JOURNAL OF MOLECULAR SPECTROSCOPY **165**, 195–204 (1994)

Microwave Spectrum, Structure, and Dipole Moment of the *trans-cis* Isomer of Ethyl Vinyl Ether

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Microwave spectra of the *trans-cis* isomer of ethyl vinyl ether and its nine deuterated species were measured. A plausible molecular structure was obtained from the observed moments of inertia by an application of a diagnostic least-squares technique. The dipole moment and its direction were determined by the Stark effect measurements of several low J transitions for the normal and two deuterated species. © 1994 Academic Press, Inc.

INTRODUCTION

The microwave spectra of the normal species of the *trans-cis* (*tc*) isomer (*trans* for the CH_3–CH_2–O–CH= part and *cis* for the –CH_2–O–CH=CH_2 part) of ethyl vinyl ether were already reported by Owen and Sørensen (*1*), and the approximate structure and dipole moment and its most probable direction were proposed on the basis of a comparison of the experimental data with those of the *cis* isomer of methyl vinyl ether reported by Cahill *et al.* (*2*).

We also worked on the microwave spectra of the *cis* isomer of methyl vinyl ether (*3*) and found that the proposed structure of Cahill *et al.* is fairly different from the r_s structure obtained by us, and the direction of the dipole moment proposed is also different from the actual direction determined by us.

The present work on the *tc* isomer of ethyl vinyl ether was undertaken in connection with our work on *c*-methyl vinyl ether, and spectra of nine deuterated species were measured. Although we also studied the spectra of the ^{13}C and ^{18}O species, samples decomposed rapidly in the waveguide cell and we could not obtain reliable rotational constants necessary to solve the r_s structure of the molecule.

We were also trying to find conditions in which we could obtain reliable molecular structures to replace the r_s structure by using a series of molecules whose r_s structures were already reported as test molecules. We found that reasonable structures can be obtained from the differences of the observed moments of inertia between the normal and the deuterated species without data for the skeletal substituted species, such as the ^{13}C and ^{18}O species, if sufficient data are available for deuterated species by applying the diagnostic least-squares method proposed by Nösberger *et al.* (*4*) and Curl (*5*).

Details of these investigations will be published separately (*6*).

We then applied the method to the present molecule and determined a reasonable structure of the molecule. We obtained the dipole moment and its direction in the molecule by the Stark effect measurements of several low J transitions for the normal and two deuterated species.

0022-2852/94 $6.00

EXPERIMENTAL DETAILS

The sample of the normal species of ethyl vinyl ether was prepared by the following reactions: hydrochloric acid was passed through a mixture of acetaldehyde and ethanol at about 0°C and the resultant α-chloroethyl ethyl ether was refluxed with pyridine at about 120°C. The sample thus obtained was distilled in a vacuum line. The samples of nine deuterated species were prepared by the same reactions with appropriate deuterated species of acetaldehyde and ethanol.

The microwave spectra were measured by a conventional 100-kHz Stark modulation spectrometer at dry ice temperature. Since the samples decomposed rapidly in the waveguide cell, we exchanged the samples in the cell frequently.

MICROWAVE SPECTRA

The *tc* isomer of ethyl vinyl ether has *a* and *b* components of the dipole moment, and strong *b*-type and medium *a*-type transitions are expected.

In Table I, the observed frequencies of the transitions with $J \leqq 7$ and $K_p \leqq 1$ are listed, and they could be fitted by a rigid rotor Hamiltonian without any centrifugal terms. The rotational constants thus obtained are listed in Table II.

METHOD OF DETERMINATION OF MOLECULAR STRUCTURES

The present data are insufficient for the determination of the r_s coordinate values of skeletal heavy atoms but are sufficient for obtaining values of all the hydrogen atoms in the molecule by the substitution method. Although the conventional least-squares method seems to be useful for the present case, a simple application of the method to obtain the structural parameters from the observed moments of inertia has not yet been successfully carried out.

The following three situations exist for structural parameters and moments of inertia of the molecules: (i) The dependence of moments of inertia on structural parameters is much different from one parameter to the other, (ii) some of the parameters are highly correlated with each other, and (iii) observed moments of inertia contain fairly large contributions from the molecular vibrations which are very different between isotopic species.

