

RAMAN SPECTROSCOPY OF LOW PRESSURE GASES AND VAPORS¹

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ABSTRACT

Raman spectra of gases and vapors at pressures of a few atmospheres were obtained with a carefully diaphragmed Raman tube of large volume, irradiated by five high intensity mercury lamps with water-cooled electrodes. Frequencies and intensity contours of 32 of the 35 fundamental bands of CH_4 , CH_2Cl_2 , CH_3Cl , CHCl_3 , CCl_4 , and CH_3Br were measured. Vibrational assignments, based on the intensity contours of the bands, showed no discrepancies in previous assignments. The integrated intensities of the bands, determined on the same intensity scale for all compounds of the series, show the inadequacy of the bond polarizability theory of Raman intensities. Depolarization factors, calculated from the intensity distribution in totally symmetric bands, are somewhat greater than those measured for the liquid. Asymmetries in the Q branches of some totally symmetric bands are explained quantitatively in terms of anharmonicity and isotope effect.

INTRODUCTION

Since its discovery the Raman effect has been used, with only few exceptions, in the study of substances in the condensed phases. The lack of systematic investigations on compounds in the gaseous state is due to the experimental difficulties in obtaining satisfactory Raman spectograms when the density of the scattering substance is low. Nevertheless, it is important to study the spectra of gases at low pressures, since the present theories of molecular structure and of Raman scattering are strictly applicable only to molecules which are free from the perturbing influence of neighboring molecules. In addition, the comparison of the Raman spectra of a substance in the gaseous and the condensed phase can lead to some understanding of the effect of intermolecular forces on the vibration and rotation of molecules.

With the experimental methods developed in the present investigation reasonably complete Raman spectra can be obtained for gases at pressures of a few atmospheres. Special attention was directed to the accurate measurement of intensities since intensity data are important in the development of molecular spectroscopy. The relative integrated intensities of the bands of a given molecule and of chemically related molecules furnish data for testing theories of Raman intensities. Also, the contours of the bands of freely rotating molecules are probably better criteria for the assignment of vibrational frequencies than the frequently used depolarization factors.

EXPERIMENTAL METHODS

Since the density of a gas at a pressure of a few atmospheres is lower than the liquid density by two or three orders of magnitude, the Raman scattering of the gas is very weak compared with that of an equal volume of liquid. This reduction

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in scattered intensity must be counterbalanced by increasing the volume of the scattering medium and by increasing the radiation density of the exciting light. In addition, the intensity of the stray light entering the spectrograph must be kept low relative to the Raman intensity by careful design of the Raman tube, if satisfactory spectra are to be obtained.

The Raman tube shown in Fig. 1 is made of standard wall Pyrex tubing, 35 mm. in internal diameter, and can withstand gas pressures of at least 10 atmospheres. The illuminated portion, 60 cm. long, is separated from the window

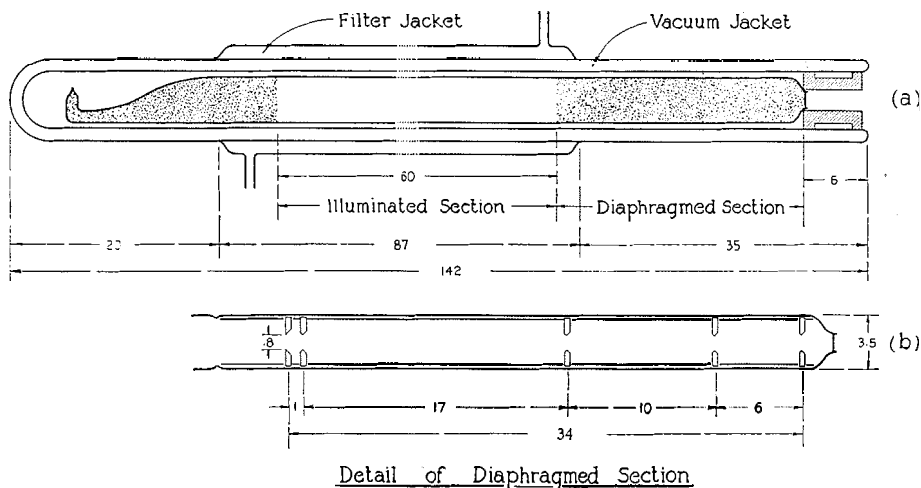


FIG. 1. Raman tube for low pressure gases.

by a diaphragmed section, and is terminated in a cone which serves as a light trap. The diaphragms, made of opaque black glass, have apertures 8 mm. in diameter with sharply beveled edges to minimize reflections. A condensing lens forms an image of the slit of the spectrograph at and within the aperture of the back diaphragm, and an image of the collimator lens at and within the diaphragm nearest the window.

