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Far Infrared Spectra and Internal Rotation of Ethyl Fluoride and Deuterated Species

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Far infrared spectra were measured of ethyl fluoride CH_3CH_2F and deuterated species CH_3CD_2F, CD_3CH_2F, and CD_3CD_2F in the gaseous state. The potential barriers hindering the internal rotation were calculated with various models. Possibly because of isotope effects on structure relaxations due to torsional motion and to zero-point motion of other vibrational modes, the observed potential barriers are slightly different among isotopic molecules; the threefold barrier is lowered on the deuteration of the methyl group. The absorption intensities of the four isotopic species were also measured. The intensity of the torsional vibration of the methyl group is nearly doubled on deuteration of the methyl group but is reduced on deuteration of the methylene group. The observed intensity ratios among isotopic species were in good agreement with the ratios calculated with the intensity theory of our previous study.

In our previous study, infrared absorption intensities of torsion-rotation transitions of molecules with symmetric internal rotor were theoretically derived on the basis of torsion-rotation interactions and useful applications were discussed on absolute intensities, orientations of dipole transition moments, band types and deuteration effects.[1] According to the theory, the integrated absorption intensity of the internal-rotation vibration of methyl group [$-CH_3$] was expected to be nearly doubled on the deuteration of the methyl group [$-CD_3$].[1] In the present study, the far infrared spectra of deuterated ethyl fluoride [CH_3CD_2F, CD_3CH_2F, and CD_3CD_2F] were measured for the first time as well as ethyl fluoride [CH_3CH_2F], and experimental integrated intensities were compared with theoretical intensities.

As for the internal rotation of methyl groups, a number of data on barrier heights were accumulated by microwave spectroscopy[2] and far infrared spectroscopy.[3] The internal rotation barrier of ethyl fluoride [CH_3CH_2F] was previously determined as 3306 cal/mol (1156 cm^{-1}) by Herschbach with the microwave absorption spectroscopy.[4] The far infrared spectra of CH_3CH_2F were measured by Sage and Klemperer[5] and by Kinumaki and Kozuka,[6] and potential-barrier coefficients were estimated[5] as $V_3=1165$ and $V_6=-5\ cm^{-1}$. In the present study, the internal-rotation potential for the four isotopic molecules were studied with various model calculations.

Experimental

The samples of ethyl fluoride [CH_3CH_2F] and deuterated species [CH_3CD_2F, CD_3CH_2F, and CD_3CD_2F] were prepared through tosyl esters from corresponding ethanols by the method of Edgell and Parts.[7] Ethanol [CH_3CH_2OH] and the perdeuterated species [CD_3CD_2OD] were obtained from commercial sources. The ethanol with the deuterated methylene group [CH_3CD_2OH] was prepared by the reduction of acetyl chloride with lithium aluminum deuteride. The ethanol with the deuterated methyl group [CD_3CH_2OH] was prepared by the reduction of CD_3COOD with lithium aluminum hydride. The samples for spectroscopic observations were dried over phosphorous pentoxide just before measurements.

Far infrared spectra were measured with a Hitachi FIS-3 Far Infrared Spectrophotometer and a 10 cm gas cell with polyethylene windows. The spectral slit width was 2—3 cm^{-1} and the frequency accuracy was estimated to be about $\pm 0.5\ cm^{-1}$. The peak frequencies were calibrated with the absorption lines of water vapor.[8] The far infrared spectra observed for the four isotopic species are shown in Fig. 1. Mid infrared spectra were measured with a Hitachi Model-225 Infrared Spectrophotometer and a 10 cm gas cell with cesium iodide windows (gas pressure, 10 Torr). The infrared bands due to the C–H and/or C–D stretching vibrations of the four isotopic species are shown in Fig. 2.

Results on Peak Frequencies

The observed frequencies and assignments of internal-rotation transitions of ethyl fluorides are given in Table 1. The fundamental band ($1\leftarrow 0$ transition) and two hot bands ($2\leftarrow 1$ and $3\leftarrow 2$ transitions) were observed for CH_3CH_2F and for CH_3CD_2F, while for CD_3CH_2F and CD_3CD_2F the fundamental band ($1\leftarrow 0$) and three hot bands ($2\leftarrow 1$, $3\leftarrow 2$, and $4\leftarrow 3$) were observed. The peak frequencies observed for CH_3CH_2F agreed with the values reported by Sage and Klemperer[5] within $\pm 0.5\ cm^{-1}$ but were slightly lower (by 0.6—1.3 cm^{-1}) than the values reported by Kinumaki and Kozuka.[6]

As for the symmetry index (σ) of the internal-rotation wave functions of ethyl fluoride, the selection rule of the infrared absorption allows $A_1\leftrightarrow A_2$ and $E\leftrightarrow E$ transitions for the vibrational transition $\Delta v=1$.[1,3] Accordingly, in principle, two peaks are expected for each transition $\Delta v=1$. However, in the present study, splitting into two peaks was not observed (Table 1). The $4A_1\leftrightarrow 3A_2$ transition[5,6] and $4E\leftrightarrow 3E$ transition[6] of CH_3CH_2F were not observed either, with the present experimental conditions.

