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TOP-TOP AND TOP-SKELETAL TORSION COUPLING EFFECTS ON THE MICROWAVE SPECTRA OF trans-ETHYLMETHYLETHER

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Microwave spectra of trans-ethylmethylether and its four deuterated species in the ground and four lowest torsionally excited states were measured. The coupling effects among two methyl and skeletal torsions were analyzed.

In the previous paper$^{1)}$, we reported the molecular structure of trans-ethylmethylether as a preliminary work for the problem of the coupling effects among two methyl and skeletal torsions. Recently, Durig and Compton$^{2)}$ have reported a similar analysis of trans-ethylmethylether from the far-infrared and Raman spectra. Then, we will report our present results obtained from the microwave spectra in order to compare them with their results, though our works are not satisfactorily completed.

Microwave spectra in the ground and four lowest torsionally excited states (hereafter referred as (v_c, v_o, τ) = (000), (001), (002), (010), and (100) where v_c, v_o, and τ indicate the torsional quantum numbers of the CH_3C, OCH_3, and skeletal torsions, respectively) were measured for the normal and four deuterated species, $CH_3CH_2OCH_3$, $CH_3CD_2OCH_3$, $CD_3CH_2OCH_3$, $CD_3CD_2OCH_3$, and $CH_3CH_2OCD_3$ (hereafter designated as (HHH), (HDH), (DHH), (DDH), and (HHD)).

The spectra having $J\leq10$ and $K_p\leq2$ in the (000), (001), and (002) states are usually doublets due to the internal rotation of the OCH_3 group. Furthermore, the A and E components of the doublets are proved to be reversely arrayed in the (001) and (002) states as contrasted to those in the (000) state from the analysis of the odd order term contributions. This irregular array indicates that the coupling effect with the skeletal torsion is not negligible for the excited skeletal torsional states. The spectra having $J\leq10$ and $K_p\leq1$ in the (010) and (100) states are usually quartets or pairs of doublets whose components are labelled as AA, AE, EA, and EE where the first and second symbols indicate the sublevels, A or E, of the CH_3C and OCH_3 torsions, respectively. Some of the low J transitions exhibit quintet structures whose EE component splits further into two components EE_+ and EE_- due to the differences of the odd order term contributions. For these states, the differences of two components $\Delta\nu$(AA-EA) and $\Delta\nu$(AE-EE) correspond to the splittings due to the CH_3C torsion while $\Delta\nu$(AA-AE) and $\Delta\nu$(EA-EE) correspond to those due to the OCH_3 torsion. CH_3C splittings in the (010) state and OCH_3 splittings in the (100) state are proved to be reversely arrayed as contrasted to those in the (000) state. This behavior is similar to that of the OCH_3 splittings in the (001) and (002) states as pointed above. This irregularity is considered to be mainly due to the coupling effect between the tops.

Vibrational energy levels; According to the vibrational spectra reported[2,3], the present five isotopic species are classified into three classes from the patterns of the six lowest vibrational energy levels, that is;

		$v_\tau = 1$	$v_\tau = 2$	$v_o = 1$	$v_c = 1$	$v_d = 1$
Class A	(HHH)	115.4	227.2	201.8	248.0	288.0
	(HDH)	111.0	222.0	202.0	240.0	282.0
Class B	(DHH)	108.0	216.0	230.0	175.0	262.0
	(DDH)	104.0	208.0	220.0	170.0	260.0
Class C	(HHD)	106.1	209.7	163.0	242.7	277.0

where the levels are given in cm^{-1} and v_d indicates the quantum number of the lower skeletal deformation vibration.

Top-skeletal torsion coupling; According to the extended bootstrap method[4,5], the perturbation coefficients $W_{v\sigma}^{(n)}$ in the effective rotational Hamiltonian are simply proportional to the effective pure torsional energy difference of the A and E sublevels $\omega_1^{(v)}(\mathrm{eff})$ $[=8(E_{vA}-E_{vE})/27F]$ if the barrier V_3 is sufficiently high and the top-skeletal torsion coupling terms are small. $\omega_1^{(v)}(\mathrm{eff})$ can be expanded by the coupling parameters $X(=F_\tau'/F)$, $Y(=V_{3\tau}/V_3)$, and $Z(=V_{3\tau}'/V_3)$ as

