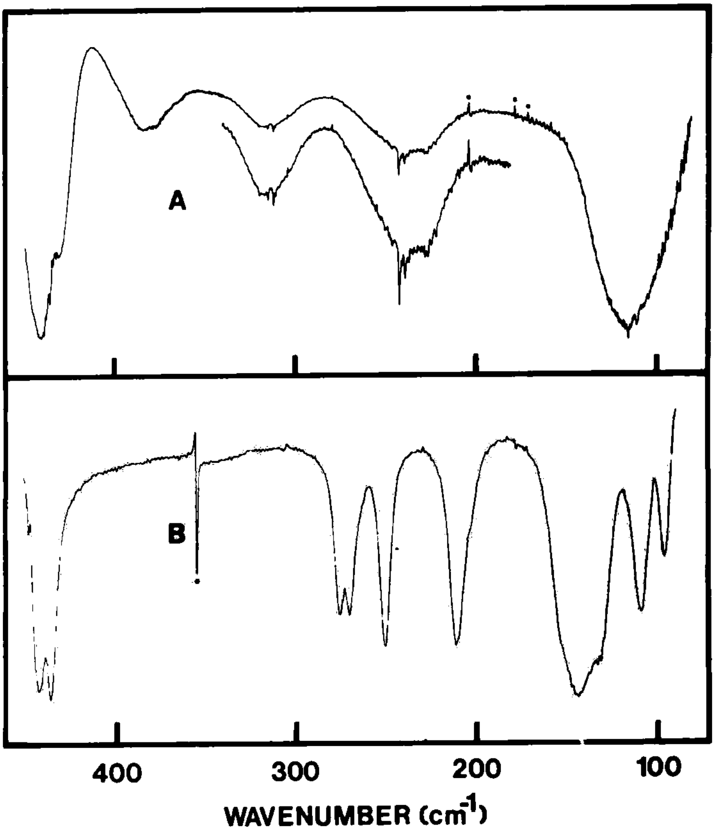


FIGURE 1 Far infrared spectra of (A) gaseous and (B) crystalline diethylether between 450 and 80 cm^{-1}. The asterisks in spectrum A indicate "negative" water peaks and in spectrum B an instrumental artifact from the 60 Hz.

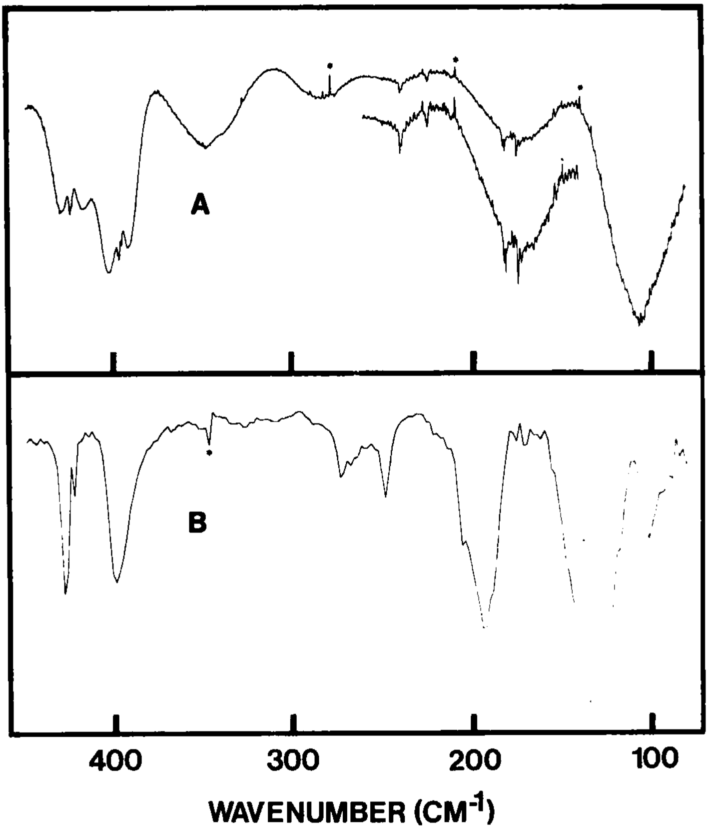


FIGURE 2 Far infrared spectra of (A) gaseous and (B) crystalline diethylether-d_5 between 450 and 80 cm^{-1}. The asterisks in spectrum A indicate "negative" water peaks and in spectrum B an instrumental artifact from the 60 Hz.

their ambient vapor pressures in 12 cm cells over activated 3Å molecular sieves. Interferograms for both the sample and reference cells were taken 2500 times, averaged, apodized by using a boxcar apodization function, and then transformed. The effective resolution was 0.25 cm^{-1} and no spectral enhancement was performed. The spectra of the solids were recorded by condensing the samples onto a silicon plate held at liquid nitrogen temperature. The samples were annealed until no further changes in the spectra were observed. Far infrared spectra between 450 and 80 cm^{-1} for gaseous and solid diethylether-d_0 and diethylether-d_5 appear in Figs. 1 and 2, respectively.

The mid-infrared spectra between 450 and 550 cm^{-1} were recorded on a Digilab Model FTS-14C Fourier transform interferometer equipped with a high intensity Glowbar source, Ge/KBr beamsplitter and a TGS detector. The spectra of the gases were recorded at their ambient vapor pressures by using a 10 cm cell fitted with KBr windows. The spectra of the annealed solids were recorded by condensing the samples onto a CsI plate held at liquid nitrogen temperature. The effective resolution of all of the mid-infrared spectra as well as the far infrared spectra of the solids is 2 cm^{-1}.