For situation (iii), we can largely reduce the vibration effect if we use only the differences of the moments between the isotopic and the normal species in a manner similar to the case when the r_s structure is solved, as is pointed out by Nösberger *et al.* (*4*). For situations (i) and (ii) it seems adequate to apply the diagnostic least-squares method proposed by Curl (*5*).

In this method, situation (i) is settled by the careful choice of the initial parameter values and their estimated uncertainties, which act as kinds of weighted parameters, and situation (ii) is settled by the use of special linear combinations of parameters instead of the parameters themselves. These linear combinations are automatically found by diagonalization of the coefficient matrix of the left side of the normal equation in the least-squares procedures and they are independent of each other.

For example, the observed values of the CH bond lengths fall into the range from $r_{\min} = 1.070$ to $r_{\max} = 1.110$ Å for the molecules whose structures have been reported. The value of 1.09 ± 0.02 Å may then be considered to be a reasonable initial value and estimated uncertainty for the CH bond.

In the conventional least-squares procedure, the estimated uncertainties of the initial values are usually set to be equal, and the CH value outside the above interval happens to be obtained in order to fix the other sensitive parameters.

TABLE I

Observed Frequencies of Ethyl Vinyl Ether ($CH_3CH_2OCH=CH_2$) (MHz)[a]

Transition	EtOVy[b]	CD_3CH_2OVy	s-CH_2DCH_2OVy	a-CH_2DCH_2OVy	$CH_3CHDOVy$
$1_{10}\leftarrow 1_{11}$	13828.98(2)	12606.23(1)	13489.92(-1)	13393.67(0)	12867.93(1)
$2_{11}\leftarrow 2_{12}$	14174.10(-1)	12882.41(1)	13816.02(1)	13709.01(0)	
$3_{12}\leftarrow 3_{13}$	14703.61(2)	13304.95(0)	14315.93(1)	14192.19(1)	13750.94(-1)
$4_{13}\leftarrow 4_{14}$	15431.36(1)	13883.70(-3)	15002.44(2)	14855.22(1)	14487.93(0)
$5_{14}\leftarrow 5_{15}$	16375.54(2)	14631.59(-1)	15892.19(4)	15713.83(1)	15446.63(1)
$6_{15}\leftarrow 6_{16}$	17557.77(-1)	15564.15(4)	17005.10(3)	16786.86(-2)	16650.38(-1)
$7_{16}\leftarrow 7_{17}$	19002.34(-2)	16698.84(-2)	18363.46(-6)	18095.59(0)	18125.01(0)
$2_{02}\leftarrow 1_{01}$	10583.72(1)	9502.07(2)	10115.11(2)	10222.73(-1)	10515.50(-1)
$2_{12}\leftarrow 1_{11}$	10251.18(1)	9234.78(2)	9800.55(0)	9918.27(-1)	10181.16(-2)
$2_{11}\leftarrow 1_{10}$	10928.87(1)	9778.23(1)	10441.21(3)	10538.08(0)	10863.60(1)
$3_{03}\leftarrow 2_{02}$	15859.84(2)	14241.98(0)	15158.22(0)	15320.52(0)	15756.10(1)
$3_{13}\leftarrow 2_{12}$	15372.85(0)	13849.37(-1)	14697.26(1)	14874.06(1)	15267.52(0)
$3_{12}\leftarrow 2_{11}$	16389.31(0)	14664.52(-2)	15658.14(1)	15803.70(1)	16291.05(1)
$1_{11}\leftarrow 0_{00}$	18785.13(0)	17087.74(0)	18230.04(0)	18197.86(-1)	17787.90(-1)
$2_{12}\leftarrow 1_{01}$	23741.29(0)	21569.24(-1)	22970.15(-1)	23002.06(0)	22707.89(-1)
$3_{13}\leftarrow 2_{02}$	28530.41(-2)	25916.61(2)	27552.29(-3)	27653.37(0)	27459.90(0)
$4_{14}\leftarrow 3_{03}$	33160.55(-1)	30135.36(-2)	31983.83(-1)	32158.70(-1)	32052.68(1)

