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THE RAMAN AND INFRARED SPECTRA AND STRUCTURES OF ETHYL
CHLORIDE, BROMIDE AND IODIDE

Key Words: Raman, Infrared, Structure, C_2H_5I , C_2H_5Br ,
 C_2H_5Cl

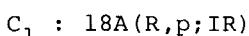
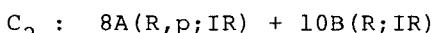
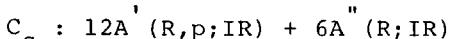
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ABSTRACT

The Raman, infrared and proton NMR spectra of the liquid molecules, C_2H_5-X ($X=Cl, Br, I$) have been recorded. And the molecular structures have been studied on the basis of these spectra. Consequently a non-rigid structure in which a CH_2 group rotates freely with respect to the three hydrogen atoms of CH_3 group is established.

INTRODUCTION

The obtained Raman spectra and the polarization data of C_2H_5-X ($X=Cl, Br, I$) do not seem to be explained according to the possible symmetries; C_s , C_2 or C_1 for a rigid structure of CH_3-CH_2-X . That is, considered as a rigid structure, the selection rules for every symmetries predict 18 fundamentals to be both in Raman and infrared active, as shown by the following irreducible representations;



On the other hand, the selection rules derived from a non-rigid structure in which the CH_2 group rotates freely with respect to the CH_3 group yield 8 fundamentals [$4A_1(R,p;IR) + 4E(R;IR)$] due to $CH_3-(Y)-X(Y=CH_2)$ which has C_{3v} symmetry and 3 additional fundamentals due to the CH_2 group. The obtained vibrational spectra of CH_3-CH_2-X can be explained according to a non-rigid structure (C_{3v}) and the obtained NMR spectra strongly support a non-rigid structure for these molecules, too.

EXPERIMENTAL

All samples were purchased from commercial sources, and purified by distillation.

The Raman spectra of the liquids^{*1} were recorded on JEOL JRS-S1B spectrophotometer using Ar^+ (4880 Å) laser. The infrared spectra were measured both in gaseous and liquid state^{*2} with Shimadzu IR-450 spectrometer whose gas cell had a path of 10 cm and KRS-5 windows. The differences between the infrared spectra of gaseous and liquid samples are hardly discernible, but those for gaseous state are shown, so as to indicate the band types; a parallel type or a perpendicular one. The NMR spectra of the samples were measured with JEOL PS-100 spectrometer operating at 100 MHz and TMS was used as internal standard.

RESULTS AND DISCUSSION

The obtained Raman and infrared spectra of C_2H_5-X and CH_3-I which has a C_{3v}^{1-3} symmetry are shown in Fig. 1. The previous literature⁴⁻⁶ have reported that the structures of C_2H_5-X were C_s with a bent $C-C_X$ chain. In the case of

