

The Raman Spectra of Glycol and some Organic Chlorine Compounds

By

V. N. THATTE, M.Sc., AND S. M. SHAHANE, M.Sc.

(College of Science, Nagpur.)

(Plate V.)

(Received for publication, 16th May, 1931.)

ABSTRACT.

Results of the study of the Raman spectra in glycol, per-chlor ethylene, chloral, tetra-chlor ethane and penta-chlor ethane are reported in this paper. The spectrum of glycol resembles that of glycerine and likewise shows a continuous spectrum which is divided into two distinct portions. The strong shift $\Delta\nu$ 1570 in per-chlor ethylene is due to the double bond C=C. The spectra of chloral and acetaldehyde are compared and the effect of substituting the hydrogen atoms by chlorine atoms on the scattered spectrum is discussed. A comparative study of the Raman spectra in the chlorine substituted compounds of C_2H_6 is made and it is shown that as the number of chlorine atoms increases the value of corresponding shift also increases.

Introduction.

The paper describes the study of the Raman spectra in glycol, perchlor ethylene, chloral and the tetra- and penta-chlor ethanes. The liquids were distilled in vacuum and were contained in Wood's tubes. Mercury arc was used as the source and the spectrum of the scattered light was taken with

a Hilger E_2 spectrograph using Ilford high speed Iso-zenith plates. The results are collected in Tables 1 to 5. Only the Raman lines excited by the incident line λ 4358.3 of mercury are given in the tables, though the complete spectrum was measured for the correct allocation of the lines. The intensity was visually estimated, taking the intensity of the strongest line as 10 and that of the line that was but just visible on the negative as 0. Where the letter d is added it denotes that the line is diffuse.

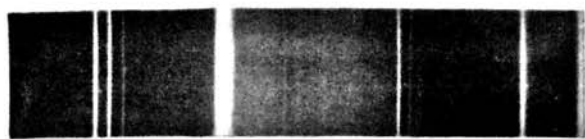
Discussion of Results.

Glycol.—The prominent Raman lines in the scattered spectrum of this liquid are the two sharp lines corresponding to the frequency shifts 871 and 1463 and the two diffuse lines corresponding to the shifts 1070 and 2909. The last of these shifts is the well-known aliphatic C-H frequency. This line extends over about 50 wave-numbers and a close examination shows it to consist of two lines, a diffuse line at λ 5002 and a comparatively sharper and fainter component at λ 4986. The incident light was filtered through a solution of quinine sulphate and the incident line λ 4047 was not sufficiently strong to excite this frequency whereby the above structure could be confirmed. In glycerine the value of this shift is almost the same, *viz.*, 2920. The two frequency shifts 1070 and 1463 are equally prominent in the spectrum of glycerine, the first being very broad and the second sharp as in glycol. The Raman line corresponding to $\Delta\nu$ 871 is very sharp in glycol while in glycerine we have, in this position, a pair of faint and diffuse lines corresponding to $\Delta\nu$ 841 and $\Delta\nu$ 923 respectively. On the other hand the strongest shift 485 of glycerine is very feeble in glycol.

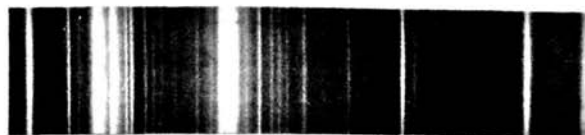
The continuous spectrum in the scattering of glycol is similar to that in glycerine¹ though the intensity is much less.

¹ Venkateswarang Ind. Jour. Phys., 3, 105, 1928.

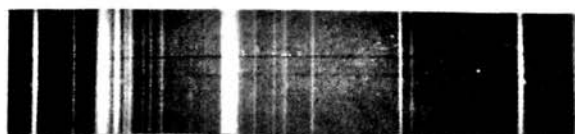
-43583



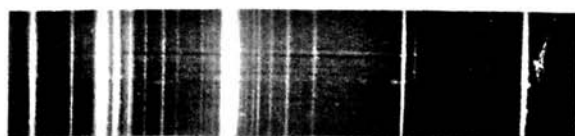
(a)



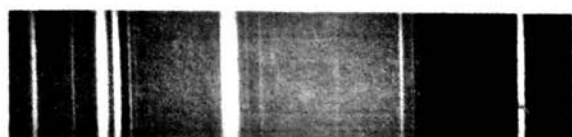
(b)



(c)



(d)



(e)

(a) Glycol, (b) Chloral, (c) Tetrachlorethane,
(d) Pentachlorethane, (e) Perchlorethylene.

This continuous spectrum is distinctly seen to consist of two portions with a clear gap between, which makes the lines appear more prominent than in glycerine. The first portion extends from λ 4358 to λ 4530 and the second portion extends from λ 4600 to λ 4800. That the continuous spectrum is a genuine phenomenon and not due to the presence of impurities is, more or less, generally recognised and also it is clear that it is not fluorescence in the ordinary sense of the term. The explanation is not quite clear but it is significant that it is not exhibited by freshly distilled liquids and becomes more and more conspicuous with increasing period of exposure to light of the mercury arc. This supports the explanation suggested by Pal and Sengupta,² viz., that it is due to some kind of photo-chemical dissociation of the molecule, the actual kinetic energy acquired by the dissociated parts being taken from the incident quantum of light.