Transition	CH_3CD_2OVy[b]	$EtOCD=CH_2$	$EtOCH=CHD$	$EtOCH=CHD_t$	$EtOCH=CD_2$
$1_{10}\leftarrow 1_{11}$	12019.92(0)	12840.03(1)	12662.66(2)	13778.20(2)	12659.26(-1)
$2_{11}\leftarrow 2_{12}$	12367.60(-2)	13199.60(1)	13030.87(2)	14094.62(1)	12996.40(-1)
$3_{12}\leftarrow 3_{13}$	12902.85(1)	13752.65(1)	13597.71(-1)	14579.22(1)	13514.35(-1)
$4_{13}\leftarrow 4_{14}$	13641.70(-1)	14515.38(1)	14380.40(-1)	15243.77(0)	14227.59(0)
$5_{14}\leftarrow 5_{15}$	14605.11(1)	15508.73(0)	15401.12(0)	16103.69(-1)	15154.90(1)
$6_{15}\leftarrow 6_{16}$	15817.70(5)	16757.55(-1)	16686.05(-1)	17177.55(0)	16318.64(2)
$7_{16}\leftarrow 7_{17}$	17306.18(-4)	18289.07(0)	18263.76(1)	18486.20(0)	17743.47(-2)
$2_{02}\leftarrow 1_{01}$	10447.64(0)	10350.53(-1)	10396.80(0)		
$2_{12}\leftarrow 1_{11}$	10114.62(1)	10005.68(1)	10044.20(1)	9771.01(1)	
$2_{11}\leftarrow 1_{10}$	10795.32(-2)	10710.09(-2)	10765.02(2)	10393.20(-1)	
$3_{03}\leftarrow 2_{02}$	15653.15(-1)	15507.48(1)	15575.70(-1)	15101.86(0)	14852.30(-1)
$3_{13}\leftarrow 2_{12}$	15167.39(1)	15003.96(0)	15061.48(1)	14653.21(1)	14378.60(0)
$3_{12}\leftarrow 2_{11}$	16188.38(1)	16060.54(2)	16142.57(0)	15586.46(1)	15370.27(1)
$1_{11}\leftarrow 0_{00}$	16907.05(1)	17666.74(-1)	17504.54(0)	18508.11(-2)	17288.20(0)
$2_{12}\leftarrow 1_{01}$	21794.18(2)	22493.47(0)	22346.44(1)	23238.07(-1)	21917.12(-1)
$3_{13}\leftarrow 2_{02}$	26513.88(-2)	27146.87(-1)	27011.09(-2)	27814.49(-1)	26383.28(1)
$4_{14}\leftarrow 3_{03}$	31075.58(-1)	31636.33(-1)	31508.49(0)	32244.17(1)	30694.96(0)

[a] Figures in parentheses indicate the difference between the observed and calculated frequencies attached to the last digit.

[b] CH_3CH_2- and $-CH=CH_2$ are abridged as Et and Vy in the name rows, respectively.

In the diagnostic least-squares procedure, the structural parameter r(CH) is replaced by $\zeta = (x - x_0)/\sigma$, where $x_0 = (r_{\min} + r_{\max})/2$, $\sigma = (r_{\max} - r_{\min})/2p$, and $p = 1.645$ when 90% of the actual r(CH) values are in the range from $r_{\min}$ to $r_{\max}$. This modification of the parameters produces the change of the weights for individual parameters.

As already mentioned earlier, we worked recently on this subject using a series of molecules whose r_s structures were already established (*6*), and the purposes of our work are (i) whether the parameters obtained by this method depend on the initial values, (ii) whether the so obtained parameters are close to the r_s structural parameters

TABLE II

Observed Rotational Constants of *tc*-Ethyl Vinyl Ether (MHz)[a]

Species[b]	A	B	C	RMS[c]
EtOVy	16307.044(13)	2816.925(3)	2478.082(2)	.014
CD_3CH_2OVy	14846.982(18)	2512.489(4)	2240.757(3)	.020
s-CH_2DCH_2OVy	15859.984(24)	2690.375(5)	2370.059(4)	.026
a-CH_2DCH_2OVy	15795.769(9)	2711.994(2)	2402.096(2)	.009
$CH_3CHDOVy$	15327.912(10)	2801.199(2)	2459.994(2)	.010
CH_3CD_2OVy	14463.482(18)	2783.925(4)	2443.560(3)	.020
$EtOCD{=}CH_2$	15253.383(10)	2765.583(2)	2413.361(2)	.011
$EtOCH{=}CHD_c$	15083.592(11)	2781.352(2)	2420.948(2)	.011
$EtOCH{=}CHD_t$	16143.154(11)	2676.078(3)	2364.975(2)	.012
$EtOCH{=}CD_2$	14973.732(10)	2645.046(3)	2314.465(2)	.011

a. Figures in parentheses indicate the uncertaities attached to the last digit calculated from 2.5 times the standard deviation.
b. CH_3CH_2- and $-CH{=}CH_2$ are abridged as Et and Vy, respectively.
c. The root mean square deviation between the observed and calculated frequencies.