Raman spectra were recorded by using a Cary Model 82 spectrophotometer equipped with a Spectra Physics 171 argon ion laser tuned to the 5145 Å line. Gaseous samples were examined at their ambient vapor pressure in standard Cary multipass cells. The spectra of the liquids at room temperature were recorded with the samples sealed in glass capillaries. The spectra of the liquids at low temperature and those of the crystalline solids near their triple point were recorded by inserting the glass capillaries into a cell similar to the one described by Miller and Harney.[17] The temperature of the sample was monitored with an iron-constantan thermocouple referenced to 0°C. The spectra of the crystalline solids at 20K were recorded in a Cryogenic Technology Inc. Spectrim cryostat equipped with a Lake Shore Cryotronics Model DTL 500 temperature controller. The laser power at the sample was varied from 3 to 0.5 W depending upon the phase being investigated. The resolution was varied from 4 to 1 cm^{-1}. Depolarization ratios were measured by using the standard Cary accessories. The Raman spectra of gaseous, liquid and solid diethylether-d_0 and d_5 appear in Figs. 3 and 4, respectively. The observed infrared and Raman frequencies below 550 cm^{-1} for diethylether-d_0 and diethylether-d_5 appear in Tables I and II, respectively. The infrared frequencies quoted below 450 cm^{-1} are expected to be accurate to ± 0.5 cm^{-1} for measurements of the gas phase and to ± 1 cm^{-1} for the solid phase. Frequencies quoted above 450 cm^{-1} are also accurate to $\pm$ 1 cm^{-1}. The Raman frequencies are expected to be accurate to $\pm$ 2 cm^{-1}.

RESULTS AND DISCUSSION

The interpretation of the low frequency vibrational spectrum of diethylether is highly complex due to the anticipated presence of seven normal modes per conformer in the spectral region below 500 cm^{-1}. These normal modes can be described as three bending motions, two methyl torsions and two asymmetric CH_3CH_2-0 torsions. As an aid in assigning these modes, a low temperature study of the low frequency region of the Raman spectrum of diethylether was undertaken, and additionally the infrared and Raman spectra of $CH_3CH_2OCD_2CD_3$ below 500 cm^{-1} were investigated. The assignments presented herein are based on the results of these studies utilizing group frequencies, depolarization ratios, band contours, and expected spectroscopic activities. Based on the number of observed fundamentals in the spectra of the fluid phases, it is evident that only two conformers are present. One conformer

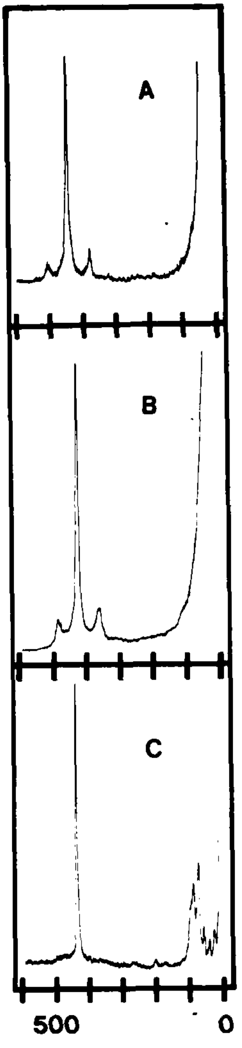


FIGURE 3 Low frequency Raman spectra of (A) gaseous, (B) liquid and (C) crystalline diethylether between 600 and 10 cm^{-1}.

has been assigned to the *trans-trans* structure as identified by the microwave study,[12] whereas the other conformer has been assigned to the *trans-gauche* structure. For the deuterated compound the *trans-gauche* structure gives rise to two non-equivalent conformers. In one conformer the heavy atom skeleton of the OCH_2CH_3 moiety constitutes a plane and the CD_2CD_3 group is rotated out of the plane. The second conformer arises when the OCD_2CD_3 moiety is in

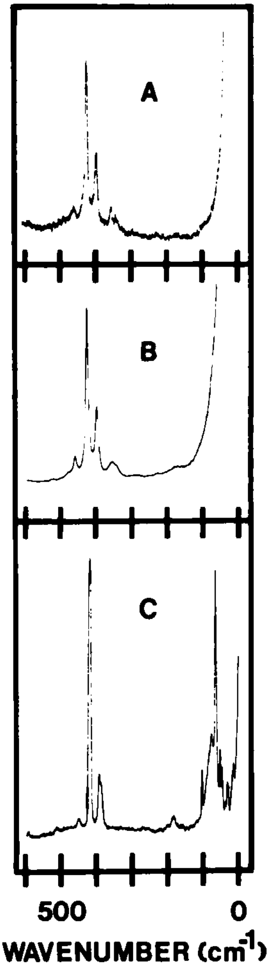


FIGURE 4 Low frequency Raman spectra of (A) gaseous, (B) liquid and (C) crystalline diethylether-d_5 between 600 and 10 cm^{-1}.

the plane and the CH_2CH_3 group is rotated out of the plane. These two conformers are also possible for the light compound; however, they are spectroscopically equivalent. The Raman spectra of the low temperature and room temperature liquids did not differ significantly. In the spectra of the annealed solids, only bands due to the *trans-trans* conformer were observed. The low frequency intramolecular fundamentals observed in the Raman spectra were found to have identical frequencies and similar intensities in both crystalline phases. A discussion of the assignments for the individual modes follows.

TABLE I
Observed vibrational spectrum of diethylether-d$_0$ below 550 cm^{-1}, and proposed assignments.[a]

Gas				Liquid		Solid (Phase II)						
Raman	Int. & Pol.	IR	Int.	Raman	Int. & Pol.	Raman	Int.	IR	Int.	Conformer	Symmetry Species	Assignment
503	w,p	503.5	m	500.5	w,p					t-g	A	C-O-C bend
441	s,p	441	s	441	s,p	444	s	441	s	t-t	A$_1$	C-O-C bend
		435.5 Q A/B	m					434	s	t-t	B$_1$	C-C-O antisym. bend
		433.7										
		432										
		430.2 P										
373	w,p	372.5	w	377	w,p					t-g	A	C-C-O antisym. bend
		314	w									
		313	w,br							t-g	A	C-C-O sym. bend
		310	w									
		309.5	vw									
						273	vw	273	m	t-t	A$_2$	CH$_3$ torsions
						267	vw	268	m			
		241.8	w			252	vw	248	m	t-t	B$_2$	CH$_3$ torsions
						246	vw					
		240.2	w							t-g		
		233	w,br							t-g	A	C-C-O sym. bend
		226.3	w							t-t	B$_2$	CH$_3$ torsions
		224	w							t-g	A	
						207	vw	208	m	t-t	A$_1$	C-C-O sym. bend
						201	vw					
		115	s	115	w,sh	141	w	139	s	t-t	B$_2$	O-CH$_2$CH$_3$ torsion
						132	w	130	s,sh	t-t	A$_2$	O-CH$_2$CH$_3$ torsion