Successive separations of hot bands usually increase with decreasing peak frequencies, although systematically anomalous cases have also been observed.[9] As shown in Table 1, for the four isotopic molecules of ethyl fluoride, systematic anomaly was not observed but for CD_3CH_2F some irregularity was found in successive separations of hot bands.

Internal Rotation Potential

The Hamiltonian for the internal rotation of a rigid

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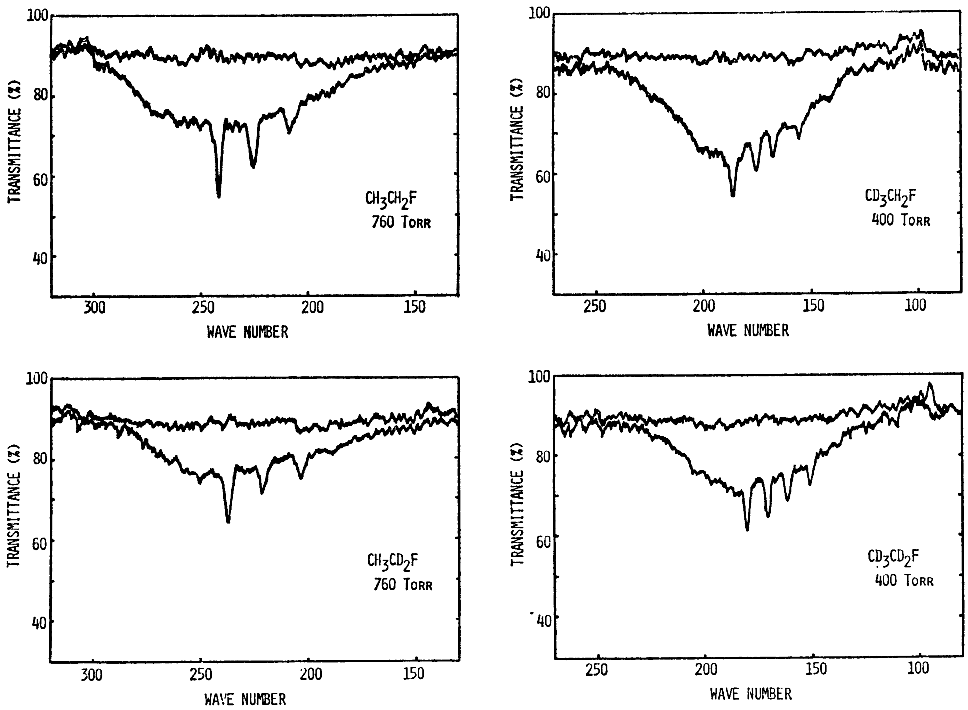

Fig. 1. Far infrared spectra of four isotopic species of ethyl fluoride in the gaseous state at 300 K (path length 10 cm).

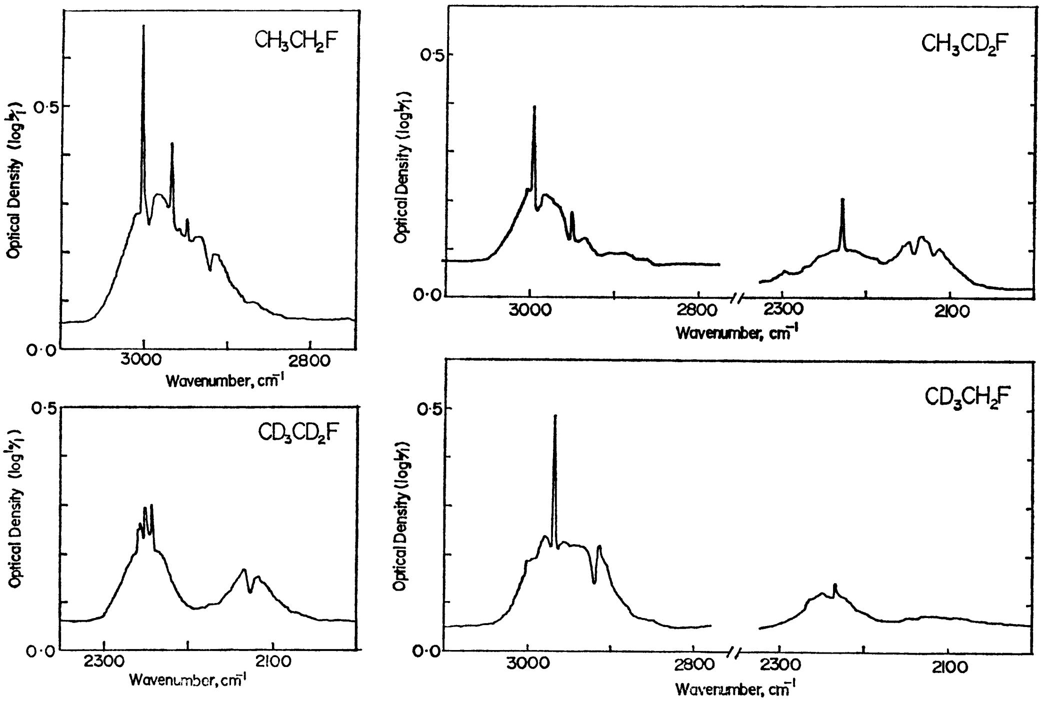

Fig. 2. Infrared spectra of four isotopic species of ethyl fluoride in the gaseous state at 300 K (path length 10 cm, gas pressure 10 Torr).