Moments of Inertia of tc-Ethyl Vinyl Ether (amu·Å²)[a]

Species	I_a	I_b	I_c	P_c[b]	ΔP_c[c]
EtOVy	30.99127(3)	179.40698(19)	203.93837(17)	3.22994(17)	
CD_3CH_2OVy	34.03897(4)	201.14556(32)	225.53807(30)	4.82323(33)	1.59329(52)
s-CH_2DCH_2OVy	31.86485(5)	187.84593(35)	213.23351(36)	3.23864(38)	0.00870(57)
a-CH_2DCH_2OVy	31.99439(2)	186.34850(14)	210.38959(18)	3.97665(17)	0.74671(36)
$CH_3CHDOVy$	32.97096(2)	180.41417(13)	205.43790(17)	3.97362(16)	0.74368(35)
CH_3CD_2OVy	34.94152(4)	181.53363(26)	206.81956(25)	4.82779(28)	1.59785(47)
$EtOCD{=}CH_2$	33.13206(2)	182.73760(13)	209.40754(17)	3.23106(16)	0.00112(35)
$EtOCH{=}CHD_c$	33.50502(2)	181.70156(13)	208.75128(17)	3.22765(16)	-0.00229(35)
$EtOCH{=}CHD_t$	31.30590(2)	188.84950(21)	213.69190(18)	3.23175(21)	0.00181(40)
$EtOCH{=}CD_2$	33.75084(2)	191.06511(22)	218.35543(19)	3.23026(21)	0.00032(40)

a. Figures in parentheses indicate the uncertainties attached to the last digit.
b. $P_c = (I_a + I_b + I_c)/2$.
c. $\Delta P_c = P_c(\text{isotopic}) - P_c(\text{normal})$.

when only the differences of the moments of inertia are used, and (iii) how we can recognize that the procedures are effective.

It is concluded that (i) the obtained values are not affected by the initial values, if the actual values are in the range of the estimated uncertainties, (ii) the values obtained are close to the r_s values, and for most molecules, the values are the r_s values themselves, and (iii) we may conclude that the least-squares procedures are effective if the calculated uncertainties of the obtained values are smaller than the initial estimated uncertainties.

In the course of these studies, we found that the moments of inertia for the isotopic species with the skeletal heavy atom are not always necessary for obtaining reasonable skeletal parameters for some of the molecules if a sufficient number of moments of inertia for the deuterated species are available.

This can be understood from the fact that the separation between two hydrogen atoms is generally determined not only from the parameters directly related to their positions but also from the positions of the skeletal heavy atoms such as the carbon and oxygen atoms, and the moments of inertia for the deuterated species implicitly contain some information about the skeletal structural parameters.

STRUCTURE

Before the application of the diagnostic least-squares method to the present molecule, we tested the method using *c*-methyl vinyl ether, whose r_s structure is well established.

As reported previously (*3*), moments of inertia for four skeletal isotopic species and 10 deuterated species are available for *c*-methyl vinyl ether. The established r_s structure is given in the r_s column of Table IV.

The diagnostic least-squares procedures were carried out by the use of the r_s parameters as the initial values and 0.04 Å and 2° as the initial estimated uncertainties for the bonds and angles, respectively.

In Table IV, the numbers in the DLS column are the parameters obtained by the use of all the available moments of inertia, and those in the DLS-SK-DF column are the values obtained by using moments of inertia only for the 10 deuterated species and not those for the skeletal isotopic species. The differences among the r_s, DLS, and DLS-SK-DF values are very slight. The values are especially almost identical for the DLS and DLS-SK-DF cases. The calculated uncertainties of the obtained parameters largely decrease from the initial estimated uncertainties, and this indicates that the procedures are effective for this molecule.

