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FERMI RESONANCE BETWEEN METHYL TORSIONAL AND SKELETAL BENDING EXCITED STATES OF ETHYL FLUORIDE BY MICROWAVE SPECTRA

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Microwave spectra of ethyl fluoride and its deuterated species were measured in the ground, methyl torsional and skeletal bending excited states. Fermi resonance between the second excited methyl torsional state and the first excited skeletal bending state was analyzed in relation to the methyl internal rotation.

Recently we remeasured the microwave spectra of ethyl fluoride and its deuterated species (CD_3CH_2F) in the ground, first and second excited methyl torsional and first excited skeletal bending states in order to investigate the coupling effects between the methyl torsion and the skeletal bending vibration, though the r_s structure of this molecule was already well determined.$^{1)}$ For convenience, we will hereafter designate the vibrational state as (v τ) where v and τ are the vibrational quantum numbers of the skeletal bending and methyl torsional vibrations, respectively. Furthermore, the vibrational transition will be denoted as $(v'\ \tau') \leftarrow (v\ \tau)$.

About fifteen microwave transitions of a- and b-types were measured for each species and for each state. The spectra of the normal species in the (0 1) and (0 2) states and of the deuterated species in the (0 2) state exhibit doublet structures due to the internal rotation of the methyl group. Furthermore, the spectra of the b-type in the (1 0) state also exhibit doublet structures with small spacings for both species. Since the corresponding spectra in the (0 0) state are singlets, the doublet structures of the spectra in the (1 0) state indicate the existence of some coupling effects between the methyl torsion and the skeletal bending vibration.

The rotational constants R_A were first determined by a least-squares fit of the observed A component frequencies with a modified rigid rotor expression which included the $-d_{JK}[J(J+1)\langle P_z^2\rangle]$ and $-d_{EJ}[J(J+1)E_r]$ terms of the centrifugal distortion formula. Second, the A-E splitting analysis was carried out by the standard PAM-bootstrap method.$^{2)}$ The higher order contributions to the A-E splittings were found to be negligible for the present molecule. Then, the unperturbed rotational constants R_0 were obtained by the following formula.

$$R_0 = R_A - Fg^2 W_{vA}^{(2)}, \quad W_{vA}^{(2)} = -(\pi^2/2)\omega_1, \quad R = A,\ B,\ \text{and}\ C, \qquad (1)$$
$$g = \alpha,\ \beta,\ \text{and}\ \gamma, \quad \alpha = I_\alpha\lambda_a/I_a, \quad \beta = I_\alpha\lambda_b/I_b, \quad \gamma = I_\alpha\lambda_c/I_c$$

The results are listed in Table 1.

Table 1 Quantities Obtained from Microwave Spectra[a)]

State		(0 0)	(0 1)	(0 2)	(1 0)
CH_3CH_2F					
A	(MHz)	36070.12 (66)	35961.47 (79)	35886.26 (57)	36347.78 (37)
B	(MHz)	9364.53 (4)	9340.29 (4)	9315.83 (3)	9367.05 (2)
C	(MHz)	8199.63 (4)	8189.96 (4)	8180.16 (3)	8182.00 (2)
$d_{JK}\times 10$	(MHz)	-2.64 (64)	-2.11 (71)	-0.95 (50)	-2.18 (33)
$d_{EJ}\times 10$	(MHz)	1.69 (19)	1.70 (21)	1.75 (15)	1.73 (10)
F	(GHz)	192.46	192.34	192.47	191.87
(α, β)		(0.1852, 0.0337)	(0.1846, 0.0336)	(0.1852, 0.0334)	(0.1835, 0.0348)
s		79.6 [b)]	79.7 (8)	80.1 (1)	63.4 (15)
$\omega_1\times 10^4$		-0.020 [b)]	1.227(94)	-31.835(298)	-0.116(18)
CD_3CH_2F					
A	(MHz)	29258.66 (39)	29177.29 (57)	29194.64 (42)	29364.19 (60)
B	(MHz)	2972.49 (2)	7953.69 (3)	7949.96 (4)	7963.75 (4)
C	(MHz)	7105.33 (2)	7102.95 (3)	7100.33 (4)	7094.39 (4)
$d_{JK}\times 10$	(MHz)	-1.29 (20)	-1.25 (29)	-0.85 (20)	-1.24 (30)
$d_{EJ}\times 10$	(MHz)	1.15 (7)	1.16 (11)	0.96 (13)	0.83 (16)
F	(GHz)	110.69	--	110.60	112.17
(α, β)		(0.3002, 0.0573)	(-- , --)	(0.2995, 0.0571)	(0.3084, 0.0543)
s		183.5 [b)]	--	183.6 (9)	64.4 (10)
$\omega_1\times 10^4$		-1.1×10^{-4} [b)]	--	-0.337(20)	-0.103(11)

a) Unperturbed rotational constants about the methyl internal rotation. Figures in parentheses indicate the uncertainties attached to the last significant figures.

b) Calculated from the observed V_3 value obtained from the (0 1) state for CH_3CH_2F and from the (0 2) state for CD_3CH_2F.

