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plates used. Neither the prism nor the grating instrument showed any sign of splitting in the so-called doublets at 240–277 and 346–367 or the triplet 450–471–488 cm^{-1}, respectively. Only single very broad bands were observed with our instruments. It can be pointed out that large dispersion and resolving power might conceivably make any slight changes of intensity across such broad diffuse lines and tend to be less obvious than on photographs taken at lower dispersion. In view of the total situation, it seems very doubtful that these slight intensity changes across a broad band (if they exist) will have a very profound physical meaning.

The polarization method of Cleveland[4] requires critical anlysis to display some of its shortcomings. The method of excitation is essentially that described by Wood and Rank.[6] However, if improperly used, large convergence errors are introduced (later corrected empirically by comparing results with good data obtained by better methods). Douglas and Rank[7] have discussed this type of illumination in the first paragraphs of the experimental part of their paper. When the arc and scattering tube are near the paraxial foci of the cylindrical lens, the convergence error is very small, since the spherical aberration of the cylindrical lens causes most of the light from the outer zones to be ineffective in producing illumination in the scattering tube. Previously Rank[8] had measured ρ_n for a number of typical Raman lines using the photoelectric spectrograph. Intensity measurements with the photoelectric spectrograph are obtainable with many times the accuracy possible by means of photographic photometry. These results showed that, when properly used, the cylindrical lens method introduced only very small convergence errors. The $\Delta\nu = 459$ line of CCl_4 can be used as an example. Cleveland[4] gives $\rho_n = 0.072$ after empirically correcting for convergence error. Rank[8] obtained $\rho_n = 0.064$ uncorrected for convergence error. Douglas and Rank[7] obtained $\rho_n = 0.013$ by the method of polarized incident light which is free of convergence error to the third order of approximation.

The modification of the method of polarized incident light of Douglas and Rank[7] used by SK is essentially a differential method in its operation and is free of the vicissitudes of quantitative photographic photometry, convergence error, and the transmission factor of the spectrograph for the two kinds of plane polarized light. The theory demands only that one know which lines are more strongly polarized except in the case where all lines may belong to polarized classes. In this event quatitative ρ values are desirable and should be obtained by means of a good experimental method essentially free of convergence error.

ZMCD have tried to interpret the line observed at 201 cm^{-1} by SK as being a blend of 260 cm^{-1} excited by $\lambda 4347$ and 1780 cm^{-1} by $\lambda 4078$ and thus not as a real molecular frequency. It may be pointed out that $\lambda 4347$ is very weak in the low-pressure "Toronto type" lamps which are now almost universally used in the more modern laboratories. Even without the use of any filter, excitation by $\lambda 4078$ is weaker than that of $\lambda 4358$ by an order of magnitude. We have used a $NaNO_2$ filter in an efficient manner as was pointed out above in the discussion of the proper use of cylindrical lens filters in conjunction with polarization methods.

An additional argument in support of interpreting the frequency at 201 cm^{-1} as a real molecular frequency and not as a blend is that, while the frequency at 201 cm^{-1} increases in intensity with an increase of temperature, the bands at 260 and 1780 cm^{-1} decrease in intensity.

We feel that the most conspicuous features of the spectrum of oxalyl chloride are the existence of very broad bands in both the Raman and infrared spectra, and the large variation in the intensity of these bands with temperature. Unless these effects are explained, the assignments may not be correct. It would appear that there are too many Raman lines for a completely *trans*-structure which requires only six active fundamentals. There are also a few coincidences, all of which may not be accidental. The assignment made with the help of the normal coordinate treatment is not entirely satisfactory as it proposes a strongly depolarized frequency for an A_g fundamental, a strongly polarized frequency for the B_g fundamental, and considers a very strong band in the

infrared at 1058 cm^{-1} as a combination band, and a fairly strong Raman band at 189 cm^{-1} as a difference band.

We believe that further experimental work is needed to elucidate the structure of this molecule.