[a] Abbreviations used: w, weak; m, medium; s, strong; v, very; p, polarized; dp, depolarized; sh, shoulder; br, broad; P, Q and R indicate P, Q and R rotational-vibrational branches; sym., symmetric; antisym., antisymmetric; A/B, hybrid band contour; t-t, *trans-trans;* t-g, *trans-gauche.*

TABLE II
Observed vibrational spectrum of diethylether-d_5, $CH_3CH_2OCD_2CD_3$, below 550 cm^{-1}, and proposed assignment.[a]

Gas				Liquid		Solid (Phase II)						
Raman	Int. & Pol.	IR	Int.	Raman	Int. & Pol.	Raman	Int.	IR	Int.	Conformer	Symmetry Species	Assignment
460	w,p	463	w	461.2	w,p	460†	w			t-g/g-t	A	C-O-C bend
		428 R										
426	s,p	424 Q A/B	m	427.5	s,p	428	s	428	m	t-t	A′	C-O-C bend
		423 Q				422	w					
		417 P										
		402.5 R										
		397.5 Q										
398.9	m,p	396.8 Q A/B	m	400	m,p	402	m	400	m	t-t	A′	C-C-O antisym. bend
		395.5 Q				397	m					
		391.5 P										
349	w,p	347	w,br	363.5	w,p					t-g/g-t	A	C-C-O antisym. bend
342	vw,p	340	vw,sh	353	w,p,sh					g-t/t-g	A	C-C-O antisym. bend
		282	w,br	297	vw,p,br	273†	vw	273†	w	t-g/g-t	A	C-C-O sym. bend
						267†	vw	267†	w			
		239.5	w			250	vw	250	w	t-t	A″	
		238.5	w							t-g/g-t	A	CH_3 torsions
		224.1	w							t-g/g-t	A	
		223.9	w							t-t	A″	
		210.5	w									
		182	w							t-g/g-t	A	
		181	w			205	vw,sh	205	w	t-t	A″	CD_3 torsions
		174.2	w							t-t	A″	
174	vvw,br	174	w,br	190	vw,p,br	195	w,br	195	m	t-t	A′	C-C-O sym. bend
		173.9	w							t-g/g-t	A	CD_3 torsion
		106	s			134	w	134	s	t-t	A″	$O-CH_2CH_3$ torsion

[a] For abbreviations used see Table I.

† Residual from t-g/g-t conformer.

Skeletal Bending Modes

The three skeletal bending modes can be described as a C-O-C bend, a symmetric C-C-O bend and an antisymmetric C-C-O bend. For the *trans-trans* conformer, C_{2v} symmetry, these modes are represented by the irreducible representations $\Gamma = 2A_1 + B_1$; thus, all of the bending modes are both infrared and Raman active. The A_1 modes are symmetric modes that give rise to polarized Raman lines. The B_1 mode is the antisymmetric bending mode and it is expected to be depolarized in the Raman effect. In the case of $CH_3CH_2OCD_2CD_3$, the symmetry of the *trans-trans* conformer is lowered to C_s. All of the skeletal bending modes are of the A′ species; thus, three bands with both infrared and Raman activity are expected and the Raman lines should appear polarized.

The C-O-C bending mode of the *trans-trans* conformer has been assigned to the strong polarized Raman band observed at 441 cm^{-1} in the spectrum of gaseous diethylether. Its infrared counterpart is also strong in intensity. In the Raman spectra of the deuterated compound, the C-O-C bending fundamental is observed at 426 cm^{-1} and the corresponding infrared band exhibits PQR structure characteristic of an A/B hybrid. This band contour is anticipated for such motions in the skeletal plane.

The symmetric O-C-C bending fundamental of *trans-trans* diethylether has been assigned to a band observed only in the spectra of the crystalline solids. In the infrared spectrum, the band appears at 208 cm^{-1} and is of medium intensity, whereas in the Raman effect the band is split into two weak components. In the spectra of the deuterated species this bending fundamental is observed in all three physical phases. It appears as a very weak, broad band at 174 cm^{-1} in the gas phase and shifts to 195 cm^{-1} upon crystallization.

The final bending mode of the *trans-trans* conformer, the antisymmetric C-C-O bend, has been assigned to a band of medium intensity that appears at 435.5 cm^{-1} in the infrared spectrum of gaseous $CH_3CH_2OCH_2CH_3$. This band possesses an A/B hybrid band contour, as expected, and several "hot-bands" appear on its low frequency shoulder. In the infrared spectrum of the crystalline solid this mode shifts to 434 cm^{-1} and is strong in intensity. No corresponding bands were observed in the Raman effect. As observed in the case of the C-C-O symmetric bending fundamental, the C-C-O antisymmetric bending mode also appears in all three physical phases upon deuteration. For the gaseous compound, the symmetric bending mode appears at 396.8 cm^{-1} and exhibits the PQR fine structure of an A/B hybrid in the infrared spectrum. In the infrared spectrum of the annealed solid this mode appears at 400 cm^{-1}. The corresponding Raman band splits into the two components observed at 402 and 397 cm^{-1}.

For both diethylether and diethylether-d_5, the *trans-gauche* conformers have C_1 symmetry. All of the normal modes are therefore of the A symmetry species and are expected to be both infrared and Raman active. The Raman lines should be polarized. For $CH_3CH_2OCH_2CH_3$, bands due to the *trans-gauche* conformer are anticipated to be fairly intense, since the equivalence of the two possible *trans-gauche* structures produces a two-fold statistical advantage. In the case of $CH_3CH_2OCD_2CD_2$ where the two *trans-gauche* structures are not equivalent, the bending modes are anticipated to occur in pairs separated by only a few wavenumbers. These pairs are indicated by the notations "t-g/g-t" and "g-t/t-g" in Table II.