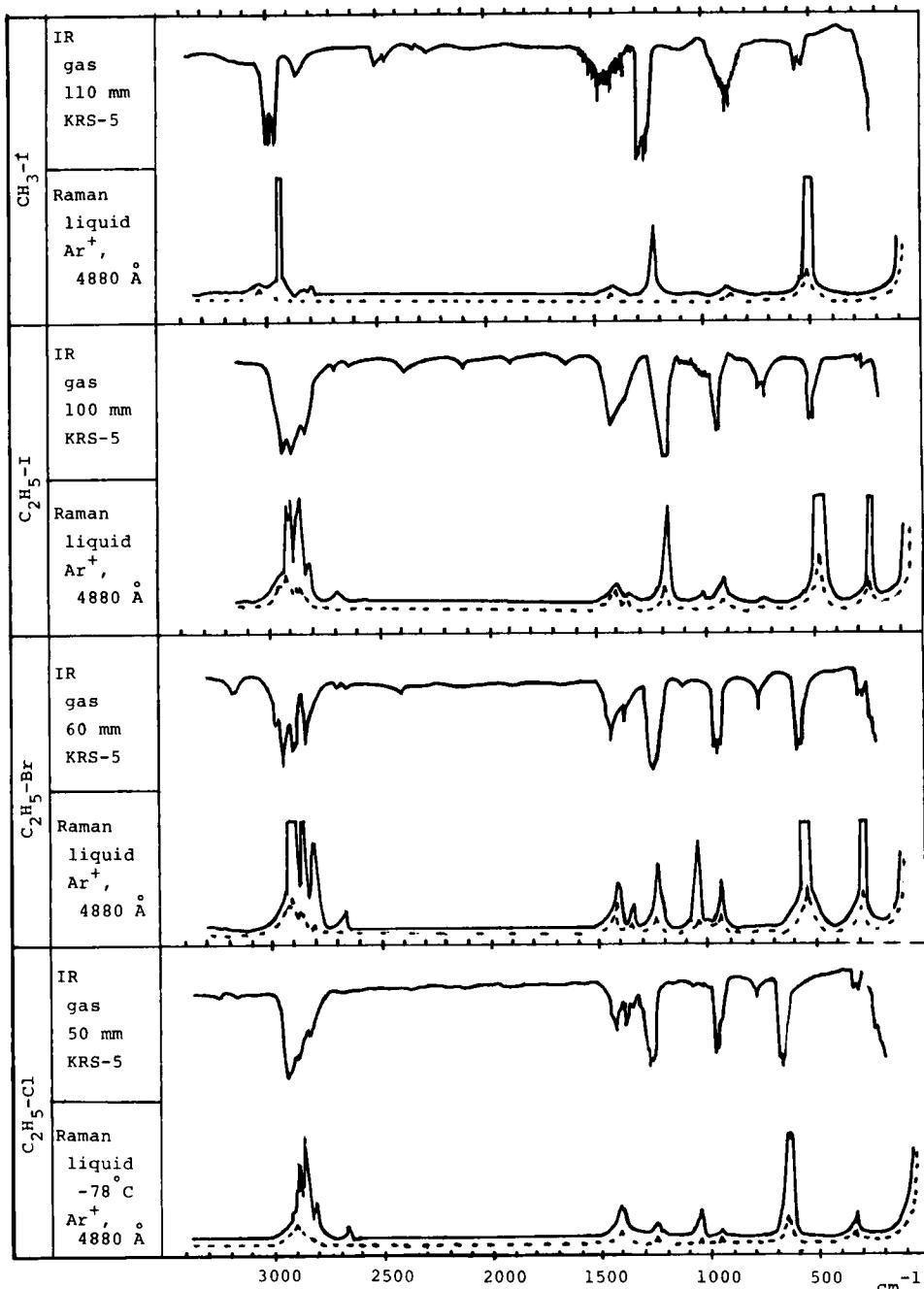


Fig. 1 Raman and infrared spectra of $\text{CH}_3\text{-I}$, $\text{C}_2\text{H}_5\text{-I}$, $\text{C}_2\text{H}_5\text{-Br}$ and $\text{C}_2\text{H}_5\text{-Cl}$
 (*) means that polarization state or band contour is ambiguous.

a bent chain, there would appear 18 fundamentals, all of which are both Raman and infrared active for C_2H_5-X . However the obtained spectra indicate the general simplicity of the spectra and resemble very closely to the spectra of CH_3-I with C_{3v} symmetry, except the appearance of $\nu_a C-C-X$, $\delta C-C-X$, νCH_2 , δCH_2 and ρCH_2 . There are some possible reasons for the simplicity as not expected; accidental overlapping and disappearing of weak bands. In this case, the C_s symmetry for a molecule might be erroneously taken as a C_{3v} . However it is supported by several spectroscopic arguments, as follows, that the CH_3-CH_2-X type molecules would have a non-rigid structure, in which a CH_2 group rotates freely with respect to the three hydrogen atoms of a CH_3 group. (1) The obtained spectra of CH_3-CH_2-X resemble closely to that of CH_3-I having C_{3v} symmetry. (2) It has been reported that a non-rigid molecule accompanied with an internal rotation can have the higher symmetry than the symmetry possible for a molecule considered a rigid structure^{7,8}. (3) A parallel type infrared band(A_1 species) shows a PQR structure with a proper P-R separation: 14 cm^{-1} for C_2H_5-I , 15 cm^{-1} for C_2H_5-Br and 19 cm^{-1} for C_2H_5-Cl . The presence of P, Q, and R branches demands that the major axis symmetry should be threefold or greater^{1,9-10}. (4) In a NMR spectrum of CH_3-CH_2-X there are two sets of equivalent nuclei, those of methyl group and those of methylene group. The signal of CH_2 , which appears at a lower field, is split into a quartet by the three equivalent protons in CH_3 , whereas the signal of CH_3 is a triplet resulting from a spin-spin interaction with the two equivalent protons in CH_2 . The spacing of the individual components in the two signals is identical. This can be explained on the basis of internal rotation occurring at a sufficiently rapid rate for the effective chemical shifts and spin coupling constants to be averaged¹¹.