methyl group with respect to a rigid frame may be written as[10,11)]

$$H = Fp_\alpha^2 + V_3(1-\cos 3\alpha)/2 + V_6(1-\cos 6\alpha)/2 + \cdots \quad (1)$$

where α is the internal-rotation angle ($\alpha=0$ for the staggered form), V_3 and V_6 are the threefold and sixfold barriers in the Fourier expansion of the potential energy, and F is equal to one-half of the inverse reduced moment of inertia. The F values for the four isotopic molecules were calculated, as given in Table 1, from molecular structure parameters reported by Nygaard.[12)]

Calculation-I. In the rigid-top-rigid-frame model, the potential function may be taken common for all the isotopic molecules. In the first approximation, the threefold barrier (V_3) was taken into account but the sixfold barrier (V_6) was neglected. With the F values

Table 1. Observed frequencies (cm^{-1}) for torsional transitions of ethyl fluorides

Transition	CH_3CH_2F	Δ[a]	CH_3CD_2F	Δ[a]	CD_3CH_2F	Δ[a]	CD_3CD_2F	Δ[a]
1←0	242.2		237.7		186.4		180.7	
		16.5		16.4		10.9		9.3
2←1	225.7		221.3		175.5		171.4	
		17.3		17.4		7.7		9.5
3←2	208.4		203.9		167.8		161.9	
						12.4		10.9
4←3					155.4		151.0	
F (cm^{-1})[b]	6.460		6.174		3.771		3.501	

a) The separation (cm^{-1}) between the observed frequencies. b) Calculated from the structure of Ref. 12.

of Table 1, the potential barrier V_3 of ethyl fluoride molecule was calculated by the method of least squares, with reference to the observed transitions of the four isotopic species. Equal weight was given to each of the observed transitions in the least-squares treatment. Since splitting of the $A_1 \leftrightarrow A_2$ and $E \leftrightarrow E$ transitions was not observed in the present experimental conditions, the calculated transition frequencies were taken as the weighted average of the calculated $A_1 \leftrightarrow A_2$ (weight=1) and $E \leftrightarrow E$ (weight=2) transition frequencies.

The potential barrier was thus obtained as $V_3=1142$ cm^{-1}. The torsional frequencies calculated with this barrier are given in Table 2, together with deviations from the observed values. The calculated frequencies agree fairly well with the observed frequencies, although there are systematic deviations greater than experimental errors; the frequencies calculated for CH_3CH_2F or CH_3CD_2F molecules with the CH_3 group are lower than the observed frequencies whereas the frequencies calculated for CD_3CH_2F or CD_3CD_2F molecules with the CD_3 group are higher than the observed frequencies.

Calculation II. The sixfold barrier (V_6) as well as the threefold barrier (V_3) were taken common for all the isotopic molecules. These barriers were thus calculated as $V_3=1152\pm8$ and $V_6=-6\pm4$ cm^{-1}, with reference to the observed frequencies of the four isotopic molecules. The method of least squares was used in similar manners as Calculation-I, although the V_6 term was treated with the second-order perturbation method.

Calculated transition frequencies agreed with observed frequencies, slightly better than the results of Calculation-I. However, the systematic deviations for the CH_3- and CD_3-groups were little reduced.

Calculation-III. The use of common potential function for the isotopic molecules of ethyl fluoride results in systematic frequency deviations for the CH_3- and CD_3-groups. Accordingly, potential barriers were then calculated for each isotopic molecules, where the F values of Table 1 were used.

In Calculation-III, the three-fold barrier was taken into account but the sixfold barrier was neglected. For each isotopic molecule, the value of V_3 was calculated, as shown in Table 3, by the method of least squares. The V_3 values calculated for the CH_3- group are higher than those calculated for the CD_3- group. Agreements between the calculated and observed frequencies were much improved as compared with the case of Calcula-

Table 2. Calculated frequencies (cm^{-1}) of torsional transitions of ethyl fluorides