Bands due to the *trans-gauche* conformers are observed only in spectra recorded from samples held in their fluid phases. The only exceptions are the three weak bands observed in the spectra of crystalline diethylether-d_5, which are assigned as residuals from the *trans-gauche/gauche-trans* conformers. These bands were rather intense in spectra recorded immediately following sample deposition; however, as annealing progressed they became weaker and weaker in intensity. The fact that these weak bands never completely vanished from the spectra of crystalline diethylether-d_5 indicates that a poor quality molecular crystal may be formed by the deuterated compound. With all of the additional weight of the deuterium atoms concentrated in one end of the molecule, the process of annealing may become more difficult. Also, since the deuterium substituted compound is not symmetric, the individual molecules can be arranged in several different relative orientations within the crystal lattice.

The C-O-C bending fundamental of the *trans-gauche* conformer of diethylether appears as a weak polarized Raman line at 503 cm^{-1} in the spectrum of the gas. Its infrared counterpart is of medium intensity. In the spectra of the gaseous deuterated compound, this mode is observed at 460 cm^{-1} and is also weak in intensity. The symmetric C-C-O bending mode of *trans-gauche* diethylether is only observed in the far infrared spectrum of the gas. It appears as a broad band of weak intensity centered at 313 cm^{-1}. A considerable amount of fine structure is observed on this band. However, due to the asymmetric shape of this band, it is probable that these Q-branches are actually components of an underlying combination band. The symmetric C-C-O bending mode of *trans-gauche* diethylether-d_5 also appears as a broad band of weak intensity. It is centered at 282 cm^{-1} in the infrared spectrum of the gas and shifts to 297 cm^{-1} in the Raman spectrum of the liquid. The remaining skeletal bending fundamental of the *trans-gauche* conformer is the antisymmetric C-C-O bending mode. This mode has been assigned to a weak band appearing at 373 cm^{-1} in both the infrared and Raman spectra of the gas. In the spectra of the deuterated compound bands attributed to both the *trans-gauche* and the *gauche-trans* conformers are observed. In the spectra of the gas these bands are observed at 349 and 342 cm^{-1}, and both are weak in intensity and polarized in the Raman effect.

Torsional Modes

The torsional modes of diethylether include two methyl torsions and two asymmetric O-CH_2CH_3 torsions per conformer. In the case of the *trans-trans* conformer (C_{2v} symmetry), one of the methyl torsions is both infrared and Raman active whereas the other is Raman active only. For the deuterated species, (C_s symmetry), both methyl torsions are A″ modes and thus infrared and Raman active. Since the *trans-gauche* conformers of both isotopic species have C_1 symmetry, the methyl torsions as well as all of the other modes fall in the A symmetry block. A summary of the methyl torsional data observed for diethylether and diethylether-d_5 is presented in Table III. Both the A_2 and B_2 methyl torsional fundamentals of the *trans-trans* conformer are observed in the infrared spectra of crystalline diethylether. They appear centered at 273 and 248 cm^{-1}, respectively. This infrared activity of the A_2 mode is due to the lower site symmetry in the crystal. Also, both torsional fundamentals were found to be split into two components each. In the spectra of the crystalline deuterated compound, the methyl torsions are observed at 250 and 205 cm^{-1}, the latter being assigned to the CD_3 top. The infrared spectra of gaseous diethylether and diethylether-d_5 are fairly complex as a number of torsional transitions are observed (see Figs. 1 and 2). Since only one methyl torsional series is anticipated in the infrared spectrum for the *trans-trans* conformer of diethylether, the two strong Q-branches observed at 241.8 and 226.3 cm^{-1} have been assigned as the $1 \leftarrow 0$ and $2 \leftarrow 1$ transitions of the B_2 mode, respectively. In the infrared spectrum of gaseous diethylether-d_5, two series of strong Q-branches are observed. The first, starting at 239.5 cm^{-1} has been assigned to the CH_3 torsion while the other series, starting at 181 cm^{-1} has been assigned to the torsion of the CD_3 group. Torsional transitions assigned to the *trans-gauche* conformers were observed in the infrared spectra of both isotopic species. These transitions are much weaker and in general were found to be shifted only a few wavenumbers from the torsional frequencies observed for the *trans-trans* conformers. The fact that only one series is observed for the *trans-gauche* conformer of diethylether is probably due to the near degeneracy of the energy levels of the two torsions. The analysis of the methyl torsional data has been confined to that obtained from the investigation of the gaseous samples as it is in this phase that intermolecular interactions are at a minimum.

Calculations of the barrier height to internal rotation were carried out using both uncoupled and coupled top treatments. The results of these calculations appear in Table IV. For the uncoupled top case, the potential function for a 3-fold torsional oscillation can be written as $V(\alpha) = (V_3/2)(1 + \cos 3\alpha) + (V_6/2)(1 + \cos 6\alpha)$, where V_3 and V_6 are the potential function coefficients. The reduced moment of inertia constants, $F = h^2/8\pi^2 I_r$, where I_r is the reduced moment of inertia for the internal rotation, were calculated using the

TABLE III

Summary of the methyl torsional data observed for diethylether and diethylether-d_5.

Diethylether						Diethylether-d_5					
Gas	Solid	Conformer	Symmetry Species	Assignment $v' \leftarrow v$	Obs.-Calc.[a]	Gas	Solid	Conformer	Symmetry Species	Assignment $v' \leftarrow v$	Obs.-Calc.[a]
	273	t-t	A_2	$1 \leftarrow 0$	—	239.5	250	t-t	A″	$1 \leftarrow 0$	0.5
241.8	248	t-t	B_2	$1 \leftarrow 0$	0.3	238.5		t-g/g-t	A	$1 \leftarrow 0$	0.2
238.5		t-g	A	$1 \leftarrow 0$	0.6	224.1		t-g/g-t	A	$2 \leftarrow 1$	−0.1
226.3		t-t	B_2	$2 \leftarrow 1$	−0.2	223.9		t-t	A″	$2 \leftarrow 1$	−0.3
224.0		t-g	A	$2 \leftarrow 1$	−0.5						
						182		t-g/g-t	A	$1 \leftarrow 0$	0.3
						181	205	t-t	A″	$1 \leftarrow 0$	−0.3
						174.2		t-t	A″	$2 \leftarrow 1$	0.3
						173.9		t-g/g-t	A	$2 \leftarrow 1$	−0.2

[a] Based on gas phase data, uncoupled top treatment.

