RAMAN SPECTRA OF 1,2-DICLOROETHANE AND 2-CHLOROETHANOL

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ABSTRACT

Raman spectra of 1,2-dichloroethane and 2-chloroethanol have been recorded using both the 4358 Å and the 2537 Å excitations In the spectra obtained with the latter excitation, many new Raman lines are found for the first time. Assignments of these lines are discussed. When the exciting wavelength is changed from 4358 Å to 2537 Å, the relative intensities and depolarization ratios of some of the Raman lines of the two substances are seen to change also. These changes are explained on the basis of the resonance Raman effect.

1. INTRODUCTION

The Raman spectrum of 1,2-dichloroethane and 2-chloroethanol has been studied by numerous investigators[1-5]. The problem of internal rotation in substituted ethanes has been studied in detail by Mizushima[2]. It is now well known that both in the gaseous and liquid states 1,2-dichloroethane exists as a mixture of two rotational isomers, having the trans- and the gauche- forms respectively. The trans- form of the molecule belongs to the symmetry point group C_{2h} and the gauche- form to the point group symmetry C_2. Complete vibrational assignments from normal coordinate analyses for these two forms has been given by Nakagawa and Mizushima[6]. The molecular structure of 1,2-dichloroethane has also been studied by X-ray[7], electron diffraction[8] and infrared[2,9] methods.

The Raman spectrum of 2-chloroethanol has also been the subject of numerous investigations[10-15]. Infrared obsorption[16-18], electron diffraction[19,20] and microwave[21] studies of 2-chloroethanol have also been reported in the literature. These studies have shown that the 2-chloroethanol molecule also exists in two rotational isomeric forms — the trans- and the gauche-ones. Whereas in 1,2-dichloroethane the trans- form is more stable, in 2-chloroethanol the guache- form is the more stable one. In the latter case, the chlorine atom and the hydroxyl groups take part in the formation of an internal hydrogen bond.

All these earlier studies on the Raman spectra of the above two compounds had been carried out using the visible mercury 4358 Å excitation methods. Pure 1,2-d.chloroethane and 2-chloroethanol were found to be sufficiently transparant to the 2537 Å mercury radiation. It was thought worthwhile, therefore, to re-examine the Raman spectra of the above two liquids using the 2537 Å excitation, with a view to find out the changes if any, which take place in the spectra, as the exciting frequency in this case will be much closer to the electronic absorption frequencies of the compounds.

2. EXPERIMENTAL DETAILS

Two sets of Raman spectra were recorded for each compound, one using the visible mercury 4358 Å excitation and the other using the ultraviolet mercury 2537 Å radiation. A Toronto type helical mercury arc was the sources of the visible radiation, while a water-cooled, magnet-controlled quartz mercury arc served to produce an intense beam of the ultraviolet radiation. A saturated solution of sodium nitrite was used to cut off all radiations of wavelength less than 4358 Å in the first case; for the ultra-violet studies, a filter of dilute acetic acid was used to cut off all radiations of wavelength less than 2537 Å   The visible Raman spectra were recorded using a Hilger two prism spectrograph on Ilford Astra III plates. For the ultraviolet Raman spectra, a Hilger medium quartz spectrograph was used, the spectra being photographed on Ilford Zenith Astronomical plates. For the depolarization measurements, a double image prism was inserted in the path of the scattered light. The light coming out of the double image prism was condensed on to the slit of the spectrograph using a crystal quartz lens. The lens was so chosen that by its optical activity and biref-ringence the two componets of the scattered light coming out of the double image prism, were effectively depolarized. Thus the two beams did not suffer unequal reflection losses inside the spectrograph. The Raman spectra were microphotometered using a Moll microphotometer.

Analar quality 1, 2-dichloroethane, and 2-chlorcethanol were used in the study. Both the liquids were distilled twice before use. For the ultraviolet study, the samples were kept in a high optical quality fused silica Wood's tube.

3. RESULTS

Figures 1a and 1b show the Raman spectra and the microphotometer tracings of 1, 2-dichloroethane as excited by the 2537 Å and the 4358 Å radiations, respectively. Figures 2a and 2b show the corresponding Raman spectra of 2-chloroethanol. The observed Raman frequency shifts, their visually estimated relative intensities, and depolarization ratios of 1, 2-dich-loroethane are listed in Table 1. The frequency shifts of the Raman lines of 2-Chloroethanol, along with their visually estimated relative intensities are given in Table 2.