The calculated uncertainties for the DLS-SK-DF case are larger than those for the DLS case, and the root-mean square deviation (RMS) between the observed and the calculated moments of inertia for all the species used increases slightly for the DLS-SK-DF case as expected.

These facts indicate that the r_s-like structure is reasonably obtained without the moments of inertia for the skeletal isotopic species for *c*-methyl vinyl ether. Details of the results will be included in a forthcoming paper (*6*).

From the results for *c*-methyl vinyl ether described above, we expect that an application of the diagnostic least-squares procedures will also give us fruitful results for the present molecule, *tc*-ethyl vinyl ether.

The initial structural parameters were transferred from the corresponding r_s values for *c*-methyl vinyl ether and *trans*-ethyl methyl ether (*7*, *8*), and the estimated un-

TABLE III

Differences between the Observed and the Calculated Quantities Related to Moments of Inertia (amu · Å^2)

Species	δI_a[a]	δI_b[a]	δI_c[a]	$\delta \Delta I_a$[b]	$\delta \Delta I_b$[b]	$\delta \Delta I_c$[b]
EtOVy	0.02185	1.56182	1.50490			
CD_3CH_2OVy	0.02397	1.51826	1.46968	0.00191	-0.04646	-0.03614
s-CH_2DCH_2OVy	0.02172	1.55442	1.47997	0.00001	-0.00586	-0.02324
a-CH_2DCH_2OVy	0.02262	1.54336	1.49789	0.00060	-0.02068	-0.00837
$CH_3CHDOVy$	0.02289	1.52665	1.47329	0.00020	-0.03562	-0.03203
CH_3CD_2OVy	0.02735	1.51048	1.44184	0.00382	-0.05234	-0.06383
$EtOCD=CH_2$	0.02287	1.54063	1.48249	0.00094	-0.01975	-0.02105
EtOCH=CHD	0.02126	1.54107	1.48813	-0.00120	-0.02186	-0.01848
EtOCH=CHD	0.02137	1.54973	1.48870	-0.00042	-0.01425	-0.01829
$EtOCH=CD_2$	0.02552	1.52682	1.47293	0.00315	-0.03824	-0.03572
ave	0.02314	1.53732	1.47998			
dev[d]	0.00421	0.02449	0.01791			

a. $\delta I_g = I_g(\mathrm{obs}) - I_g(\mathrm{calctd})$, g = a, b, c.

b. $\Delta I_g = I_g(\mathrm{isotopic}) - I_g(\mathrm{normal})$, $\delta \Delta I_g = \Delta I_g(\mathrm{obs}) - \Delta I_g(\mathrm{calctd})$, g = a, b, c.

c. Average of δI.

d. dev $= \delta I_g(\max) - \delta I_g(\min)$.

TABLE IV

Structural Parameters[a] of *tc*-Ethyl Vinyl Ether and *c*-Methyl Vinyl Ether

	tc-Ethyl Vinyl Ether(X=C)		c-Methyl Vinyl Ether(X=O)		
	initial[b]	DLS-SK-DF[d]	r_s	DLS	DLS-SK-DF[c]
Skeleton					
r(CC) (Å)	1.521{7}	1.522(6)			
r(CO) (Å)	1.420	1.415(4)	1.420{1}	1.420(1)	1.420(1)
r(OC=) (Å)	1.350	1.348(6)	1.350{1}	1.350(1)	1.350(1)
r(C=C) (Å)	1.339	1.343(4)	1.339{1}	1.339(1)	1.339(1)
α (CCO)	108° 9' {23'}	107°26' (18')			
α (COC)	116° 5'	115°39' (16')	116° 5' {5'}	115°59' (3')	115°58' (4')
α (OC=C)	128° 1'	128°17' (18')	128° 1' {6'}	128° 6' (3')	128° 4' (5')
CH_3 Group					
r(CH_s) (Å)	1.089{8}	1.088(8)	1.077{5}	1.077(2)	1.077(2)
r(CH_a) (Å)	1.092{7}	1.095(3)	1.102{1}	1.103(1)	1.103(1)
α (XCH_s)	110°30' {38'}	110°57' (33')	106°51' {44'}	107° 7' (13')	106°57' (21')
α (XCH_a)	110° 8' {34'}	110°19' (23')	110°15' {5'}	110°15' (4')	110°10' (8')
α (H_aCH_a)	108°38' {36'}	108°52' (43')	107°59' {3'}	108° 9' (7')	108°17' (12')
CH_2 Group					
r(CH) (Å)	1.100{3}	1.104(4)			
α (OCH)	110°19' {28'}	109°38' (33')			
α (HCH)	107°24' {17'}	107°11' (43')			
OCH= Group					
r(CH) (Å)	1.086	1.090(6)	1.086{1}	1.086(2)	1.086(2)
α (OCH)	110°18'	110°58' (32')	110°18' {5'}	110°30' (9')	110°33' (14')
$C=CH_2$ Group					
r(CH_c) (Å)	1.096	1.093(5)	1.096{1}	1.096(1)	1.096(2)
r(CH_t) (Å)	1.077	1.082(8)	1.077{1}	1.077(2)	1.077(2)
α ($C=CH_c$)	121°56'	122°26' (29')	121°56' {5'}	122° 1' (8')	121°55' (12')
α ($C=CH_t$)	118°20'	118°41' (34')	118°20' {7'}	118°39' (13')	118°28' (24')
species used		10		15	11
RMS(amu·Å^2)[e]		0.0134		0.0044	0.0077