$$\omega_1^{(v)}(\mathrm{eff}) = \omega_1^{(v)}(1 + AX^2 + BXZ + CZ^2 + DY + EY^2) \qquad (1)$$

where F_τ', $V_{3\tau}$, and $V_{3\tau}'$ are the coefficients of the kinetic coupling term and of the potential coupling terms $\tau^2(1-\cos 3\alpha)$ and $\tau\sin 3\alpha$, respectively. The coefficients A, B, C····· can be calculated from the effective pure torsional Hamiltonian by the second order perturbation theory, where the skeletal torsion is approximated by harmonic oscillator with frequency ν. At first, observed frequency $\nu(\tau=0\rightarrow1)$ was used without any correction. When some of the terms in the perturbation sums are large, the corresponding 2×2 secular equations are directly solved in the calculations as we did in the cases of the other molecules . From $\omega_1^{(v)}(\mathrm{eff})$ values determined from the observed splittings for each state, V_3, $V_{3\tau}$, and $V_{3\tau}'$ values can be obtained. The results are as follows (see also Table 1).

The OCH_3-skeletal torsion coupling; First, the irregular array of the A and E components found in the (001) and (002) states can be interpreted by the presence of the X^2 dependent term. Second, for Class A species, the barriers V_3 obtained from the (002) and (010) states cannot coincide with those obtained in the (000) and (001) states even after Y and Z dependent terms are introduced. For the (010) state, this fact may be due to the presence of the top-top coupling contributions, while the reason for the (002) state is unresolvable at present. Third, for Class B species, not only the barriers V_3 for the (002) and (010) states but also those for the (000) and (001) states never coincide with one another in the reasonable range of the Y and Z values. For example, in order to get coincidence of the V_3 values for the (000) and (001) states, the Y value should be about 2.5 which cannot be accepted. This fact is also unresolvable at present. For Class C species, we have no data useful for the OCH_3-skeletal torsion coupling. Fourth, though the theory assumes harmonic oscillator for the skeletal torsion, the observed $\nu(\tau=0\rightarrow1)$ was used in the actual calculation. Fortunately, Durig and Compton reported the observed

Table 1. The OCH_3-Skeletal and Top-Top Torsion Coupling (V in cal/mol)

OCH -skeletal torsion coupling								
class	species		$V_3(OCH_3)$				$V_{3\tau}$	$V_{3\tau}'$
		$\nu(cm^{-1})$	(000)	(001)	(002)	(010)		
A	(HHH)	115.4	2574	2574	3162	2752	-64	142
	(HDH)	111.0	2555	2574	----	2687	153	-13
	(HHH)	120.4	2585	2585	3176	2744	-39	78

top-top torsion coupling without corrections of top-skeletal torsion coupling												
			$V_3(CH_3C)$			$V_3(OCH_3)$					V_{33}	V_{33}'
		$\nu(cm^{-1})$	(000)	(010)	(100)	(000)	(001)	(002)	(010)	(100)		
A	(HHH)	-----	----	3397	3350	3102	----	----	3196	3174	135	0
	(HDH)	-----	----	3391	3351	3095	----	----	3187	3157	134	0
B	(DHH)	-----	3372 (assumed)			2868	----	----	2818	2813	57	14
	(DDH)	-----	3372 (assumed)			2723	----	----	2742	2729	27	-14
C	(HHD)	-----	3110	3102	3002	----	----	----	2808	----	-15	15
with corrections of top-skeletal torsion coupling												
A	(HHH)	120.4	----	3338	3292	2950	2951	3576	3044	3001	116	0
	(HDH)	111.0	----	3308	3297	2931	2930	----	3005	2945	116	0
with corrections of top-skeletal torsion coupling and V_6 terms												
	$V_6(CH_3C) = 81$		$V_6(OCH_3) = -159$									
A	(HHH)	120.4	----	3256	3257	3088	3095	3754	3091	3131	116	0

Durig and Compton	(HHH) (HHD)	$V_3(CH_3C)$	3077 3106	$V_3(OCH_3)$	2613 2808	V_{33}	161 0	V_{33}' 0 0

frequencies of a series $\tau-1\rightarrow\tau$ ($\tau\leq 7$) for the (HHH) species and the harmonic frequency ν_0 can be estimated by fitting them with the formula $\nu(\tau-1\rightarrow\tau)=\nu_0-2\alpha\tau$. Using the corrected frequency $\nu_0=120.4$ cm^{-1}, the calculation was repeated. The V_3 values, however, are not so much affected, while the $V_{3\tau}$ and $V_{3\tau}'$ values are slightly shifted.