Perchlor ethylene.—This liquid has been studied by Pringsheim and Rosen³ and the present results agree well with theirs. The Raman spectrum of the liquid is quite simple and the lines come out very pronounced though there appears a general continuous background. Many of the lines are close to the exciting line and have corresponding anti-Stokes lines also. In this respect this spectrum is comparable with the spectra of chloroform and carbon tetrachloride. The strong shift 1570 which is present also in the spectrum of $C_2H_2Cl_2$ but not in the spectra of $C_2H_2Cl_4$ and $C_2H_4Cl_2$ ⁴ is to be attributed to the C=C bond. The shift 452 is the same as the strongest shift in carbon tetrachloride.

Chloral (Tri-chlor acetaldehyde).—The scattering in this liquid is strong and the Raman lines come out prominent and free from any background effect. The intensity of the lines is comparable to that in the spectra of the simple halogen

² Pal and Sengupta: Ind. Jour. Phys., 5, 13, 1930.

³ Pringsheim and Rosen: Zeits fur. Phys., 50, 741, 1928.

Bhagvantam and Venkateswaran: Proc. Roy. Soc. A., 127, 365, 1930.

compounds like carbon tetrachloride and chloroform. It will be interesting to compare the spectrum of this liquid with that of acetaldehyde. The scattering in acetaldehyde⁵ is generally very feeble and the smallest frequency shift is 521. In chloral the three hydrogen atoms of acetaldehyde are replaced by chlorine atoms. The effect of this substitution on the Raman spectrum is at once evident from the presence of strong lines close to the exciting lines and corresponding to low frequency shifts. The anti-Stokes lines corresponding to these shifts also appear on the plate.

The effect of this substitution is again noticed in the structure of the band at 3.3μ which is due to the aliphatic C-H linkage. In chloral this has the value 3.5μ ($\Delta\nu$ 2860). Though the line is a little diffuse it does not show any structure. In acetaldehyde this band consists of three almost equally spaced components corresponding to shifts 2850, 2922 and 2997 respectively, of which the central one is the strongest and the end components rather faint. The simple structure of this aliphatic shift in chloral is easily understood as we have here only one hydrogen atom. This low component at 3.5μ is present in all the aliphatic aldehydes, but not in the aromatic aldehydes.

The strongest shift in this spectrum is $\Delta\nu$ 444 which corresponds to $\Delta\nu$ 459 of carbon tetrachloride. This frequency is so strong that the corresponding Raman line is excited by such comparatively feeble lines as λ 4916 and the companions of λ 4358 and 4047. The line corresponding to $\Delta\nu$ 256 is broad extending over about 33 wave-numbers, but terminating in quite sharp edges. The line, as a whole, is stronger on the violet side and shading off towards the red. Its anti-Stokes line is equally broad and is strong at the red end and shades off towards the violet.

Another sharp shift is the one at 1761 which is due to

⁵ Venkateswaran and Bhagavantam : Proc. Roy. Soc. A., 128, 253, 1930.

the carbonyl group C:O and is present in all aldehydes at about 1680 and in the ketones at 1710.

Tetra- and Penta-chlor ethane.—The first of these liquids has been studied by Pringsheim and Rosen (*l. c.*) and the results are in good agreement. As in the other chloro compounds the spectra of these liquids are characterised by low frequency shifts that are also strong. It will be interesting to compare the Raman spectra of the chlorine substituted products of ethane. The corresponding strong shifts in the spectra of the four compounds $C_2H_4Cl_2$, $C_2H_2Cl_4$, C_2HCl_6 and C_2Cl_6 are set forth in Table 6. It will at once be seen that as we go up the series to higher substituted compounds, the value of many of the shifts steadily increases. The shift $\Delta\nu 2980$ is about the same in the three liquids and it is also significant that this shift being due to the C-H bond is absent in C_2Cl_6 . In ethylene chloride the band corresponding to this shift consists of no less than five components (2845, 2874, 2920, 2963 and 3004) and this is evidently due to the large number of hydrogen atoms that we have in this molecule.

Attention has already been drawn by various investigators in the field to the effect of scattering on the incident lines themselves. This effect is one of broadening the lines and this has been explained as due to the purely rotation frequencies of the molecule. In the spectra of these two compounds this broadening effect is especially noticeable and also it is seen that it is quite unsymmetrical with respect to the incident line. The line $\lambda 4358$ broadens to about 80 wave-numbers on the longer wave length side, where it terminates in a definitely sharp edge, and to a much less extent on the shorter wave-length side. Of course it is difficult to judge the broadening on the latter side as we have the two close companions $\lambda 4347$ and $\lambda 4339$. But at $\lambda 4046$ this unsymmetrical broadening is quite conspicuous.