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TABLE 1

Raman Spectrum of 1,2-Dichloroethane

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7537 Å excitation		4538 Å excitation		Assignments		Species	
Frequencies $(cm^{-1})(a)$	ρ	Frequencies (cm^{-1})	$\rho^{(b)}$			Trans C_{2h}	Gauche C_1
125(3)	dp	125(4)	0.63	ν'_{10}	torsion		a
223(0)		223(1)		ν_{18}	C-Cl bending	b_u	
265(2)	0.47	263(2)	0.31	ν'_6	C-Cl bending		a
301(8)	0.54	300(8)	0.40	ν_6	C-Cl bending	a_g	
414(4)	0.94	412(4)	0.81	ν'_{18}	C-Cl bending		b
465(0)	. .			ν_5-ν_6	or ν_{16}-ν^9	A_g or B_g	
537(0)				ν'_5-ν_6	or $2\nu_6$	A_g	A
650(10)	0.13	652(10)	0.18	ν'_5	C-Cl stretching		a
680(8)	0.88	678(6)	dp	ν'_{17}	C-Cl stretching		b
752(10)	0.39	754(10)	0.23	ν_5	C-Cl stretching	a_g	
883(4)	0.18	881(3)	0.88	ν'_{13}	CH_2 rocking		b
944(5)	0.34	942(4)	0.26	ν'_9	CH_2 rocking		a
990(1)		989(1)	p	ν_{13}	CH_2 rocking	b_g	
1032(1)		1032(1)		ν'_4	C-C stretching		a
1054(3)	0.57	1052(4)	0.47	ν_4	C-C stretching	a_g	
1145(2)	dp	1143(2)	dp	ν'_{12}	CH_2 twisting		b
1169(0)				ν'_2-ν'_6			A
1209(7)	0.71	1206(6)	0.65	ν'_8	CH_2 twisting		a
1264(0)		1262(1)	dp	ν'_3, ν_{12}	CH_2 wagging	b_g	a
1305(9)	0.35	1303(7)	0.45	ν_3, ν'_{16}	CH_2 twisting	a_g	b
1432(8)	0.72	1439(8)	0.82	ν'_2, ν'_{15}	CH_2 bending		a, b
1444(6)		1443(5)	dp	ν_2	CH_2 bending	a_g	
1507(1)				$2\nu_3$		A_g	

TABLE 1—(contd.)

2537 Å excitation		4358 Å excitatio		Assignmets	Species	
Frequencies (cm⁻¹)(a)	ρ	Frequencies (cm⁻¹)(a)	ρ(b)		Trans C_{2h}	Cauch C_1
1630(0)	..	..	..	$\nu'_{17} + \nu'_9$		B
2062(1)	..	..	..	$\nu_3 + \nu_5$	A_g	
2095(1)	..	..	..	$\nu_8' + \nu'_{13}$ or $\nu'_2 + \nu'_5$		B or A
2260($\frac{1}{2}$)	..	..	..	$\nu_8' + \nu'_4$		A
2316(0)	..	..	..	$\nu'_2 + \nu'_{13}$		B
2470(1)	..	..	..	$\nu_2'' + \nu'_4$ or $\nu'_8 + \nu'_3$		A
2525($\frac{1}{2}$)	..	..	..	$\nu'_8 + \nu'_{16}$		B
2569(1)	..	..	..	$\nu'_2 + \nu_{12}$ or $\nu_3 + \nu_{12}$		A
2603(0)	..	..	..	$2\nu_3$ or $2\nu'_{16}$	A	A
2712($\frac{1}{2}$)	..	..	..	$\nu_2 + \nu_{12}$	B_g	
2744(1)	..	..	..	$\nu_2 + \nu_3$	A_g	
2844(5)	p	2841(4)	p	$2\nu_2'$		A
2875(5)	p	2875(4)	p	$2\nu_2$	A_g	
2958(10)	0.23	2960(10)	0.23	$\nu_1\ \nu'_1\ \nu'_{14}$ CH stretching a_g		a,b
3005(8)	1.00	3007(7)	dp	$\nu_{11}\ \nu'_7\ \nu'_{13}$ C-H stretching b_g		a,b

(a) Numbers within brakets give the relative intensities estimated vissually.
(b) Values reported by Neu et al. (4).