TABLE IV
Potential Function Coefficients and Dispersions, in cm^{-1}, Calculated for the Methyl Rotors of Diethylether.

		Diethylether				**Diethylether-d_5**			
		t-t		*t-g*[a]		t-t		t-g/g-t[a]	
Case	Coefficient	Value	Dispersion	Value	Dispersion	Value	Dispersion	Value	Dispersion
uncoupled	V_3	1254.5	53.0	1235.8	57.8	1249.3	54.3	1282.3	46.6
CH_3 top	F	5.769	—	5.767	—	5.670	—	5.472	—
uncoupled	V_3	—	—	—	—	1302.5	41.3	1285.9	47.0
CD_3 top	F	—	—	—	—	3.028	—	3.050	—
coupled	V_{30}					1222.8	5.5	1279.0	2.6
C_{3v} tops	V_{03}					1310.3	7.7	1301.1	3.6
	$1/2(V_{30} + V_{03})$					1266.5	—	1290.0	—
	g^{44}					11.462		10.957	
	g^{55}					6.149		6.107	
	g^{45}					−0.731		−0.283	
	σ^b					0.63		0.30	

[a] g^{45}, g^{44}, g^{55} and F calculated using a 119° C-C-O-C dihedral angle.
[b] σ is the standard deviation of the fitted frequencies in cm^{-1}

structural parameters for diethylether reported in the microwave study of Hayashi and Kuwada.[12] The C—O—C—C dihedral angle of the *trans-gauche* conformer was assumed to be 119° in accord with the corresponding dihedral angle found in ethylmethylether.[8] The F values utilized in the calculations appear in Table IV along with the potential function coefficients and their dispersions. Only V_3 coefficients were required to satisfactorily fit the observed transitions; however, the dispersions are fairly large.

The Hamiltonians for two coupled C_{3v} top systems have been set up by Groner and Durig[6] for a range of compounds. The *trans-trans* conformer of diethylether-d_5 is designated as a $C_{3v}(T) - C_s(F) - C_{3v}(\overline{T})$ system where T = top, F = frame and the bar indicates that the tops are not equivalent. The *trans-gauche* conformer is similarly denoted as a $C_{3v}(T) - C_1(F) - C_{3v}(\overline{T})$ system.

The internal rotation Hamiltonian for the general C_1 case with nonequivalent tops has been derived[6] as

$$H_I = (\tfrac{1}{2})\,(g^{44}\hat{p}_o^2 + 2g^{45}\hat{p}_o\hat{p}_1 + g^{55}\hat{p}_1^2) + V(\tau_0,\tau_1),$$

with $V(\tau_0,\tau_1)$ in standard form as

$$\begin{aligned} V(\tau_0,\tau_1) = {} & (\tfrac{1}{2})[V_{30}(1 - \cos 3\tau_0) + V'_{30} \sin 3\tau_0 + V_{60}(1 - \cos 6\tau_0) \\ & + V'_{60} \sin 6\tau_0 + V_{03}(1 - \cos 3\tau_1) + V'_{03} \sin 3\tau_1 + V_{06}(1 - \cos 6\tau_1) \\ & + V'_{06} \sin 6\tau_1 + V_{33}(\cos 3\tau_0 \cos 3\tau_1 - 1) + V'_{33}(\sin 3\tau_0 \sin 3\tau_1) \\ & + V''_{33} \sin 3\tau_0 \cos 3\tau_1 + V'''_{33} \cos 3\tau_0 \sin 3\tau_1]. \end{aligned}$$

For the C_s case with nonequivalent tops, this expression is simplified by the following restrictions:

$$V'_{30} = V'_{03} = V'_{60} = V'_{06} = V''_{33} = V'''_{33} = 0$$

The kinetic coefficients g^{44}, g^{45} and g^{55} were calculated using the structural parameters discussed previously. Since the torsional series of both tops were observed only in the case of diethylether-d_5, coupled top calculations were carried out for the two conformers of the deuterated species only. The values obtained for the kinetic coefficients and the potential function coefficients are reported in Table IV. The smaller dispersions obtained for the potential function coefficients of the coupled top treatment make these results more favorable. Even though no potential coupling coefficients were utilized in the calculation, the smaller dispersions obtained with the coupled top treatment indicate that there is kinetic coupling between the two tops. Very little if any potential coupling was anticipated between the two methyl tops of diethylether because of the large separation between the two tops.

From the potential function coefficients appearing in Table IV, it can be concluded that the barrier to methyl rotation for the *trans-trans* conformer of diethylether is on the order of 1250 cm^{-1} or 3.6 kcal/mole. Comparison with the corresponding methyl torsional barriers in ethylmethylether[8] and propane[18] shows an increase in barrier height in diethylether. The value calculated for the C-CH_3 barrier in ethylmethylether is 1076 cm^{-1}, while for propane a value of 1147 cm^{-1} was obtained. The barrier to methyl rotation for the *trans-gauche* conformer of diethylether was determined to be slightly higher than the value obtained for the *trans-trans* conformer. This trend was also observed for the methyl torsional barriers of ethylmethylether.[8]