a. Figures in round parentheses indicate the uncertainties attached to the last digit.

b. The initial parameter values for the analysis by the diagnostic least squares method and estimated uncertainties were taken to be 0.04 Å and 40' for the bond and angle, respectively. These values were transferred from those of the corresponding r_s values of trans-ethyl methyl ether and c-methyl vinyl ether. Figures in { } indicate the uncertainties of the r_s values.

c. *The parameter values obtained by the diagnostic least squares method.*

d. The parameter values obtained by DLS without the data for skeletal substituted species, that is, $^{13}CH_3OVy$, $CH_3{}^{18}OVy$, $CH_3O^{13}CH=CH_2$, and $CH_3OCH=^{13}CH_2$ for the $CH_3OCH=CH_2$ case.

e. The root mean square deviation between the observed and calculated moments of inertia of all the species used.

certainties of these values were taken to be 0.04 Å and 2° for the bonds and angles, respectively. Results are given in Tables IV and V. The calculated uncertainties of the parameters become much smaller than the initial estimated uncertainties for all the parameters although they are larger than those for the DLS-SK-DF case of *c*-methyl vinyl ether. The procedures are then found to be also effective for the present molecule.

TABLE V

Atom Coordinate Values (Å) for *tc*-Ethyl Vinyl Ether

Hydrogen atom		x_a	x_b	x_c
H_s (CH_3)	DLS-SK-DF[a]	-2.90865	0.96489	0.0
	r_s[b]	-2.90606(10)	0.95968(32)	0.0
	δ[c]	-0.00159	0.00521	0.0
H_a (CH_3)	DLS-SK-DF	-2.49345	-0.50482	±0.89063
	r_s	-2.49087(8)	-0.51085(36)	±0.88742(22)
	δ	-0.00258	0.00603	±0.00321
H_n (CH_2)	DLS-SK-DF	-0.54395	1.09905	±0.88863
	r_s	-0.51380(176)	1.09901(92)	±0.88945(158)
	δ	-0.03015	-0.00004	±0.00082
H_o (-CH=)	DLS-SK-DF	1.82434	-1.48504	0.0
	r_s	1.81840(10)	-1.48472(13)	0.0
	δ	0.00594	-0.00032	0.0
H_t (=CH_2)	DLS-SK-DF	3.08325	0.58135	0.0
	r_s	3.08104(7)	0.57902(37)	0.0
	δ	0.00221	-0.00233	0.0
H_c (=CH_2)	DLS-SK-DF	1.51429	1.60421	0.0
	r_s	1.50837(12)	1.60452(12)	0.0
	δ	0.00592	-0.00031	0.0

Skeletal Atom by DLS-SK-DF	x_a	x_b	x_c
C_m (CH_3)	-2.26310	0.08910	0.0
O	-0.02793	-0.69395	0.0
C_c (=CH_2)	2.00408	0.62661	0.0
C_n (CH_2)	-0.79606	0.49441	0.0
C_o (-CH=)	1.30936	-0.52436	0.0

a. See the footnotes c. and d. in Table IV.

b. The r_s coordinate values. Figures in parentheses indicate the uncertainties attached to the last digit.

c. The differences between the coordinate values obtained by DLS and by the substitution method.