	Calcn-I		Calcn-II	
	$V_3=1141.6\pm4.2$[a]		$V_3=1151.6\pm7\ 5$[a] $V_6=-6.4\pm4.0$[a]	
	ν_{calcd}	δ[b]	ν_{calcd}	δ[b]
CH_3CH_2F				
1 ←0	242.1	−0.1	241.3	−0.9
2E←1E	225.1	−0.7	225.1	−0.6
2A←1A	225.0		225.0	
3A←2A	206.0	−3.3	206.8	−2.3
3E←2E	204.7		205.7	
4E←3E	183.6		185.2	
4A←3A	172.5		174.8	
(rmsd)		(1.9)		(1.5)
CH_3CD_2F				
1 ←0	237.1	−0.6	236.2	−1.5
2 ←1	220.8	−0.5	220.8	−0.5
3A←2A	202.6	−1.9	203.4	−1.1
3E←2E	201.7		202.6	
4E←3E	181.4		182.9	
4A←3A	172.8		174.8	
(rmsd)		(1.2)		(1.1)
CD_3CH_2F				
1 ←0	187.9	1.5	187.1	0.7
2 ←1	178.4	2.9	178.1	2.6
3 ←2	167.9	0.1	168.2	0.4
4E←3E	156.2	0.7	156.9	1.4
4A←3A	156.0		156.7	
5A←4A	143.5		144.6	
5E←4E	141.3		142.6	
6E←5E	128.0		129.6	
6A←5A	114.2		116.8	
(rmsd)		(1.7)		(1.6)
CD_3CD_2F				
1 ←0	181.4	0.7	180.6	−0.1
2 ←1	172.6	1.2	172.3	0.9
3 ←2	163.0	1.1	163.2	1.3
4E←3E	152.2	1.2	152.9	1.8
4A←3A	152.1		152.8	
5A←4A	140.4		141.4	
5E←4E	139.2		140.3	
6E←5E	126.3		127.7	
6A←5A	117.8		119.9	
(rmsd)		(1.1)		(1.2)
rmsd[c]		1.5		1.4

a) Errors are standard deviations (cm^{-1}) calculated by the method of least squares. b) $\delta=\nu_{calcd}-\nu_{obsd}$. c) Root-mean-squared deviation.

tion-I.

Calculation-IV. The sixfold barrier (V_6) as well as the threefold barrier (V_3) were calculated, as shown in Table 3, for each isotopic molecule by the method of least squares. The V_3 values calculated for the CH_3-group were systematically higher (by 30—35 cm^{-1}) than those calculated for the CD_3-group. The systematic variations of the calculated V_3 values possibly indicate the isotope effects on structure relaxations due to torsional motion and to zero-point motion of other vibrational modes.

For each isotopic molecule of ethyl fluoride, the agreements between the calculated and observed frequencies were improved, by the incorporation of the V_6 term, as compared with the case of Calculation-III. However, for the molecule of CD_3CH_2F, there are some noticeable frequency deviations for the 2←1 and 3←2 transitions. These deviations are due to the irregularity of successive separation of hot bands (Table 1). One of the origins for this irregularity may be ascribed to the Fermi resonance interaction between the second excited state of the torsional vibration and the first excited state of the skeletal C-C-F bending vibration. For the isotopic molecules of CH_3CH_2F, CH_3CD_2F, CD_3CH_2F, and CD_3CD_2F, the separations between the second excited torsional level and the ground level were calculated as 467.9, 459.0, 361.9, and 352.1 cm^{-1}, from the observed torsional transitions (Table 1). On the other hand, the separations between the first excited bending level and ground level were observed as the infrared bands[13] at 415, 409, 370, and 364 cm^{-1}. Accordingly, the separation between the second excited torsional level and the first excited bending level is smallest for CD_3CH_2F and some Fermi resonance effect may in fact be expected between these levels.

Calculation-V. The second excited torsional levels are perturbed by Fermi resonances whereas the first excited torsional levels are practically free from Fermi resonance interactions. Accordingly, from the observed fundamental transitions (1←0), the threefold barrier was calculated, as shown in Table 3, for each of the four isotopic molecules. The threefold barriers of the CH_3- group were calculated to be higher than those of the CD_3- group.

Calculation-VI. In Calculations III—V, the F values (Table 1) obtained by the microwave analyses[12] were used and the potential barriers were calculated for each isotopic molecule. Instead, the transition frequencies of the four isotopic molecules may also be reproduced by the least-square adjustments of F values for the four isotopic molecules and a common value of V_3. As shown in Table 4, the value of V_3 (1172±14 cm^{-1}) thus calculated is higher than those of the Calculations-I—II whereas the values of F thus calculated are smaller than the F values from the microwave analyses. The attempt of determining the value of V_6 as well as V_3 and F values was not successful because of ill conditions for the least-squares adjustments.

Calculation-VII. The results of Calculations-I—VI imply that actual internal-rotation modes are accompanied with relaxations of the structures of the rotor and/or frame. Theoretical methods on nonrigid models were derived for the interpretation of microwave spectra by Kivelson[14] and by Kirtman.[15]

Table 3. The calculated frequencies and deviations (cm^{-1}) of torsional transitions of ethyl fluorides