The two asymmetric O-CH_2CH_3 torsions can be considered as skeletal bending motions. They can be best described as geared and anti-geared torsional oscillations of the ethyl moieties about the O-C bonds. Under the C_{2v} symmetry restrictions of the *trans-trans* conformer, the geared motion is represented by the B_2 symmetry species and is thus both Raman and infrared active. The anti-geared mode falls in the A_2 symmetry block and is therefore Raman active only. The asymmetric torsions of *trans-trans* diethylether-d_5 are both A″ modes. The O-CH_2CH_3 torsions of the *trans-gauche* conformers are A modes for both isotopic species. The B_2 asymmetric O-CH_2CH_3 torsion of *trans-trans* diethylether has been assigned to a strong band observed at 115 cm^{-1} in the infrared spectrum of the gas. The A_2 asymmetric torsion is observed as a weak shoulder on the exciting line in the Raman spectrum of the liquid. Both torsional modes are observed in the spectra of the crystalline solids. This can be attributed to lower site symmetry in the crystal. In the spectra of the deuterium-substituted compound only one of the asymmetric torsions is observed. This mode appears as a strong band at 106 cm^{-1} in the infrared spectrum of the gas. It is observed in both the infrared and Raman spectra of the molecular crystal. No asymmetric torsions were observed for the *trans-gauche* conformer. These modes probably differ very little in energy from those of the *trans-trans* conformer and thus produce the strong unresolvable bands observed. The lack of information on the asymmetric torsions of the *trans-gauche* conformers prohibits the determination of the potential function for this asymmetric motion. The energy difference between the two conformers was determined by Perchard *et al.*[14] to be 1.37 kcal/mole. This value for ΔH is very similar to the one found for ethylmethylether[8].

LATTICE MODES

D. André *et al.*[19] have found the crystalline structure of the stable modification of diethylether to be $P2_12_12_1 \equiv D_2^4$. This space group is non-centric and has no special positions and only four general positions. Crystallographically, it was determined that there are eight molecules per unit cell. These molecules are associated into four asymmetric units of two independent ether molecules each. It is these asymmetric units that sit on the four general positions. This crystal symmetry accounts for the two molecules per unit cell sitting on nonequivalent sites reported by Perchard *et al.*[14] It is also consistent with the splitting of several torsional and skeletal bending modes reported herein. From the group theoretical considerations of Halford[20] and Hornig[21] one can predict the following representations for the intermolecular fundamentals of the stable form of diethylether:

$$\Gamma = 12A + 12B_1 + 12B_2 + 12B_3.$$

The acoustical translations fall into the species:

$$\Gamma(AT) = B_1 + B_2 + B_3.$$

Thus, 45 spectroscopically active lattice modes are expected. The representations for the optical translations and librations are then:

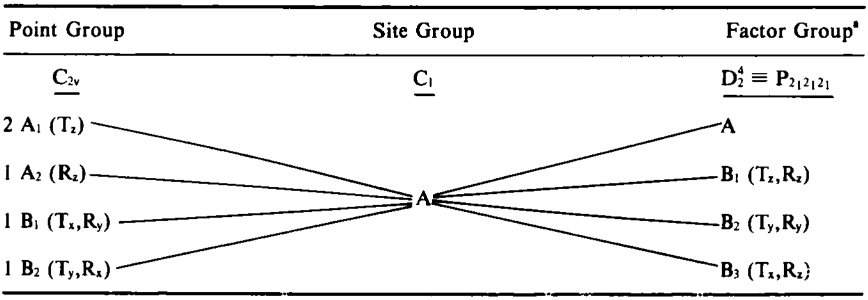
$$\Gamma(OT) = 6A(R) + 5B_1(IR,R) + 5B_2(IR,R) + 5B_3(IR,R)$$

$$\Gamma(OL) = 6A(R) + 6B_1(IR,R) + 6B_2(IR,R) + 6B_3(IR,R)$$

Table V gives the factor group analysis of diethylether based on C_{2v} molecular symmetry. André *et al.*[19] concluded from their single-crystal x-ray diffraction study that even though the two molecules constituting the asymmetric unit occupy a general position, they have nearly perfect C_{2v} symmetry. The large degree of uncertainty in the bond angles as determined by the x-ray study as well as the contacts found when hydrogen atoms are involved indicates that the ether molecules may be distorted from perfect C_{2v} symmetry. André *et al.*[19] also neglected to correct their data for absorption, thus adding another source of error into the calculation of the structural parameters. In an attempt to determine more accurate structural parameters it is suggested that a low temperature neutron diffraction study be undertaken.

TABLE V

Vibrational Representation of the Skeletal and Torsional Modes of Gaseous *trans-trans*-Diethylether and the Correlation Table to the D_2^4 Unit Cell Group.



[a] The A modes are Raman active only whereas all other modes are both Raman and Infrared active.

Theoretically, the intermolecular fundamentals may be distinguished by analyzing the observed frequency shifts of a motion upon deuteration of the molecule. The shift factor for a translation upon deuteration of diethylether should be proportional to the square root of the mass of $CH_3CH_2OCD_2CD_3$ to that of $CH_3CH_2OCH_2CH_3$, or 1.03. Similarly, those shift factors associated with the librations depend upon the moments of inertia around the three principal axes of a molecule and its isomer. The principal moments of inertia for diethylether were determined using the structural parameters obtained from the microwave study.[12] The theoretical shift factor for a libration which occurs about the "a" principal axis of diethylether is 1.15, while a value of 1.06 is calculated for librations about the "b" and "c" axes. There is a small difference between the shift factors calculated for the librations about the "b" and "c" axes, with the "b" axis having a slightly smaller factor than the "c", but the calculated difference is probably smaller than can be detected experimentally. The observed shift factors are usually smaller than the predicted values due to the large amount of anharmonicity associated with intermolecular fundamentals. Also, in the case of a non-centric cell, the librations and translations may mix.

From the Raman spectra of the stable modification of diethylether and diethylether-d_5 shown in Figure 5, ten discernible bands are observed which could be assigned as intermolecular fundamentals. It is quite clear that not nearly as many lattice modes are being observed as one predicts from the group theoretical considerations. Two of these ten bands are also observed in the infrared spectra of the crystalline solids. Because of the great similarity between the spectra of the two isotopic species, most of the corresponding lattice modes were easily identified. The frequencies for the observed intermolecular fundamentals of the stable modification of diethylether, their shift factors, and their assignments are given in Table VI. Since it was not possible to differentiate between the librations about the "b" and "c" axes with confidence, they are tentatively assigned with the librations about the "b" axis having the smaller of the observed shift factors. Also, since translations generally occur at lower frequencies than librations, the bands which are observed above 80 cm^{-1} have been tentatively assigned to two-phonon transitions, although the bands at 107 and 94 cm^{-1} may be associated with the intramolecular asymmetric rotation. However, it appears clear from the Raman spectrum that the bands at 42, 49, 61 and 77–79 cm^{-1} are librational modes. The breadth of the 79 cm^{-1} Raman line is somewhat surprising and it may be made up of several lattice modes which could include two phonon bands of the translations. However the simplicity of the lattice spectrum is more consistent with what one might expect for a crystal with two molecules per unit cell.