In order to know whether the parameters obtained are close to the r_s parameters in a manner similar to the cases for other molecules, r_s coordinates of the hydrogen atoms were solved and compared with the values calculated from the obtained structure. From Table V, it is found that the differences between two kinds of the coordinates are very small except that of the x_a coordinate of the H_n hydrogen atom in the CH_2 group, for what reason is not presently known.

When the r_s structure of a molecule is well established, it is well known that the differences between the observed and the calculated moments of inertia are small, positive, and constant for all the isotopic species used.

In the present DLS treatment, this tendency for the differences of moments of inertia is also found, as seen in Table III, in a manner similar to the cases for the r_s treatment.

From the results mentioned above, we believe that the plausible structure is reasonably obtained and this structure may be close to the r_s structure of *tc*-ethyl vinyl ether.

From the structure listed in Table IV, it is found that the structural parameters of the present molecule (EVE) are roughly equal to those of the corresponding parameters of *c*-methyl vinyl ether (MVE) and *trans*-ethyl methyl ether (EME).

However, the following remarks are in order although the uncertainties of their values are overlapping each other: (i) r(CC–O) is smaller than that of MVE, similar to those of r(CC–O) and r(C–O) for EME, (ii) r(C$=$C) is larger than that of MVE, (iii) α(CCO) and α(COC) of EVE are slightly smaller than those of EME and MVE, respectively, (iv) α(OCH) in the CH_2 group is smaller than that of EVE while that of the OCH$=$ group is larger than that of MVE, and (v) the difference of the two r(CH) bonds lengths is smaller than that of MVE and the difference of the two α(C$=$CH) angles is also smaller than that of MVE.

DIPOLE MOMENT

Stark effect measurements were carried out for several low J transitions of the normal and two deuterated species. The spectrometer was calibrated with OCS spectra (9) before and after measurements of the samples. Results are given in Table VI.

The dipole moment of the normal species is 0.995 D, making an angle of 57°51′ with the a-inertial axis. This value of the dipole moment is larger by 0.03 D than that

TABLE VI

Stark Effect[a] and Dipole Moment

transition	M	$CH_3CH_2OCH=CH_2$ Obs	$CH_3CH_2OCH=CH_2$ Calc	$CD_3CH_2OCH=CH_2$ Obs	$CD_3CH_2OCH=CH_2$ Calc	$CH_3CD_2OCH=CH_2$ Obs	$CH_3CD_2OCH=CH_2$ Calc
$2_{11}\leftarrow 2_{02}$	1	1.628(3)	1.626	0.844(2)	0.835		
$2_{11}\leftarrow 2_{02}$	2			1.935(3)	1.937		
$1_{11}\leftarrow 0_{00}$	0					1.962(6)	1.973
$2_{12}\leftarrow 1_{01}$	0	-0.588(1)	-0.589			-0.349(1)	-0.347
$2_{12}\leftarrow 1_{01}$	1					0.182(3)	0.176
$2_{02}\leftarrow 1_{01}$	0	-0.596(2)	-0.597	-0.617(3)	-0.631		
$2_{02}\leftarrow 1_{01}$	1	0.084(0)	0.084	0.128(0)	0.128		
$2_{11}\leftarrow 1_{10}$	1					-5.311(12)	-5.332
μ_a(D)		0.529(2)		0.541(6)		0.534(4)	
μ_b(D)		0.842(3)		0.836(11)		0.837(11)	
μ_{total}(D)		0.995(3)		0.996(10)		0.993(10)	
$\alpha(\mu\times a)$[b]		57°51′, 122° 9′ (12′)		57° 6′, 122°54′ (46′)		57°27′, 122°33′ (40′)	
$\alpha(a\times CH_2\text{-}O)$[c]		57° 7′		57° 1′		56°40′	
$\alpha(a\times \text{bisec})$[d]		114°57′		114°50′		114°29′	
$\alpha(a\times CH\text{-}O)$[e]		172°47′		172°40′		172°19′	
$\alpha(\mu(A)\times CH_2\text{-}O)$[f]		44′		5′		47′	
$\alpha(\mu(B)\times \text{bisec})$[g]		7°12′		8° 4′		8° 4′	

a. Stark coefficients in $\Delta\nu/\varepsilon^2(\times 10^5)$ MHz/(V/cm)^2.
Figures in parentheses indicate the experimental uncertainties attached to the last digit. See also Fig. 1.