	Calcn-III		Calcn-IV		Calcn-V	
CH_3CH_2F	$V_3=1153.4\pm8.3$		$V_3=1170.7\pm7.8$ $V_6=-11.4\pm4.4$		$V_3=1142$	
1 ←0	243.5	1.3	241.9	−0.3	242.2	0.0
2E←1E	226.4	0.7	226.4	0.7	225.1	(−0.6)
2A←1A	226.3		226.4		225.0	
3A←2A	207.4	−1.8	208.8	−0.3	206.0	(−3.2)
3E←2E	206.2		207.7		204.8	
4E←3E	185.0		187.7		183.7	
4A←3A	174.4		178.2		172.6	
rmsd		1.3		0.5		(1.9)
CH_3CD_2F	$V_3=1150.6\pm3.8$		$V_3=1157.7\pm6.2$ $V_6=-4.6\pm3.4$		$V_3=1147$	
1 ←0	238.1	0.4	237.4	−0.3	237.7	0.0
2 ←1	221.8	0.5	221.8	0.5	221.4	(0.1)
3A←2A	203.7	−0.8	204.2	−0.3	203.2	(−1.3)
3E←2E	202.8		203.4		202.3	
4A←3A	182.4		183.5		182.0	
4E←3E	174.1		175.6		173.6	
rmsd		0.6		0.4		(0.7)
CD_3CH_2F	$V_3=1126.8\pm6.9$		$V_3=1137.4\pm12.7$ $V_6=-6.8\pm6.8$		$V_3=1124$	
1 ←0	186.7	0.3	185.8	−0.6	186.4	0.0
2 ←1	177.1	1.6	176.8	1.3	176.9	(1.4)
3 ←2	166.6	−1.2	166.9	−0.9	166.4	(−1.4)
4E←3E	154.8	−0.7	155.6	0.1	154.6	(−0.9)
4A←3A	154.6		155.4		154.3	
5A←4A	142.2		143.4		141.9	
5E←4E	139.7		141.2		139.5	
6E←5E	126.6		128.3		126.4	
6A←5A	111.9		114.7		111.5	
rmsd		1.1		0.9		(1.1)
CD_3CD_2F	$V_3=1129.2\pm1.3$		$V_3=1126.5\pm2.3$ $V_6=1.6\pm1.2$		$V_3=1133$	
1 ←0	180.4	−0.3	180.6	−0.1	180.7	0.0
2 ←1	171.6	0.2	171.6	0.2	171.9	(0.5)
3 ←2	161.9	0.0	161.9	0.0	162.3	(0.4)
4E←3E	151.2	0.1	151.0	−0.1	151.5	(0.5)
4A←3A	151.0		150.9		151.4	
5A←4A	139.3		139.0		139.6	
5E←4E	138.0		137.7		138.4	
6E←5E	125.2		124.8		125.5	
6A←5A	116.1		115.5		116.6	
rmsd		0.2		0.1		(0.4)

In the present study, however, the empirical method by Ewig and Harris[16] was used for the interpretation of the far infrared spectra of ethyl fluorides.

The Hamiltonian for the internal rotation of a molecule with structure relaxations may be written in a one-dimensional approximation as,

$$H = p_\alpha F(\alpha) p_\alpha + V_3(1-\cos 3\alpha)/2 + V_6(1-\cos 6\alpha)/2 + \cdots \quad (2)$$

where $F(\alpha)$ is a function of the internal-rotation angle α (for the rigid model of Eq. (1), F is independent of α). The function $F(\alpha)$ may be evaluated with an *a priori* knowledge or an assumption on the molecular

Table 4. The calculated frequencies and deviations (cm^{-1}) of torsional transitions of ethyl fluorides [Calculation-VI][a)]

	CH_3CH_2F		CH_3CD_2F		CD_3CH_2F		CD_3CD_2F	
	$F=6.298\pm0.109$		$F=6.011\pm0.104$		$F=3.569\pm0.061$		$F=3.332\pm0.057$	
1 ←0	242.7	0.5	237.5	−0.2	185.7	−0.7	179.7	−1.0
2E←1E	226.2	0.4	221.7	0.4	176.7	1.2	171.4	0.0
2A←1A	226.1							
3A←2A	207.6	−1.4	204.1	−0.2	166.9	−0.9	162.3	0.4
3E←2E	206.7		203.5					
4E←3E	185.9		183.6		156.0	0.5	152.2	1.2
4A←3A	177.5		177.2		155.9		152.2	
5A←4A					143.9		141.0	
5E←4E					142.7		140.4	
6E←5E					129.5		127.9	
6A←5A					121.3		122.9	
rmsd		0.9		0.3		0.9		0.8

a) The threefold barrier was calculated to be $V_3=1172.6\pm14.0\ cm^{-1}$. The values of F are given in the unit of cm^{-1}. The overall rmsd was $0.8\ cm^{-1}$.

Table 5. The calculated frequencies and deviations (cm^{-1}) of torsional transitions of ethyl fluorides [Calculation-VII][a)]

	CH_3CH_2F		CH_3CD_2F		CD_3CH_2F		CD_3CD_2F	
	$\bar{F}=6.027\pm0.117$		$\bar{F}=6.001\pm0.105$		$\bar{F}=3.615\pm0.153$		$\bar{F}=3.532\pm0{\cdot}027$	
	$\bar{V}_3=1211.3\pm17.3$		$\bar{V}_3=1174.0\pm14.9$		$\bar{V}_3=1161.4\pm36.2$		$\bar{V}_3=1122.0\pm6.3$	
1 ←0	241.9	−0.3	237.5	−0.2	185.9	−0.5	180.5	−0.2
2E←1E	226.2	0.5	221.7	0.4	176.8	1.3	171.6	0.2
2A←1A	226.2							
3A←2A	208.5	−0.2	204.1	−0.2	166.8	−1.0	161.9	0.0
3E←2E	208.0		203.5					
4E←3E	188.0		183.6		153.7	0.2	151.0	−0.1
4A←3A	182.6		177.4		155.6		150.9	
5A←4A					143.4		139.0	
5E←4E					142.1		137.6	
6E←5E					128.8		124.7	
6A←5A					119.3		114.8	
rmsd		0.4		0.3		0.9		0.2

a) The values of $\bar{F}$ and $\bar{V}_3$ are given in the unit of cm^{-1}.