The vibrational frequencies of (1 0)←(0 0), (0 1)←(0 0), and (0 2)←(0 1) transitions for the normal and deuterated species were reported by Sugeta et al.[3)] They are (414.0, 242.2, 225.7) and (370.0, 186.4, 175.5) cm^{-1}, respectively. The vibrational frequencies of (0 2)←(0 0) were calculated by (0 2)←(0 0)=(0 2)←(0 1) +(0 1)←(0 0). They are 467.9 and 361.9 cm^{-1} for the normal and deuterated species, respectively. Then the frequency differences between (0 2)←(0 0) and (1 0)←(0 0) are -53.9 and 8.1 cm^{-1}. Since the (1 0) and (0 2) states belong to the same symmetry species, Fermi resonance may occur strongly between these states for the deuterated species, while it may be weak for the normal species even when it exists. As are seen in the table, the rotational constants of the (0 2) state for the deuterated species are irregularly shifted from those of the (0 0) state as compared with the shifts of those of the (0 1) state. Then, the existence of the Fermi resonance is very probable.

Morino and Saito[4)] had analyzed the Fermi resonance between ν_1 and $2\nu_2$ states of oxygen difluoride from the microwave spectra. When ν_1 and $2\nu_2$ are replaced by the (1 0)←(0 0) and (0 2)←(0 0) vibrations which usually are designated by ν_{11} and $2\nu_{18}$, respectively, our situation for ethyl fluoride is similar to that of oxygen difluoride.

Table 2 Quantities Related to Fermi Resonance[a)]

state			(0 0)	(0 2)	(1 0)
F	(cm^{-1})	CH_3CH_2F	6.415	6.416	6.396
		CD_3CH_2F	3.690	3.687	3.739
$\Delta E(v\ \tau)$	(cm^{-1})	CH_3CH_2F	$-0.438(--)\times10^{-4}$	$-0.689(\ 6)\times10^{-1}$	$-0.207(39)\times10^{-3}$
		CD_3CH_2F	$-0.131(--)\times10^{-6}$	$-0.419(25)\times10^{-3}$	$-0.130(14)\times10^{-3}$

			A	B	C
CH_3CH_2F	$\alpha_v(R)$	(MHz)	-279.04(49)	-2.67(2)	17.62(4)
	$\alpha_\tau(R)$	(MHz)	140.71(196)	23.86(9)	9.53(12)
	β (R)	(MHz)	16.03(46)	-0.19(2)	-0.07(3)
	Fermi[b)]	(MHz)	-1.39(26)	-0.15(3)	-0.01(0)
CD_3CH_2F	$\alpha_v(R)$	(MHz)	-181.59(1637)	2.55(135)	13.60(65)
	$\alpha_\tau(R)$	(MHz)	104.03(1559)	27.67(133)	4.80(66)
	β (R)	(MHz)	11.33(814)	4.44(68)	1.21(31)
	Fermi[b)]	(MHz)	-76.06(1209)	-6.19(100)	2.60(45)

		CH_3CH_2F		CD_3CH_2F	
η [c)]		0.0030(6)		0.2365(281)	
$\lvert k_{11,\ 18,\ 18}\rvert$	(cm^{-1})	5.88 (24)		6.88 (341)	
$\lvert w_{11}-w_{18}\rvert,\ \delta_0=\lvert\nu_{11}-2\nu_{18}\rvert$	(cm^{-1})	53.9(22)	53.5(22)	8.1(22)	4.3(14)
$w_{11},\ \nu_{11}$ [d)]	(cm^{-1})	414.0(20)	414.2	370.0(20)	368.1
$w_{18},\ 2\nu_{18}$ [d)]	(cm^{-1})	467.9(10)	467.7	361.9(10)	363.8

a) Figures in parentheses indicate the uncertainties attached to the last significant figures.

b) $\eta(\alpha_v(R)-2\alpha_\tau(R)+6\beta(R))$; correction to the rotational constant from the Fermi resonance.

c) η obtained from the A-E splittings.

d) w_{11} and w_{18}; observed vibrational frequencies. ν_{11} and $2\nu_{18}$; unperturbed vibrational frequencies.

