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## **The Raman and Infrared Spectra and Structures of Ethyl Chloride, Bromide and Iodide**

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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;

$$C_s : 12A' (R,p;IR) + 6A'' (R;IR)$$

$$C_2 : 8A (R,p;IR) + 10B (R;IR)$$

$$C_1 : 18A (R,p;IR)$$

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<sup>\*1</sup> were recorded on JEOL JRS-S1B spectrophotometer using  $Ar^+$  (4880 Å) laser. The infrared spectra were measured both in gaseous and liquid state<sup>\*2</sup> 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 literature<sup>4-6</sup> have reported that the structures of  $C_2H_5-X$  were  $C_s$  with a bent  $C-C-X$  chain. In the case of

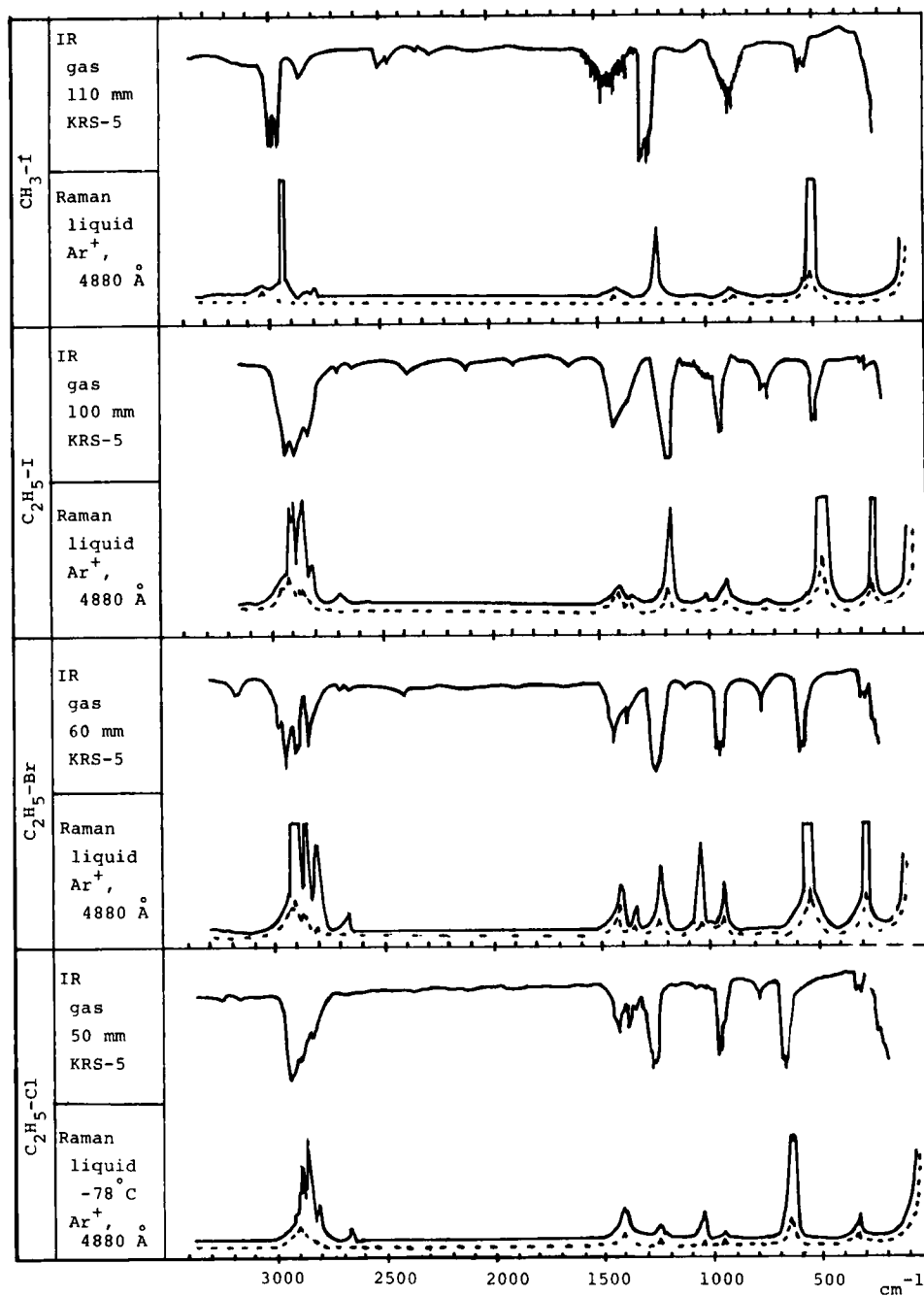


Fig. 1 Raman and infrared spectra of  $\text{CH}_3\text{-I}$ ,  $\text{C}_2\text{H}_5\text{-I}$ ,  $\text{C}_2\text{H}_5\text{-Br}$  and  $\text{C}_2\text{H}_5\text{-Cl}$   
 (\*) means that polarization state or band contour is ambiguous.