4. DISCUSSION

A study of the Tables 1 and 2 shows that besides the Raman lines already reported by earlier workers, the Raman spectra of 1,2-dichloroethane and 2-chloroethanol excited by the 2537 Å radiation contain many new lines. These lines are mainly in the region of combination and overtone bands. We have used the assignments for the fundamental vibrations of 1,2 dichloroethane as given by Nakagawa and M zushima [6]. Table 1 gives these assignments, together with our assignments of the newly observed Raman lines which have been assigned as combinations and overtones. In making the latter assignments, the following facts were taken into account : (i) only the overtones and combinations expected are those involving in general, the stronger fundamentals and (ii) the resultant states of the combinations and the overtones should belong to a Raman active species.
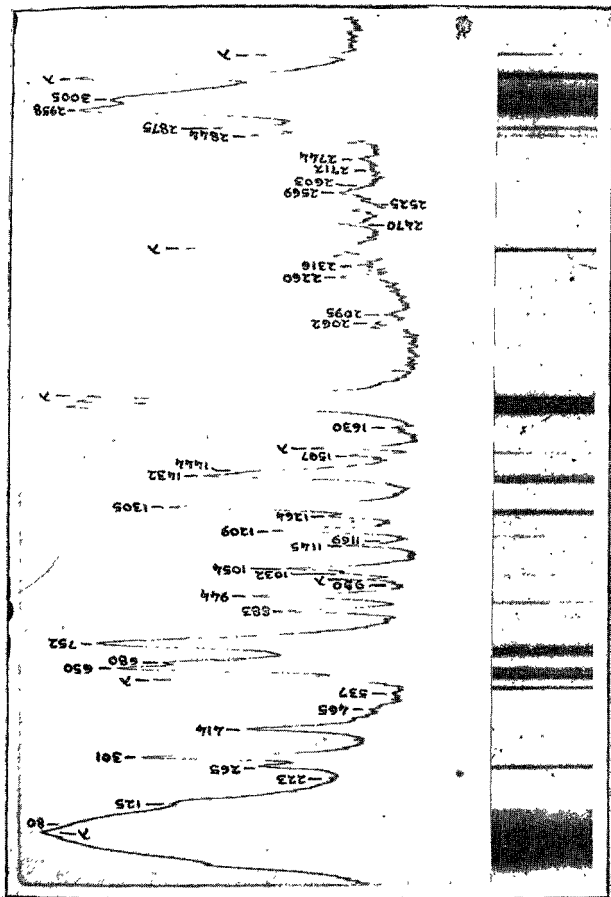
PLATE Ia

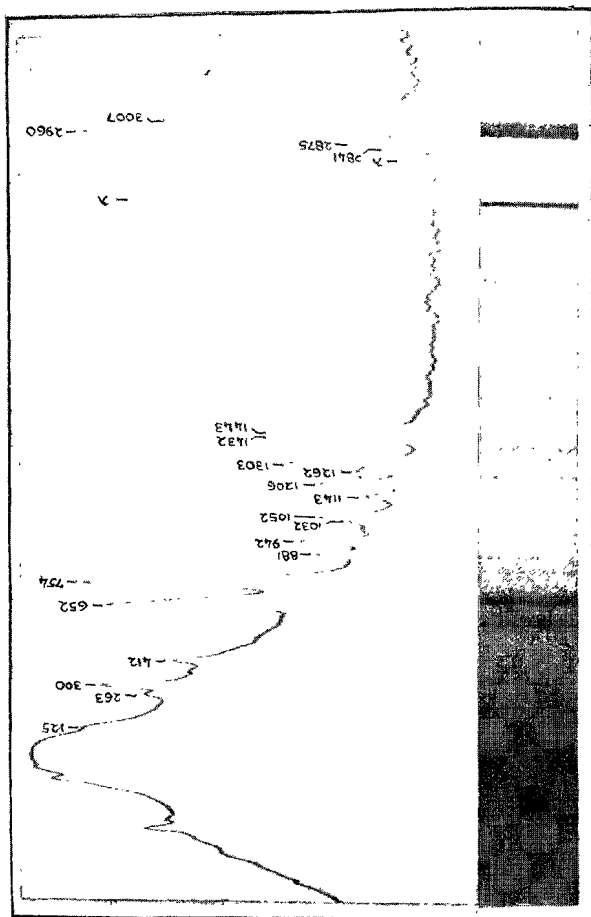Raman Spectrum and the microphotometer record of 1,2–dichloroethane (2537 Å excitation)