The CH_3C-skeletal torsion coupling; Though there are no data useful for the CH_3C-skeletal torsion coupling, the contribution from the X^2 dependent term is so small because of the smallness of the X value that the irregular array of the A and E components is probably not existing unless the contributions from the Y and Z dependent terms are large.

Durig and Compton neglected the top-skeletal torsion coupling effect in their analysis of the top-top coupling effect taking into account the results of the normal vibration calculation made by Kitagawa et al$^{3)}$. However, for the microwave spectra, the effect is explicit and the correction by the top-skeletal torsion coupling is inevitable.

Top-top torsion coupling; When the top-skeletal torsion coupling effect is neglected, the extended bootstrap method gives a similar formula to that for the top-skeletal torsion coupling problem, that is,

$$\omega_1^{(v)}(\mathrm{eff}) = \omega_1^{(v)}(1 + ax^2 + bxz + cz^2 + dy + ey^2) \qquad (2)$$

where $x=F'/F_1$, $y=V_{33}/V_3^{(1)}$, $z=V_{33}'/V_3^{(1)}$. $V_3^{(1)}$ is the barrier V_3 of the CH_3C group, V_{33} and V_{33}' are the coefficients of the potential top-top cross terms $(1-\cos 3\alpha_1)\times(1-\cos 3\alpha_2)$ and $\sin 3\alpha_1 \sin 3\alpha_2$. The results are as follows (see also Table 1).

First, using the five observed $\omega_1^{(v)}(\mathrm{eff})$ values for the (000), (010) and (100) states, $V_3(CH_3C)$, $V_3(OCH_3)$, y and z values were obtained so as to get the minimum deviations of the V_3 values for Class A and C species. For the (HHH) species, our V_3 values are found to be much larger than those by Durig and Compton, while V_{33} and V_{33}' values are close to theirs. For the (HHD) species, our values are considered to be in good agreement with theirs. Second, for Class B species, since the observed $\omega_1^{(v)}$ (eff) value for the CH_3C group is not available at present, the $V_3(CH_3C)$ value obtained for the (HHH) species was assumed at first. In order to find the influence of the assumed V_3 value, the value was reduced by about 300 cal/mol. Then, the $V_3(OCH_3)$ value is found to be lowered by about 100 cal/mol, while V_{33} and V_{33}' values are not much shifted. Therefore, the data useful for the $V_3(CH_3C)$ value are necessary to get the reliable $V_3(OCH_3)$ value. Durig and Compton did not measure the spectra of Class B species. Third, in order to find the influence of the top-skeletal torsion coupling, the calculation was repeated for Class A species using the corrected $\omega_1^{(v)}$ values. The results are obtained so as to fit the V_3 values in the (000), (001), (010), and (100) states with one another. For Class B and C species, similar calculations are impossible since the top-skeletal torsion coupling effects are not well solved. Fourth, V_3 values from the excited methyl torsional states are always slightly different from those in the ground methyl torsional states. However, as are shown in Table 1, the better results could be obtained for the (HHH) species when the V_6 term correction is introduced.

Inspite of several attempts for the better approximations, our V_3 values for the (HHH) species are always much larger than those reported by Durig and Compton. Furthermore, we cannot make clear the reason why a similar calculation is unsuccessful for Class B species and for the (002) state. It is noted that the (010) and (100) states are close to the (002) state for Class A and B species and their relative positions with respect to the (002) state are exchanged between Class A and B species. Though strong coupling effects are expected in these three states, our present approximation makes no direct connection between these states. A direct diagonalization of the energy matrix derived from the effective pure torsional Hamiltonian may be the best method in order to improve the situation. However, the dimension of the matrix to be diagonalized becomes very large in order to get accuracy useful to the microwave data which give the energy differences of the A and E sublevels. Then, some approximations are necessary in the actual calculation. On the other hand, as Durig and Compton adopted, the diagonalization method may easily be applied to the vibrational data since the dimension of the matrix can be reduced in order to get accuracy useful to the vibrational data which give no information about the A-E energy differences.

We are still working on this problem in order to get new additional data and to find a better approximation.

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