b. The angle between the dipole moment and the a-inertial axis.

c. The angle between the a-inertial axis and the $CH_2\rightarrow O$ bond.

d. The angle between the a-inertial axis and the bisector of the COC angle.

e. The angle between the a-inertial axis and the $=CH\rightarrow O$ bond.

f. The angle between the dipole moment (A) and the $CH_2\rightarrow O$ bond.

g. The angle between the dipole moment (B) and the bisector of the COC angle.

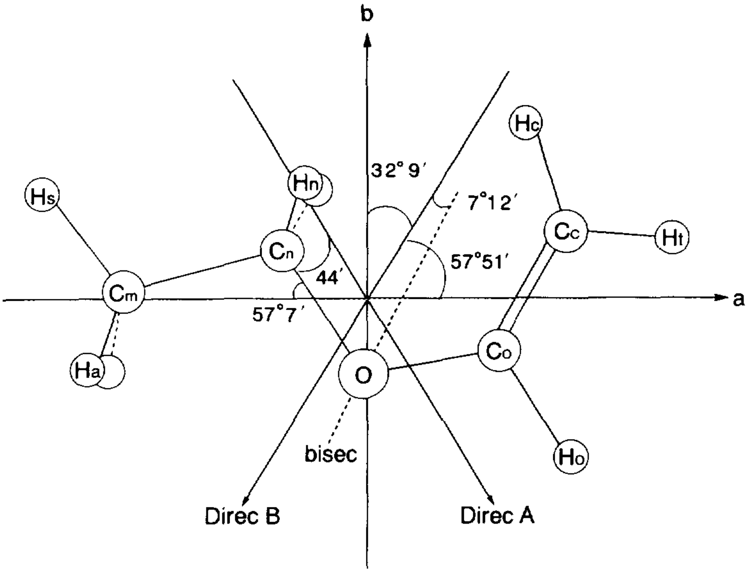

FIG. 1. Atom labeling scheme and direction of dipole moment.

of *c*-methyl vinyl ether, but much smaller than those of alkyl ethers such as dimethyl,[1] ethyl methyl, and diethyl ether (1.302, 1.174, and 1.061 D, respectively) (*11*, *7*, *12*). There are two possible directions of the dipole moments in the molecule as shown in Fig. 1 (Directions A and B). The actual direction can usually be chosen from a comparison of the results for the isotopic species. However, the rotation of the inertial axes induced by the isotopic substitution is so small for the species used (6′ and 27′ for CD_3CH_2OVy and CH_3CD_2OVy, respectively), that the direction should be estimated from other information.

Owen and Sørensen (*1*) reported that the dipole moment of this molecule makes an angle of 58°38′ with the *a*-inertial axis and is nearly parallel to the bisector of the COC angle from Stark effect measurements of the normal species. Their estimation of the direction was based on their results for *c*-methyl vinyl ether (*2*), and the direction corresponds to our Direction B. However, as reported by us (*3*), the direction of the dipole moment of *c*-methyl vinyl ether is not nearly parallel to the bisector of the COC angle but makes an angle of 12°36′ with the CH_3–O bond.

For *c*-methyl vinyl sulfide, which is the sulfur analog of *c*-methyl vinyl ether, Penn and Curl (*10*) reported their results for the molecule. Although they did not mention it explicitly, the dipole moment of this molecule makes an angle of 17°41′ with the CH_3–S bond in a manner similar to the case of *c*-methyl vinyl ether.

As the ethyl group is considered to have only a slight influence on the dipole moment, the direction of the dipole moment of *tc*-ethyl vinyl ether may be nearly close to that of *c*-methyl vinyl ether. Therefore, we conclude that Direction A in Fig. 1 is the actual direction of the dipole moment of *tc*-ethyl vinyl ether; that is, the dipole moment is nearly parallel to the CH_2–O bond.

RECEIVED: November 5, 1993

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[1] The dipole moment was remeasured by one of the present authors (unpublished data, 1975).

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