PLATE I *b*

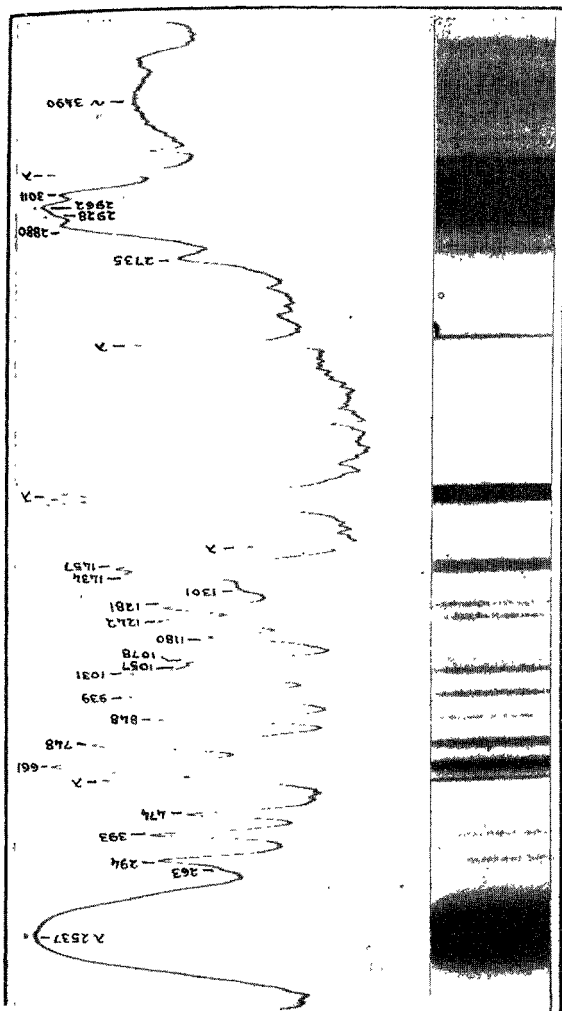Raman Spectrum and the microphotometer record of 1 2—dichloroethane (4358 Å excitation)

Plate IIa

Raman Spectrum and the microphotometer record of 2—chloro ethanol (2537 Å A excitation)
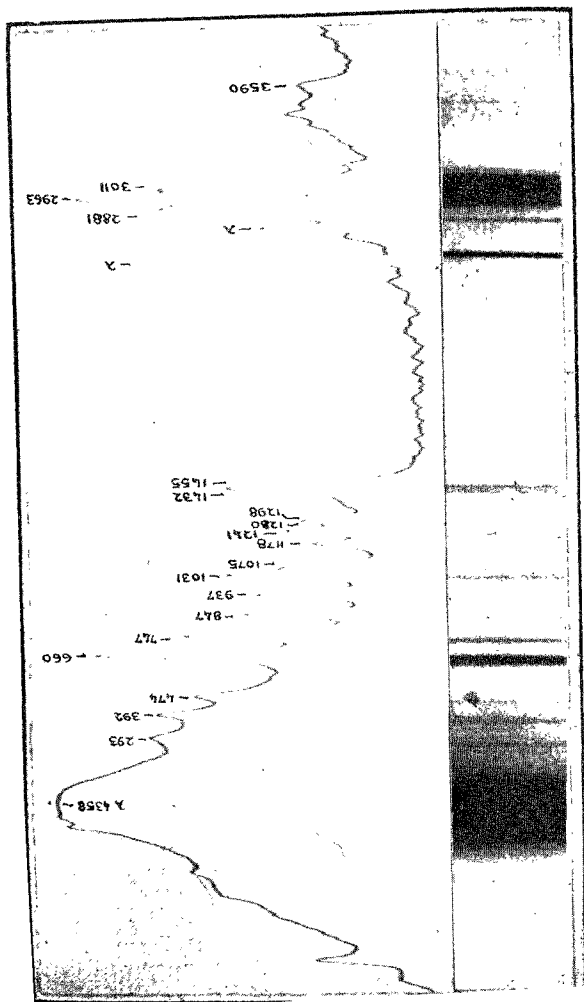
Plate II*b*

Raman Spectrum and the microphotometer record of 2—chloro ethanol (4358 Å A excitation)