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  $\nu_a C-C-X$ ,  $\delta C-C-X$ ,  $\nu CH_2$ ,  $\delta CH_2$  and  $\rho CH_2$ . 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<sup>7,8</sup>. (3) A parallel type infrared band ( $A_1$  species) shows a PQR structure with a proper P-R separation:  $14\text{ cm}^{-1}$  for  $C_2H_5-I$ ,  $15\text{ cm}^{-1}$  for  $C_2H_5-Br$  and  $19\text{ cm}^{-1}$  for  $C_2H_5-Cl$ . The presence of P, Q, and R branches demands that the major axis symmetry should be threefold or greater<sup>1,9-10</sup>. (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 averaged<sup>11</sup>.

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.<sup>\*3</sup> 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 workers<sup>12-15</sup>. Also Winther and Hummel<sup>6</sup> 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 large<sup>13</sup>, 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  $2p$  state<sup>16</sup>. 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  $\text{CH}_3\text{-I}$  and  $\text{CH}_3\text{-(Y)-X}$  ( $\text{X=I, Br, Cl; Y=CH}_3$ )

$\text{C}_{3v}$	Form. of Vibration	$\text{CH}_3\text{-I}$		$\Delta\nu_{\text{PR}}^{-1} \text{ cm}^{-1}$		$\text{CH}_3\text{-(Y)-I}$		$\Delta\nu_{\text{PR}}^{-1} \text{ cm}^{-1}$		$\text{CH}_3\text{-(Y)-Br}$		$\text{CH}_3\text{-(Y)-Cl}$		$\Delta\nu_{\text{PR}}^{-1} \text{ cm}^{-1}$	
		Raman	IR			Raman	IR			Raman	IR	Raman	IR		
$\text{A}_1$	$\nu_{\text{S}} \text{CH}_3$	(p) 2947vs	(ll) 2978vs	21		(p) 2967s	(ll) 2995s	14		(p) 2973s	(*) 3002vs	(p) 2970s	(*) 3005s	(*)	
	$\delta_{\text{S}} \text{CH}_3$	(p) 1237s	(ll) 1253vs	21		(p) 1202s	(*) 1215vs	(*)		(p) 1254s	(*) 1254vs	(p) 1282w	(ll) 1290vs	19	
	$\nu_{\text{AS}} \text{C-(Y)-X}$	nil	nil	—		(p) 1055m	(*) 1024vw	(*)		(p) 1064s	(*) 1060vw	(p) 1074m	(*) 1070vs	(*)	
	$\nu_{\text{S}} \text{C-(Y)-X}$	(p) 522vs	(ll) 535m	21		(p) 500vs	(ll) 511s	14		(p) 562vs	(ll) 576vs	(p) 658vs	(ll) 678vs	19	
$\text{E}$	$\nu_{\text{AS}} \text{CH}_3$	(d) 3040w	(ll) 3075w	—		(d) 3018wsh	(ll) 3036wsh	—		(d) 3025w	(ll) 3035wsh	(d) 2990wsh	(ll) 3023s	—	
	$\delta_{\text{AS}} \text{CH}_3$	(d) 1425w	(ll) 1477m	—		(d) 1440m	(ll) 1450s	—		(d) 1445m	(ll) 1453s	(d) 1452m	(ll) 1450s	—	
	$\rho_{\text{r}} \text{CH}_3$	(d) 882w	(ll) 886s	—		(d) 750w	(ll) 743m	—		(d) 775vw	(ll) 771m	(*)	(ll) 787m	—	
	$\delta \text{C-(Y)-X}$	nil	nil	—		(d) 980vw	(*) 990vw	—		(d) 1023vw	(*) 1015wsh	(d) 1248vwsh	(*)	—	
	Torsion	nil	nil	—		(p) 263vs	(*) 255w	(*)		(p) 292vs	(*) 284w	(p) 337m	(*) 334m	(*)	
	$2 \times \delta_{\text{AS}} \text{CH}_3$	(p) 2820w	(ll) 2845m	(*)		(p) 2862m	(ll) 2887s	14		(p) 2869m	(ll) 2888s	(p) 2833m	(*) 2896	(*)	
	$\nu_{\text{S}} \text{CH}_2$	nil	nil	—		(p) 2920s	(ll) 2937s	14		(p) 2927vs	(ll) 2944s	(p) 2937vs	(ll) 2953	20	
	$\delta_{\text{CH}_2}$	nil	nil	—		(p) 1380w	(*) 1377w	(*)		(p) 1379w	(*) 1386msh	(p) 1382w	(*) 1397msh	(*)	
	$\rho_{\text{r}} \text{CH}_2^{(*)}$	nil	nil	—		(p) 950m	(ll) 956s	14		(p) 961m	(ll) 965s	(*) 967w	(ll) 974s	19	

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

(\*\*) shows that  $\rho_{\text{r}} \text{CH}_2$  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 reported<sup>17</sup>.

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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 literature<sup>15</sup>, 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  $CH_3-CH_2-X$ .

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