dynamics of the internal-rotation and other vibrational modes. The Hamiltonian in Eq. (2) may be transformed to the reduced θ representation,[16,17)]

$$H = \bar{F}p_\theta^2+\bar{V}_3(1-\cos 3\theta)/2+\bar{V}_6(1-\cos 6\theta)/2+\cdots \tag{3}$$

on the basis of the following transformations.

$$\bar{F}^{-1/2} = (1/2\pi)\int_0^{2\pi} F(\alpha)^{-1/2}\,d\alpha \tag{4}$$

$$\theta = \bar{F}^{1/2}\int_0^{\alpha} F(\alpha')^{-1/2}\,d\alpha' \tag{5}$$

Here $\bar{F}$ is a constant independent of θ, and the transformation from α to θ is nonlinear. The angle θ has the same boundary condition as the internal-rotation angle α. The potential function $[\bar{V}(\theta)]$ of Eq. (3) is different from the potential function $[V(\alpha)]$ of Eq. (2), but these functions $\bar{V}(\theta)$ and $V(\alpha)$ have the same symmetry, same boundary condition, and same heights of the maxima and minima.[16,17)]

For the four isotopic molecules of ethyl fluoride, sufficient knowledges were not available for evaluating the functions $F(\alpha)$. Therefore, the Hamiltonian H of Eq. (3) was used for determining empirically the kinetic-energy parameter $\bar{F}$ and the potential coefficients $\bar{V}_3$ and $\bar{V}_6$.

With Eq. (3), the values of $\bar{F}$ and $\bar{V}_3$ were calculated for each isotopic molecule, by the method of least squares, with reference to the observed transition frequencies. The $\bar{V}_6$ and higher terms were neglected. The calculated results are given in Table 5. Calculated transition frequencies agreed satisfactorily with observed frequencies. However, for the molecule of CD_3CH_2F, the frequency agreements were little improved, as compared with the case of Calculation-IV, possibly because of the limitation imposed by the effect of Fermi resonance.

As compared with the F values of the rigid model (Table 1), the $\bar{F}$ values calculated with Calculation-VII were smaller for the molecules of CH_3CH_2F, CH_3CD_2F, and CD_3CH_2F but larger for the molecule of CD_3CD_2F. Furthermore, as compared with the V_3 values of Calculation-III (Table 3), the $\bar{V}_3$ values calculated with Calculation-VII were higher for the molecules of CH_3CH_2F, CH_3CD_2F, and CD_3CH_2F but lower for the molecule of CD_3CD_2F. However, systematic deuteration effects were observed on the $\bar{V}_3$ values of the four isotopic molecules; the $\bar{V}_3$ values were lowered by deuteration of the methyl group (~50 cm^{-1}) and also by the deuteration of the methylene group (~40 cm^{-1}). The attempt of determining the value of $\bar{V}_6$ as well as

$\bar{V}_3$ and $\bar{F}$ was not successful because of ill conditions for the least-squares refinements.

Isotope Effects on Absorption Intensities of Torsional Bands

The absorption intensity of a torsional band may be calculated from molecular structure parameters and molecular dipole moment, with the theory previously reported by Sugeta and Miyazawa.[1] According to this theory, the molar integrated absorption intensity of the torsional transition ($\Delta v=1$) may be expressed as,

$$\int \alpha(\nu)\mathrm{d}\nu = \frac{N}{z}\frac{8\pi^3}{3h^2c} \times 4F^2|\boldsymbol{\mu}\times\boldsymbol{\rho}|^2 \sum_{v,\sigma} [\exp(-E_{v,\sigma}/kT) - \exp(-E_{v+1,\sigma}/kT)] \times \frac{|\langle v+1,\sigma|p_\alpha|v,\sigma\rangle|^2}{E_{v+1,\sigma}-E_{v,\sigma}} \tag{6}$$

where v and σ are the vibrational quantum number and symmetry index, $E_{v,\sigma}$, is the eigenvalue of the state $v\sigma$, p_α is the angular momentum operator of the internal rotor along its symmetry axis, z is the partition function, N is the Avogadro number, and $\boldsymbol{\mu}$ is the dipole moment vector. The vector $\boldsymbol{\rho}$ is given by the moment of inertia of the internal rotor (I_α), the moment of inertia of the entire molecule (I_a, I_b, I_c), and the direction cosines of the internal-rotation axis (λ_a, λ_b, λ_c),

$$\tilde{\boldsymbol{\rho}} = [\lambda_\mathrm{a}I_\alpha/I_\mathrm{a} \quad \lambda_\mathrm{b}I_\alpha/I_\mathrm{b} \quad \lambda_\mathrm{c}I_\alpha/I_\mathrm{c}] \tag{7}$$