By the use of the formula derived by Morino and Saito, the degree of mixing η (b^2 in their notation) was calculated from the rotational constants and the vibrational frequencies of (1 0)←(0 0) and (0 2)←(0 0). On the other hand, the observed energy differences $\Delta E(v\ \tau)$ between the A and E methyl torsional sublevels for the (1 0) and (0 2) states can be shown to have the following relation to the degree of mixing η

$$\eta[\Delta E(0\ 2)+\Delta E(1\ 0)-\Delta E(0\ 0)] = \Delta E(1\ 0)-\Delta E(0\ 0) \qquad (2)$$

From the A-E splitting analysis, $\Delta E(v\ \tau)$ can be obtained as,

$$\Delta E(v\ \tau) = (27/8)F\omega_1 \qquad (3)$$

where F is in cm^{-1} and ω_1 is the second coefficient of the Fourier expansion for the periodic Mathieu eigenvalue $b_{v\sigma}$ for the (v τ) state. The ω_1 value was obtained from the A-E splitting analysis of the microwave spectra, as is listed in Table 1.

However, the η values obtained from the "A", "B", and "C" rotational constant sets and from the A-E energy differences are actually much different from one another beyond the experimental error.

This fact suggests the neccessity of some extention of the basic formula derived by Morino and Saito. Their formula had been derived on the basis of the following expansion for the rotational constants.

$$R(v\ \tau) = R(0\ 0) - \alpha_v(R)v - \alpha_\tau(R)\tau, \quad R = A,\ B,\ \text{and}\ C \qquad (4)$$

However, since the degree of mixing η can be obtained from the A-E splitting data for our case, the expansion formula can be extended to the following,

$$R(v\ \tau) = R(0\ 0) - \alpha_v(R)v - \alpha_\tau(R)\tau + \beta(R)\tau(\tau+1) \qquad (5)$$

where the coefficients $\alpha_v(R)$, $\alpha_\tau(R)$, and $\beta(R)$ can be determined from the rotational constants as;

$$\begin{bmatrix} R(0\ 0) - R(1\ 0) \\ R(0\ 0) - R(0\ 2) \\ R(0\ 0) - R(0\ 1) \end{bmatrix} = \begin{bmatrix} 1-\eta & 2\eta & -6\eta \\ \eta & 2(1-\eta) & -6(1-\eta) \\ 0 & 1 & -2 \end{bmatrix} \begin{bmatrix} \alpha_v(R) \\ \alpha_\tau(R) \\ \beta\ (R) \end{bmatrix} \qquad (6)$$

The results obtained from the above extended formula are listed in Table 2.

As are found in the table, some of the $\beta(R)$ values are not so small and this fact is considered to be some reflections of the speciality of the methyl torsion. Though the values of the cubic force constants $k_{11,18,18}$ called our special attentions, their experimental errors due to the uncertainties of the observed vibrational frequencies are so large at present that the discussion about $k_{11,18,18}$ is considered not to be fruitful until the accurate measurements of the vibrational frequencies are carried out. We are still working on the measurements of the microwave and vibrational spectra of ethyl fluoride and the other molecules similar to ethyl fluoride.

Furthermore, a situation similar to that found for the present molecule probably occurs for dimethyl sulfide. According to our preliminary search of the microwave spectra attributed to the skeletal bending excited state, they are triplets with large spacings. When the methyl torsional states are designated as (0 0), $(0\ 1)_+$, $(0\ 1)_-$, $(0\ 2)_+$, $(0\ 2)_-$, and (1 1), the vibrational frequencies of $(0\ 2)_+ \leftarrow (0\ 0)$ and $(1\ 1) \leftarrow (0\ 0)$ are reported by Durig and Griffin$^{5)}$ to be 330.0 and 333.7 cm^{-1}, respectively, while the skeletal bending frequency is 282 cm^{-1}. Since the $(0\ 2)_+$, (1 1) and skeletal bending excited states belong to the A_1A_1 symmetry species of $C_{3v}^- \times C_{3v}^+$, the Fermi resonance may occur between these states. Since the microwave spectra attributed to the $(0\ 2)_+$ and (1 1) states have not been assigned, we are working on this molecule at present.

References

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