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Absorption of 3.3-cm Microwaves in Chloroform and Ethylene Dichloride in the Liquid State

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IT is well known that many simple molecules in the vapor state exhibit absorption bands in the microwave region owing to rotational transitions. In the case of chloroform, for instance, the rotational bands lie in the region 26 417–37 554 Mc/sec.[1,2] In the liquid state, however, these rotational transitions are damped, but the angular motion of the molecules is controlled by the coefficient of viscosity which determines the relaxation time τ of the liquid. It was observed by previous workers[3] that owing to the presence of such a relaxation time many organic liquids show anomalous absorption of radio waves of wavelengths of the order of a few meters. Recently, Sen[4] studied such absorption in many liquids in the region 250–550 Mc/sec by the optical method and observed some absorption peaks, the positions and heights of which depend on the temperature of the liquid. Kastha[5] and Ghosh[6] extended these investigations to the region 550–920 Mc/sec.

We have studied the absorption of microwaves of wavelength 3.33 cm in chloroform and ethylene chloride in the liquid state at different temperatures up to the freezing points of the liquids. A klystron oscillator of type 723 A−B was used in the range 8702–9548 Mc/sec, and the absorption at the radio waves coming out through a wave guide of cross section 2.3 cm×1 cm was studied by optical method, using another wave guide and a crystal detector. The difficulties due to formation of standing waves were avoided by shifting the position of the absorption cell placed between the two wave guides till maximum deflection in the microammeter connected in series with the crystal was observed. The cell containing the liquid was placed in baths at different temperatures, and the absorption coefficient was calculated from the deflections observed with the empty cell and the cell filled with the liquid at different temperatures placed between the two wave guides at proper positions. The values of absorption coefficient were plotted against temperatures of the cell and the temperature at which the absorption was maximum was found out.

The values of τ, the relaxation time, were calculated from the frequency of the waves and the values of dielectric constant ϵ_0 and ϵ_1 for infinite and zero frequencies respectively from Debye's theory. The value of a, the radius of the rotor, was also calculated with the help of extrapolated values of η, the coefficient of viscosity. The results are given in Table I.

TABLE I. $\omega = 56\ 540$ Mc/sec.

Liquid	T°K for max abs	ϵ_1	ϵ_0	$\tau \times 10^{11}$	$\eta \times 100$	$a \times 10^8$ cm
Chloroform	228	6.12	2.094	1.523	1.12	1.5
Ethylene-chloride	263	12.7	2.084	1.214	1.20	1.426

It can be seen from Table I that the values of a are of the order of the C−Cl distance. So the rotor is a single molecule in both cases. Evidently, in the case of $C_2H_4Cl_2$ the rotational orientation is about the C−C axis, and the high value of the dielectric constant indicates a high value of permanent electric moment. Hence the molecule in this case is of gauche-type and not of the trans-type even at −10°C. Details will be published elsewhere.

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On the Structure of Oxalyl Chloride

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THE question of rotational isomerism in oxalyl chloride has been the subject of two recent papers. Saksena and Kagarise[1] have suggested that the compound is a mixture of two forms, namely, the trans- (C_{2h}) and the cis- (C_{2v}). From temperature-intensity measurements in the Raman effect, the value of ΔH for the reaction C_{2h} oxalyl chloride→C_{2v} oxalyl chloride in the liquid state was found to be 2.8 kcal/mole. On the basis of these two forms a tentative assignment was made of all fundamental frequencies.

Ziomek, Meister, Cleveland, and Decker[2] have also studied this compound and conclude that the present evidence is greatly in favor of the trans-structure for oxalyl chloride. An assignment was made assuming the sample to be in the trans-form only. They assert that it would be desirable to investigate the temperature dependence of the infrared spectrum before concluding that the 533-cm^{-1} band is due to the cis-structure as suggested by Saksena and Kagarise.[1]

Numerous investigations[3-7] in the past have shown that one of the most convincing ways of demonstrating the phenomenon of rotational isomerism is to study the Raman or infrared spectrum of the crystalline solid. Although the various stable configurations will normally be present in both the gaseous and liquid states, it often happens that only a single isomer occurs in the crystalline solid state, and accordingly a marked simplification of the spectrum occurs upon solidification.