The metastable modification of diethylether has not been studied as thoroughly as the stable one. No x-ray diffraction work has been carried out

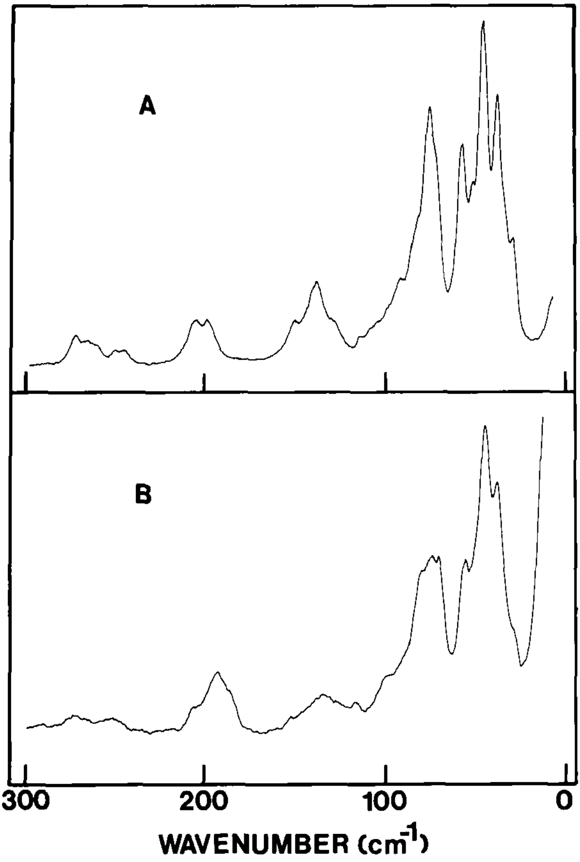


FIGURE 5 Lattice mode region of the Raman spectra recorded at 20 K (stable phase): (A) diethylether, (B) diethylether-d_5.

on this form; however, Perchard *et al.*[14] concluded from their spectroscopic study that there are two molecules per unit cell, and, unlike the stable modification, these molecules sit on identical sites. The site symmetry of a molecule in its ordered crystalline lattice must be equal to, or a subgroup of, the point group of the free molecule. Thus, for the C_{2v} symmetry of gaseous diethylether, the subgroups C_2, C_s and C_i are possible. Since the low frequency intramolecular fundamentals were found to have identical frequencies in both the stable and metastable phases, it is probable that the site symmetries of the molecules in the two modifications are also identical. Thus the molecules of the metastable modification of diethylether are tentatively placed on sites of C_i symmetry.

For a crystal with two molecules per cell, a maximum of nine optically

TABLE VI
Observed and Calculated Shift Factors for the Raman Active Lattice Vibrations and Their Assignments for the Stable Modification of Diethylether and Diethylether-d_5 at 20 K.

Diethylether	Diethylether-d_5	Observed Shift Factor	Calculated Shift Factor	Assignment
107† br	102 sh, br	1.04	—	Two phonon or
94† br	—	—	—	Asymmetric torsion
84 sh	82 s	1.02	1.03	Two phonon
79 s	77 s	1.02	1.03	Libration
77 sh	73 s	1.05	1.06	Libration b
61 s	57.5 s	1.06	1.06	Libration c
54 sh	~50 sh	—	—	Libration or Translation
49 vs	46.5 vs	1.05	1.06	Libration b
42 s	39.5 s	1.06	1.06	Libration c
33 m	32 m	1.03	1.03	Translation

†Observed also in the infrared spectrum.

active lattice modes are anticipated. From the Raman spectrum of the metastable modification of diethylether, Figure 6, a total of nine intermolecular fundamentals are readily observed. Again, the great similarity between the spectra of the two isotopic species enables the one to one correspondence between the bands to be determined. The observed fundamentals of the metastable modification of diethylether, their shift factors, and their assignments are given in Table VII; however, the assignments of these lattice vibrations were not all straightforward. The intermolecular vibrations observed for the metastable modifications were in general weaker and broader than those observed for the stable form, thus making accurate frequency determination for these modes impossible. It was also found that for many of the lattice modes, discrepancies as small as 0.1 cm^{-1} in their measured frequencies resulted in changes in their proposed assignments. Since the same librational and translational shift factors were utilized in assigning the lattice vibrations observed in the spectra of both crystalline phases, the assignment of the librations about the "b" and "c" principal axes is again tentative. The Raman band observed at 99 cm^{-1} in the spectrum of the metastable modification of diethylether was initially assigned to the A_2 geared $O\text{-}CH_2CH_3$ torsion of the *trans-trans* conformer due to its broadness and intensity. Investigation of the Raman spectrum of the deuterated species indicated that this assignment was questionable as a shift factor more characteristic of a librational mode was obtained. Thus, the assignment of the Raman lines from 78 cm^{-1} and above must be considered very tentative.