In conclusion we have great pleasure in thanking Dr. A. S. Ganesan for his help and kind interest in the work.

TABLE 1.

Glycol, $\text{CH}_2\cdot\text{OH}$ $\text{CH}_3\cdot\text{OH}$ Raman Lines excited by Hg $\lambda 4358.3$ ($\nu 22938 \text{ cm}^{-1}$)

Wave-length in vacuum A.U.	Intensity.	Wave-Number.	Wave-Number Difference.	Infra-red Wave-Length. (μ)
4992.7	2d	20029	2909	3.44
4656.6	2	21475	1463	6.83
4616.7	1d	21660	1278	7.82
4572.8	3d	21868	1070	9.34
4581.7	4	22067	871	11.5
4485.4	1	22295	643	15.6
4452.6	1	22459	479	20.9

TABLE 2.

Per-chlor ethylene, $\text{CCl}_2 : \text{CCl}_2$ Raman Lines excited by Hg $\lambda 4358.3$ ($\nu 22938 \text{ cm}^{-1}$)

Wave-length in vacuum A.U.	Intensity.	Wave-number.	Wave-number Difference.	Infra-red Wave-length (μ).
4679.9	3	21368	1570	6.37
4460.1	1	22421	517	19.3
4447.2	4	22486	452	22.1
4425.0	1	22599	339	29.5
4405.6	3	22698	240	41.7
*4322.9	3	23133	1572	
4315.6	2	23172	-234	
4277.4	1	23379	-441	

* Excited by $\lambda 4046.6$ ($\nu 24705 \text{ cm}^{-1}$).

TABLE 3.

Chloral, CCl_3CHO .Raman Lines excited by $\text{Hg}\lambda 4358.3$ ($\nu 22938 \text{ cm}^{-1}$).

Wave-length in vacuum \AA .U.	Intensity.	Wave-number.	Wave-number Difference.	Infra-red Wave length (μ).
4980.4	2d	20079	2859	3.50
4722.2	2	21177	1761	5.68
4633.3	1	21583	1355	7.38
*4579.8	4d	21835	2870	3.48
4566.5	0	21899	1039	9.62
4528.3	2d	22083	855	11.7
4508.7	3d	22204	734	13.6
1.0	4	22316	622	16.1
4446.0	10	22402	446	22.4
4420.2	2d	22623	315	31.7
4408.7	6dv	22682	6	39.1
4398.5	2d	22735	208	49.3
4320.5	1d	23145	-207	
4312.7	3dr	23187	-249	
4300.8	1d	23251	-313	
4276.7	8	23383	-445	
4244.2	0d	23562	-624	

* Excited by $\lambda 4046.6$ ($\nu 24705$).

TABLE 4.

Tetra-chlor ethane, $C_2H_2Cl_4$.Raman Lines excited by Hg λ 4358'3 (ν 22938 cm^{-1}).

Wave-length in vacuum A.U.	Intensity.	Wave-Number.	Wave-number Difference.	Infra-red wave-length (μ).
5011'9	1	19952	2986	3'34
*4605'5	3	21713	2992	3'34
4517'6	3	22136	803	12'5
4486'5	3	22289	649	15'4
4474'0	0	22351	587	17'0
4466'4	0	22389	549	18'2
4443'6	0	22504	434	23'0
4428'1	3	22583	355	28'2
4415'3	1	22649	289	34'6
4405'3	1	22700	238	42'0
4399'1	1	22763	175	57'1
4326'7	0	23112	-174	
4315'0	1	23175	-237	
4305'9	0	23224	-286	
4293'4	1	23292	-354	

* Excited by λ 4016'6 (ν 24705 cm^{-1}).

TABLE 5.

Penta-chlor ethane, C_2HCl_5 Raman Lines excited by Hg λ 4358.3 (ν 22938 cm^{-1}).

Wave-length in vacuum \AA U.	Intensity.	Wave-number.	Wave-number Difference.	Infra-red Wave-length (μ).
4644.0	0	21533	1405	7.12
*4603.4	(3)	21723	2982	3.35
4562.8	1	21916	1022	9.78
4522.3	4d	22113	825	12.1
4500.7	1	22219	719	13.9
4472.9	3	22357	581	17.2
4436.7	5	22539	399	25.1
4421.8	3	22615	323	30.9
4402.5	3	22714	224	44.6
4390.6	2	22776	162	61.7
4328.0	0	23105	-167	
4298.0	2	23267	-329	
4283.3	2	23346	-408	

* Excited by λ 4046.6 (ν 24705 cm^{-1}).

TABLE 6.

$C_2H_4Cl_2^*$	273	304	655	754	2963
$C_2H_2Cl_4$	287	354	647	801	2988
C_2HCl_5	325	400	580	825	2962
$C_2Cl_6^*$	345	434		860	

* Bhagavantam and Venkateswaran : Proc. Roy. Soc. A. 127, 366, 1930.