Some possible reasons for the simplicity are above mentioned. In opposition, there are some possible reasons for the complexity of the spectra; mistaking a Fermi doublet, a vibration-rotational band contour and/or hot bands for plural fundamentals.^{*3} In this case, a C_{3v} symmetry for CH_3-CH_2-X would be regarded as a C_s one. Such a mistaking is pointed out by some workers¹²⁻¹⁵. Also Winther and Hummel⁶ have described that in view of the large number of "hot" transitions found in the spectra of the C_2H_5-Cl and C_2H_5-Br their absence in the spectrum of C_2H_5-I is somewhat puzzling. This seems to be the example where a family of Q branches of perpendicular type band would wrongly be assigned as hot bands. A perpendicular type band consisting of a family of Q branches is not so highly resolved in the spectrum when the moments of inertia of molecule are large¹³, and so the numbers of Q branches decrease with increasing molecular weight from C_2H_5-Cl to C_2H_5-I .

The above considerations have let me decide CH_3-CH_2-X type molecules to have a C_{3v} symmetry. The CH_3 stretching, deformation and rocking which are group vibrations can easily be assigned, by comparison with those of CH_3-I which has a C_{3v} symmetry. On the other hand, the assignments of the C-C-X stretching and bending of CH_3-CH_2-X are quite clear, because of their absence for CH_3-I . The CH_2 vibrations which never appear for CH_3-I are guessed to be close to the CH_3 vibrations in frequencies. A tentative assignments of the vibrational spectra for CH_3-CH_2-X are proposed in Table 1, according to a non-rigid(C_{3v}) selection rules. The non-rigid C_{3v} model of CH_3-CH_2-X is theoretically supported as follows; It is possible to consider a 2s and a 2p_z orbital in carbon atom as being hybridized to be linear -X- by exciting one of a 2s electrons into 2p state¹⁶. A p_x and a p_y orbital of carbon atom combine with 1s orbitals of two hydrogen atom to comform CH_2 group.

Table 1. Symmetry species, selection rules, band type, P-R separation and frequency assignments of CH_3^- -I and CH_3^- -Y ($X=I, \text{Br}, \text{Cl}; Y=\text{CH}_2$)

C_{3v}	Form. of Vibration	CH_3^- -I		$\Delta\nu_{\text{PR}}$		CH_3^- (Y)-I		$\Delta\nu_{\text{PR}}$		CH_3^- (Y)-Br		$\Delta\nu_{\text{PR}}$		CH_3^- (Y)-Cl		$\Delta\nu_{\text{PR}}$	
		Raman		IR		Raman		IR		Raman		IR		Raman		IR	
			cm^{-1}		cm^{-1}		cm^{-1}		cm^{-1}		cm^{-1}		cm^{-1}		cm^{-1}		
A_1	$\nu_s \text{CH}_3$	(p) 2947vs	(II) 2978vs	21	(p) 2967s	(II) 2995s	14	(p) 2973s	(*) 3002vs	(*)	(p) 2970s	(*) 3005s	(*)				
	$\delta_s \text{CH}_3$	(p) 1237s	(II) 1253vs	21	(p) 1202s	(*) 1215vs	(*)	(p) 1254s	(*) 1254vs	(*)	(p) 1282w	(II) 1290w	(*)				
	$\nu_{as}^- \text{C-}(Y)-X$	nil	—	—	(p) 1055m	(*) 1024vw	(*)	(p) 1064s	(*) 1060vw	(*)	(p) 1074w	(*) 1074w	(*)				
	$\nu_s^- \text{C-}(Y)-X$	(p) 522vs	(II) 535m	21	(p) 500vs	(III) 511s	14	(p) 562vs	(II) 576vs	15	(p) 638vs	(III) 678s	19				
E	$\nu_{as} \text{CH}_3$	(d) 3040w	(II) 3075w	—	(d) 3018wsh	—	(d) 3025w	(II) 3036wsh	—	(d) 3035wsh	—	(d) 3091wsh	(II) 3023s	—			
	$\delta_{as}^- \text{CH}_3$	(d) 1425w	(II) 1477m	—	(d) 1440m	(II) 1450s	—	(d) 1445m	(II) 1453s	—	(d) 1452m	(II) 1450s	—				
	$\rho_r \text{CH}_3$	(d) 882w	(II) 886s	—	(d) 750w	(II) 743m	—	(d) 775vw	(II) 771m	—	(*)	(II) 787m	—				
	$\delta^- \text{C-}(Y)-X$	nil	—	(d) 980vw	(*) 990vw	—	(d) 1023w	(*) 1015wsh	—	(d) 1248wsh	(*)	(*)	—				
$2 \times \delta_{as}^- \text{CH}_3$	Torsion	nil	nil	—	(p) 263vs	(*) 255w	(*)	(p) 292vs	(*) 284w	(*)	(p) 337m	(*) 334m	(*)				
	(p) 2820s	(II) 2845m	(*)	(p) 2862m	(II) 2887s	14	(p) 2863m	(II) 2888s	15	(p) 2887m	(*) 2916	(*)					
A_2	$\nu_s \text{CH}_2$	nil	nil	—	(p) 2920s	(II) 2937s	14	(p) 2927vs	(II) 2944s	16	(p) 2937vs	(II) 2953	20				
	δCH_2	nil	nil	—	(p) 1380w	(*) 1377w	(*)	(p) 1379w	(*) 1386wsh	(*)	(p) 1392w	(*) 1397w	(*)				
	$\rho_r \text{CH}_2^{(**)}$	nil	nil	—	(p) 950m	(II) 956s	14	(p) 961m	(II) 965s	15	(*) 967w	(II) 974s	19				