TABLE 2

Raman Spectrum of 2-Chloroethanol

Frequencies (cm^{-1})		Assignments
Present study		
2537 Å excitation	4538 Å excitation	
165(1)		Torsion
263(0)		
294(4)	293(3)	C-C-Cl bending
393(5)	392(4)	
474(3)	473(3)	C-C-O bending
661(10)	660(10)	C-Cl stretching
748(5)	747(4)	
848(4)	847(4)	CH_2 rocking
939(3)	937(5)	
1031(4)	1031(5)	C-C stretching
1057(1)	1056(1)	
1078(2)	1075(2)	C-O stretching
1180(2)	1178(2)	CH_2 twisting
1242(3)	1241(3)	
1281(2)	1280(2)	CH_2 wagging
1301(2)	1293(2)	
1434(5)	1432(4)	CH_2 bending
1457(5)	1455(5)	
1598(0)		
1884(1)		
1966(1)		
2492(1)		Overtones and combinations
2610(1)		
2735(2)		
2880(4)	2881(4)	
2928(3)	2930(3)	
2962(10)	2960(10)	C-H stretching
3011(4)	3011(4)	
3460	3460	O-H stretching

The last column of Tables 2 gives the vibrational assignments for the 2-chloroethane molecule. These assignments have been made by a comparison of the Raman spectrum of 2-chloroethanol with the Raman spectra of 1,2-dichloroethane and 1,2-ethanediol 22.

A comparison of the Raman spectrum of 1,2 dichloroethane excited by the 2537 Å radiation with that obtained by the 4358 Å excitation shows that the relative intensities of the two Raman lines at Ca. 1305 cm^{-1} and a Ca. 1432 cm^{-1} are reversed. A comparison of the depolarization ratios of these two lines shows that in the 2537 Å excited spectrum, these two Raman lines have lower depolarization values. Similary, the Raman lines at 848 and 939 cm^{-1} have their intensities reversed in the 2537 Å excited Raman spectrum of 2—chloroethanol. The changes observed in the relative intensities, though small, are believed to be genuine. In the short wavelength ranges where these Raman lines occur, the variation of the sensitivity of the photographic plate cannot introduce any appreciable error. And, in our depolarization measurements, any error in the determination will only tend to increase the depolarization ratio to the limiting value. Thus the decrease in the depolarization ratios of the two 2537 Å excited Raman lines of 1,2-dichloroethane must also be genuine.

It is well known that in the phenomenon of the resonance Raman effect there is a many fold increase in the intensities of some of the Raman lines of the molecule, when the exciting frequency approaches the electronic absorption frequency of the molecule[23]. If the molecule has a non-degenerate ground and excited electronic states, the depolarization ratio tends to 0.50 as the exciting frequency approaches the electronic absorption frequency. This has been verified experimentally in the case of substituted nitrobenzenes by Rea[24]. However, in the case of saturated molecules, such as cyclohexane, 1, 4-dioxne, etc., there does not seem to be a consistent pattern in the intensity changes as the exciting frequency is in the resonance region[25],[26]. In the latter case, however, Bernard and Dupeyrat[27] have shown that the depolarization values do tend to 0.5.

Thus we can conclude that the changes observed in the spectra of 1,2 dichloroethane and 9-chloroethanol, when the exciting frequency is increased, arise due to the resonance effect. It is quite possible, in both cases, that all the lines that do change in intensity in the 2537 Å excitation, actually increase in intensity; only, say, in the case of 1,2-dichloroethane, the Ca. 1305 cm^{-1} Raman line increases intensity much more than the line at Ca. 1432 cm^{-1}.

The Raman lines at Ca. 1305 and Ca. 1432 cm^{-1} in 1,2-dichlorethane arise from the twisting and bending vibrations of the methylene group. The 848 cm^{-1} and 939 cm^{-1} lines of 2-chlorethanol arise from the methylene rocking vibrations. It is interesting to note that in cyclohexane and also in 1,4-dioxane, it is the CH_2 group frequencies which show the resonance effects[25],[26].

The electronic absorption spectrum of 1,2-dichloroethane was recorded using a Unicam absorption spectrophotometer, and it was found to be continuous below 2520 Å. This is very similar to the absorption spectrum of ethane[28], and can be connected with the fact that all the valance electrons are used up in forming the single bonds and the only non-occupied orbitals arising from the valence electrons will be antibonding ones and so will lie fairly high. In this case, therefore, it will be a good approximation to think of the continum level to be replaced by a single non-degenerate level and this might account for the changes observed in the intensities and depolarization ratios of the Raman lines on going to the resonance region. Similar explanations have been given by Albrecht[29], Tsenter and Bobovich[30] and Leite and Porto[31] to explain the resonance Raman scattering from various substances.

5. ACKNOWLEDGEMENT :

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