For the high-barrier harmonic approximation, Eq. (6) may be simplified as,[1]

$$\int \alpha(\nu)\mathrm{d}\nu \simeq (8\pi^3N/3h^2c)F|(\boldsymbol{\mu}\times\boldsymbol{\rho})|^2 \tag{8}$$

The theoretical absorption intensities of the torsional bands of the four isotopic species of ethyl fluoride were calculated, by the use of the molecular structure parameters[12] and dipole moment.[18] The results of Calculation-I were used for the intensity calculations. The theoretical intensities calculated with Eq. (6) are given for the four isotopic molecules in Table 6, where the summations in Eq. (6) were made up to the 4←3 transitions for CH_3CH_2F and CH_3CD_2F and up to the 6←5 transitions for CD_3CH_2F and CD_3CD_2F.

Table 6. Integrated absorption intensities[a] (and ratios[b]) of torsional bands of ethyl fluorides

Molecule	Experimental Intensity	Experimental Ratio	Calculated [Mathieu][c] Intensity	Calculated [Mathieu][c] Ratio	Calculated [Harmonic][d] Intensity	Calculated [Harmonic][d] Ratio
CH_3CH_2F	2.0_5		3.63		3.91	
CH_3CD_2F	1.1_5	0.5_5	2.27	0.62	2.45	0.63
CD_3CH_2F	3.8_0	1.8_5	6.29	1.73	6.62	1.69
CD_3CD_2F	2.7_5	1.3_5	4.09	1.12	4.32	1.10

a) In unit of $\mathrm{cm^{-2}\cdot atm^{-1}}$, at 300 K. b) Relative to CH_3CH_2F. c) Calculated with Eq. (6). d) Calculated with Eq. (8).

On the deuteration of the methyl group, the theoretical intensities are nearly doubled (1.7—1.8 times), as discussed previously. This intensity enhancement is due to the twofold increase in the magnitude of the $\boldsymbol{\rho}$ vector, overcoming the decrease (to about one-half) in the F values. On the other hand, the theoretical intensities are reduced (to 0.6—0.7 times) on the deuteration of the methylene group. This intensity reduction is ascribed to the decrease in the magnitude of the $\boldsymbol{\rho}$ vector and in the F values.

The experimental absorption intensities were measured for the four isotopic species of ethyl fluoride and are given in Table 6. Experimental errors in the integrated intensities were estimated to be about 20%. In the far-infrared region, experimental determinations of absolute intensities were difficult with the present instrumental conditions, and accordingly the relative intensities among the four isotopic molecules were also calculated as shown in Table 6.

The experimental intensities were lower than the theoretical intensities [from Eq. (6)], because of instrumental limitations. However, as for the relative intensities among the four isotopic molecules, observed intensity ratios agreed fairly well with experimental intensity ratios. In particular, the observed changes of the absorption intensities on deuteration of the methyl group and methylene group confirmed the validity of the intensity theory previously reported.[1]

Theoretical values of the integrated absorption intensities of the torsional bands were also calculated with the high-barrier harmonic approximation [Eq. (8)]. As shown in Table 6, the intensity values calculated with Eq. (8) are appreciably higher than the values calculated with Eq. (6). Accordingly, for calculations of the absolute intensity values, Eq. (6) rather than Eq. (8) is to be used. However, the theoretical intensity ratios calculated with Eq. (8) agree closely with the ratios calculated with Eq. (6). With this harmonic approximation, evaluations of $F|(\boldsymbol{\mu}\times\boldsymbol{\rho})|^2$ in Eq. (8) are sufficient for calculating theoretical intensity ratios.

Discussion

For studying the effects of adjustable parameters (F, V_3, and V_6) on torsional transition frequencies, Jacobian elements have been calculated. For lower transitions, the values of $\delta\nu/\delta V_3$ are nearly constant so that a small increment in V_3 results in uniform shifts of transition frequencies. On the other hand, the values of $\delta\nu/\delta V_6$ significantly decrease for higher transitions so that a small increment in V_6 results in nonuniform shifts of transition frequencies. It may be remarked that the absolute values of $\delta\nu/\delta V_6$ are minimum for the 3←2 transitions of the CH_3 group and for the 4←3 or 5←4 transitions of the CD_3 group. These higher-transition frequencies are little subjected to the effect of the sixfold barriers, as noticed previously by Fateley and Miller.[19] The values of $\delta\nu/\delta F$ also decrease for higher transitions and an increment in F results in nonuniform shifts of transition frequencies.