We have investigated the infrared spectrum of oxalyl chloride in the solid phase by means of a low-temperature cell similar to the one described by Lord, McDonald, and Miller.[8] The sample of oxalyl chloride used in this investigation was obtained from the Eastman Kodak Company and was fractionally distilled prior to being used. The spectrum was observed in the rocksalt region by means of a Perkin-Elmer 21 spectrometer, and in the 15–22μ region with the KBr prism instrument of high resolution previously described.[9] The low-temperature cell was filled and sealed, and the spectrum of the liquid at room temperature was obtained. The sample was then frozen by cooling with a dry ice-acetone mixture, and the spectrum of the crystalline solid was observed. These two spectra are shown in Fig. 1. After melting, the spectrum of the liquid was reinvestigated and found to be similar in all respects to that of the initial liquid state.

Figure 1 shows the striking changes that occur upon solidification, the outstanding ones being the complete disappearance of the two bands at 1050 and 533 cm^{-1}, respectively. According to the assignment of Saksena and Kagarise[1] these frequencies are due to the cis-form of the molecule and should disappear if only the trans-form occurs in the crystalline solid state. On the other hand, it does not appear to be possible to explain these observed temperature and solidification effects on the basis of a single molecular species of symmetry C_{2h} (trans-form) or, in fact, by any single molecular species.
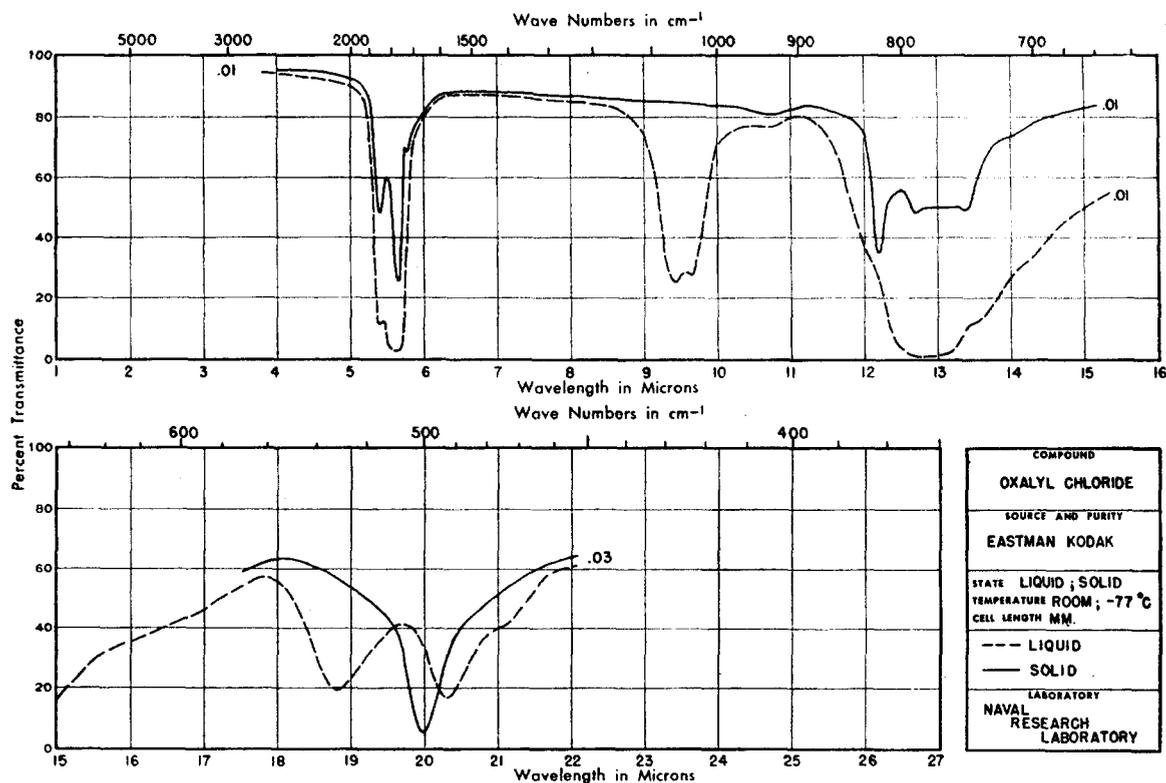

FIG. 1.