(*) shows that polarization data, P-R separations, or bands are ambiguous or unobservable.

(**) shows that $\rho_r \text{CH}_2$ band should be depolarized and perpendicular type one, but the one is against the selection rules. A clear account is not given of this violation of selection rules. The similar violation has been previously reported¹⁷.

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FOOTNOTE

*1 Generally speaking, the Raman measurement of gaseous state is very difficult.

*2 The infrared measurement in liquid state of C_2H_5Cl could not be done, because a boiling point of C_2H_5Cl is lower than a room temperature, and the present authors do not have a low temperature cell for infrared.

*3 In the literature¹⁵, the two absorption maxima at 1430 and 1475 cm^{-1} in the infrared spectrum of the vapor of CH_3-S-CH_3 are interpreted as branches of a single band and not as two separate bands. This is correct and shows that some of the previous workers mistook vibration-rotational band contours of a single band for plural fundamentals. Such a mistaking would lead a C_{3v} to a C_{2v} for CH_3-X-CH_3 type molecule or a C_{3v} to a C_s for CH_3-CH_2-X .

REFERENCES

- 1 G. Herzberg, "Molecular Spectra and Molecular Structure II" Van Nostrand Reinhold Co., New York(1945) p.314 and p.414
- 2 W. H. Bennet and C. F. Meyer, Phys. Rev., 32, 888(1928)
- 3 J. G. Moorehead, Phys. Rev., 39, 788(1932)
- 4 A. B. Dempster and G. Zerbi, J. Mol. Spectroscopy, 39, 1(1971)
- 5 S. Suzuki, J. L. Bribes and R. Gaufrès, J. Mol. Spectroscopy, 47, 118(1973)
- 6 F. Winther and D. O. Hummel, Spectrochim. Acta, 25A, 425 (1969)
- 7 D. M. Byler and D. F. Shriver, Inorg. Chem., 13, 2697(1974)
- 8 I. R. Beattie and G. A. Ozin, J. Chem. Soc., A, 370(1970)

- 9 M. Davies, "Infrared Spectroscopy and Molecular Structure" Elsvier Co., New York(1963) p.153
- 10 R. A. Kovar and G. L. Morgan, Inorg. Chem., 8, 1099(1969)
- 11 J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance", McGraw-Hill Book Co., New York(1959) p.94 and p. 377
- 12 K. Hamada and H. Morishita, J. Mol. Struct., 44, 119(1978)
- 13 K. Hamada and H. Morishita, J. Mol. Struct., 48, 191(1978)
- 14 K. Hamada and H. Morishita, Syn. React. Inorg. Metal-Org. Chem., 7, 355(1977)
- 15 D. W. Scott and M. Z. El-Sabban, J. Mol. Spectroscopy, 30, 317(1969)
- 16 W. J. Moore, "Physical Chemistry" Prentice-Hall Inc., N. J. (1962) p.537
- 17 S. G. Frankis, J. Mol. Struct., 3, 89(1969)

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