In the present study on the four isotopic molecules of ethyl fluoride, systematic deviations between the observed and calculated frequencies were found in Calculations-I—II; the transition frequencies calculated for the molecules of CH_3CH_2F and CH_3CD_2F with the CH_3- group are lower than the observed frequencies whereas the frequencies calculated for the molecules of CD_3CH_2F and CD_3CD_2F with the CD_3-

group are higher than the observed frequencies. In Calculations-III—V, systematic variations among the barrier heights of isotopic molecules were found; the threefold barriers were lowered on the deuteration of the methyl group (from CH_3CH_2F to CD_3CH_2F and from CH_3CD_2F to CD_3CD_2F). In Calculation-VI, systematic variations among the apparent F values of isotopic molecules were found. Finally in Calculation-VII, systematic variations of the $\bar{V}_3$ values were also found; the $\bar{V}_3$ values were lowered by the deuteration of the methyl group and also by the deuteration of the methylene group. All these results indicate that the observed potential barriers hindering the internal rotation are slightly but definitely different among isotopic molecules, because of the structure relaxations due to torsional motion and to zero-point motion of other modes. This effect of deuteration on potential barriers of the methyl groups has also been found for other molecules.[20)]

Recently some comments were made[16,21–23)] on the physical meaning and spectroscopic determination of the V_6 terms of the internal-rotation potential and the 3α-dependent term of $F(\alpha)$ in Eq. (2).

$$F(\alpha) = F_0 + F_3 \cos 3\alpha + \cdots \qquad (9)$$

In the least-squares refinements with reference to the observed transition frequencies,[16,22,23)] the values of $4F_0V_6+F_3V_3$ may be estimated but the values of V_6 and F_3 may not be determined independent of each other. In the present non- rigid model of Calculation-VII, however, the internal-rotation angle α is transformed into the angle θ so that $\bar{F}$ is independent of θ and 3θ-dependent term vanishes $[\bar{F}_3=0]$. Then, the values of $\bar{F}$, $\bar{V}_3$, $\bar{V}_6$,⋯in Eq. (3) may well be calculated by the method of least squares, if observed data of transition frequencies were sufficiently available.

In Calculation-VII, transition-frequency data of the present experimental study were not sufficient for the least-square adjustment of the three parameters $\bar{F}$, $\bar{V}_3$ and $\bar{V}_6$. For the molecule of CH_3CH_2F, the 4E←3E and 4A←3A transitions were observed by Kinumaki and Kozuka,[6)] although their frequencies for lower transitions were systematically higher than those of the present study. These 4E←3E and 4A←3A transition frequencies were added to the present data of the 1←0, 2←1, and 3←2 transition frequencies, and the parameters $\bar{F}$, $\bar{V}_3$, and $\bar{V}_6$ were determined, as shown in Table 7, for the molecule of CH_3CH_2F. On the other hand, model calculations were made for the molecules of CD_3CH_2F and CD_3CD_2F, and it was found that the experimental data on the fundamental (1←0) through 5A←4A and 5E←4E or more preferably 6E←5E and 6A←5A transitions were required for calculating reliable values of $\bar{F}$, $\bar{V}_3$ and $\bar{V}_6$.

After the present study was completed, high resolution far-infrared spectrum of C_2H_5F was reported by Tuazon *et al.*[24)] and the dependence of the potential parameters V_3 and V_6 on changes in selected values of F was discussed.

Table 7. Calculated frequencies and deviations (cm^{-1}) of torsional transitions of CH_3CH_2F.[a)]

Transition	Observed	Calculated	Deviation
1 ←0	242.2	241.5	−0.7
2E←1E 2A←1A	225.7	226.7 226.6	1.0
3A←2A 3E←2E	208.4	209.6 208.4	0.4
4E←3E	189.6[b)]	188.9	−0.7
4A←3A	178.4[b)]	178.5	0.1

a) $\bar{F}=6.576\pm0.128\ cm^{-1}$, $\bar{V}_3=1168.4\pm7.5\ cm^{-1}$, $\bar{V}_6=-18.4\pm6.4\ cm^{-1}$, and rmsd$=0.7\ cm^{-1}$. b) Ref. 6.

Conclusion

In the present study, several types of calculations with various models were made for analyzing the far infrared spectra and for calculating potential barrier coefficients of the four isotopic molecules of ethyl fluoride, All those calculations indicate that the observed potential barriers hindering the internal rotation are slightly different among isotopic molecules, because of the small coupling between the internal-rotation mode and other vibrational modes. For more detailed determinations of the potential barriers, however, it is desirable to observe weak far-infrared bands due to transitions between higher excited torsional states and to analyze microwave spectra of higher excited torsional states.

It has been established that the absorption intensities of C–H stretching vibrations are reduced to about one half on deuteration. In the present study, the absorption intensities of the C–H stretching vibrations of ethyl fluoride were in fact found to decrease, as shown Fig. 2, on deuteration of the methyl and/or methylene group. On the other hand, it has been anticipated theoretically[1)] that the absorption intensity of the torsional vibration of the CH_3 group is nearly doubled on deuteration of the methyl group but is reduced on deuteration of the methylene group. In the present study, the absorption intensity ratios of the torsional bands of the four isotopic molecules were in fact found to agree closely with the theoretical ratios, confirming the intensity theory previously derived.

Numerical calculations of the present study were carried out with a NEAC 2200—700 computer of Osaka University.

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