The three rather pronounced Raman lines at 30.5, 46 and 61.5 cm^{-1} all appear to have shift factors consistent with their being assigned as translational modes. The Raman lines at 37 and 53 cm^{-1} were not as easily detected since they appeared to be very dependent on the ability to anneal the sample,

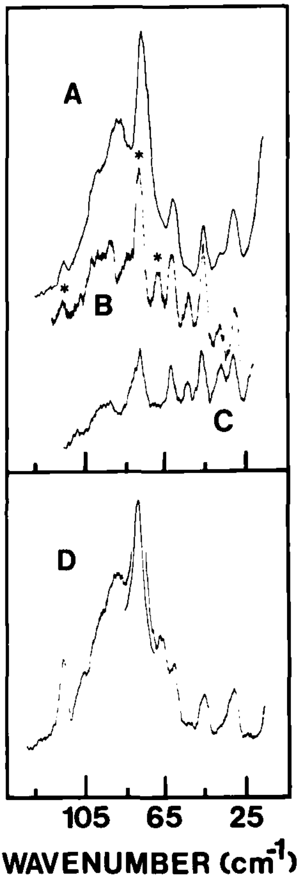


FIGURE 6 Lattice mode region of the Raman spectra recorded at 157 K (metastable phase): (A) diethylether partially annealed, (B) diethylether annealed several times, (C) diethylether annealed several times but recorded on the anti-Stokes side of the exciting line to distinguish the plasma lines, (D) diethylether-d_5. The askerisks indicate plasma lines.

and they were barely detectable in the spectrum of the -d_5 compound which did not form as good a crystal as the light sample. When we used the Miller-Harney[17] cell to obtain spectra of solids, plasma lines appeared at 65.5, 76.9 and 116.0 cm^{-1} with varying degrees of intensity. These show up clearly in the spectrum shown in Figure 6B. Also shown in this same figure (Figure 6C) is the anti-Stokes spectrum of the lattice region, and it is clear from this spectrum that the 78 cm^{-1} Raman line is strong but it is considerably broader than the lower frequency transitions. Thus it appears that there are underlying two-phonon bands associated with the 78 cm^{-1} Raman line and another libration could be assigned at about 90 cm^{-1}. Therefore, the three translational modes have been assigned and three and possibly four of the six expected librational

TABLE VII
Observed and Calculated Shift Factors for the Raman Active Lattice Vibrations and Their Assignment for the Metastable Modification of Diethylether and Diethylether-d_5 at 156 K.

Diethylether	Diethylether-d_5	Observed Shift Factor	Calculated Shift Factor	Assignment
—	105.5 m	—	—	Two Phonon or Asymmetric Torsion
99 m	95 sh	1.04	—	
92 br	88 br	1.05	1.06	Libration c or Two Phonon
78 vs	75.5 vs	1.03	1.05	Libration b
61.5 s	60 m	1.02	1.03	Translation
53 m	—	—	—	Libration
46 s	45 m	1.02	1.03	Translation
37 m	~35.5 sh	1.04	1.05	Libration b
30.5 s	30 m	1.01	1.03	Translation

modes have been observed for this crystalline phase which has two molecules per primitive cell.

By comparing the lattice mode regions of the two modifications of diethylether, Figure 5 and 6, it is evident that the two crystal structures are somewhat different. Sharpening of the Raman lines and the appearance of previously unobserved spectral features was anticipated in the spectra of the stable phase of diethylether. However, these changes, which are generally observed at low temperatures, were not nearly as pronounced as expected and apparently the coupling between the asymmetric units is quite weak. This weakness of the intermolecular forces in the stable phase was also noted by Perchard *et al.*[14] as they concluded from analysis of spectroscopic data that no association exists between the molecules of the asymmetric units. This is also reflected in the fact that the number of lattice vibrations observed is more consistent with the number of molecules in the asymmetric unit, i.e. two, than with the number of asymmetric units, i.e. the number of C_i sites per cell.

Based on the fairly loose molecular packing found by the x-ray structure analysis[19] as well as the weakness of the intermolecular interactions as concluded from spectroscopic studies[14], it is not surprising that a metastable phase exists. The stable crystalline phase is probably only slightly more energetically favorable than the metastable phase, as the metastable form was generally obtained upon cooling the liquid.

SUMMARY

The low frequency vibrational spectra of $CH_3CH_2OCH_2CH_3$ and $CH_3CH_2OCD_2CD_3$ have been investigated under relatively high resolution for all three physical phases. Bands due to the *trans-trans* and *trans-gauche* conformers have been identified and the assignments of their low frequency fundamentals are presented. Only bands attributed to the *trans-trans* conformer were observed in the spectra of the crystalline phases. A series of sharp Q-branches observed in the far infrared spectrum of gaseous diethylether has been assigned to the B_2 methyl torsion of the *trans-trans* conformer. No transitions were observed for the A_2 torsion of the *trans-trans* conformer in the Raman spectrum of the gas. Torsional Q-branch series for both the CH_3 and CD_3 moieties were observed in the spectra of gaseous diethylether-d_5. Analysis of the torsional data acquired for the methyl groups using both coupled and uncoupled top treatments yielded values for the barriers to internal rotation that are identical when the accuracy of the calculations is considered. The results of the coupled top treatment were more favorable, since lower dispersions were obtained for the potential coefficients. No potential coupling terms were required to obtain a satisfactory fit of the data. However, the lower dispersions of the coupled top treatment indicate that there is kinetic coupling between the two methyl tops. Torsional series were also observed for the methyl groups of the *trans-gauche* conformers. These Q-branches were shifted only slightly in frequency from those assigned to the *trans-trans* conformer. The value of 1250 cm^{-1} obtained for the barrier to internal rotation of the *trans-trans* conformer is slightly lower than that obtained for the *trans-gauche* conformer. Insufficient rotational fine structure was observed on the CH_3CH_2O asymmetric torsional fundamentals for the characterization of the potential function governing this motion.

The low frequency spectra of the stable crystalline phase of diethylether have been assigned in terms of the non-centric space group $P2_12_12_1 \equiv D_2^4$. This is in accord with the results of a three-dimensional single crystal x-ray diffraction study.[19] Two independent diethylether molecules associated as a pseudodimer make up the asymmetric unit. There are four of these units per unit cell and each unit sits on a general position. However, the spectrum observed in the lattice region is more nearly what is expected for two molecules per primitive cell, which indicates very weak intermolecular forces among the asymmetric units.

The results of the vibrational study of the metastable crystalline phase of diethylether indicate that there are two molecules per unit cell and the molecules sit on identical sites of C_2, C_s or C_i symmetry. The observed data in the lattice region can be satisfactorily interpreted on this basis.

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