The tube is placed inside a vacuum flask, 1.4 meters long, open at the window end. The temperature is controlled by a heating coil of chromel wire wound in an open coil on the tube, and is measured by thermocouples placed at five points along the tube. At an average temperature of 150°C. the greatest variation along the tube is about 8°C. A jacket, 1 cm. thick and completely covering the illuminated section of the Raman tube, is fused to the outer wall of the vacuum flask. Either water or a filter solution circulated through this jacket at a constant temperature eliminates the thermal exchange between the lamps and the Raman tube. A solution of sodium nitrite is used to isolate Hg4358A radiation from the higher frequencies in the mercury spectrum. A thickness of 1 cm. of this solution saturated at 25°C. transmits 90% of Hg4358A, but only 5% of Hg4078A and 1% of Hg4047A. For some spectra the faint mercury lines in the region of 5000A were removed by saturating the sodium nitrite solution with rhodamine-B.

It was found that cooling the electrodes of a low pressure mercury lamp permits the current, and hence the intensity, to be increased several-fold without a large increase in vapor density. Cooling is effected by circulating water through a finger which projects through the mercury pool into the vapor phase above (Fig. 2). The intensity of Hg4358A increases linearly with current up to at least 15 amperes, the normal operating current. In addition to the increased intensity this lamp has other desirable characteristics. There is no appreciable broadening of the spectral lines, since the hyperfine structures are resolvable. The ratio of line intensities to the intensity of the continuous background is higher than for uncooled lamps. The lamp is very stable in operation, and the intensity of Hg4358A is not noticeably reduced over a period of 1000 hr. The lamp is started by heating with a bunsen burner and applying a high voltage between two starting electrodes. Five lamps of the design shown in Fig. 2 were used with

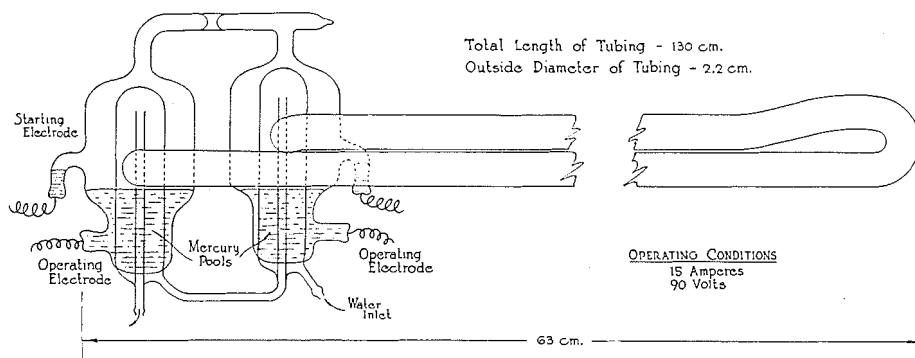


FIG. 2. High-current mercury arc with water-cooled electrodes.

the Raman tube for gases and gave a total length of discharge of about six meters. They were arranged symmetrically about the tube; thus, the transmission of the spectrograph was the same for both the isotropic and the anisotropic parts of the scattered light since both were unpolarized.

The Raman spectra were recorded photographically with a double prism glass spectrograph with two interchangeable cameras. The short camera with an F/4 lens of focal length 30 cm. gives a reciprocal linear dispersion of 225 cm.^{-1} per mm. at Hg4358A. The long camera with an F/10 lens of focal length 75 cm. gives a dispersion of 90 cm.^{-1} per mm. Antireflection coatings on the F/4 objective improved its transmission by about 30%, and reduced the stray light in the spectrograph.

The photographic plates were calibrated for intensities by replacing the slit of the spectrograph with a stepped slit and photographing the continuous spectrum of a Kipp and Zonen standard tungsten band lamp. Photographic densities were measured with a Leeds and Northrup recording microphotometer. From calibration curves determined at the wave length of each Raman band in the spectrum, the relative intensities of the bands on a given plate were evaluated from the known distribution of intensity in the spectrum of the standard lamp.

Calibration spectra were recorded on each plate with the same exposure times as the Raman spectra. Since the same optical arrangement was used for all calibration spectra, relative intensities of Raman bands on different plates and for different substances could be deduced from the known current-intensity characteristics of the standard lamp. The accuracy of such a comparison is dependent on the reproducibility of the intensity of irradiation from exposure to exposure. Relative intensities for different substances were also measured directly by mixing known amounts of the substances two at a time and photographing their superimposed Raman spectra. The relative intensities obtained by both methods were consistent, but since two photographic processes are involved in the former and only one in the latter, the relative intensities obtained by the mixture method were used to correlate the data in Tables I to VI.

The frequencies of the broad Raman bands were measured from the microphotometer trace because this method is more objective than visual measurements. To correct for nonuniformity in the pitch of the drive screw an auxiliary scanning unit was added to the microphotometer. A heavily aluminized glass plate with accurately spaced transparent rulings was attached to the plate carriage, and scanned by the image of a filament lamp. The light from this system was directed onto the phototube of the microphotometer, producing pips on the microphotometer trace spaced at intervals corresponding accurately to 0.25 mm. on the plate. Raman shifts were determined from the separations of the bands from the moderately exposed Rayleigh lines Hg4108A, Hg4916A, and Hg5026A, using the known dispersion curve of the spectrograph. An iron arc spectrum was photographed on each plate to check the constancy of the dispersion which varied slightly with temperature.

EXPERIMENTAL RESULTS

The spectra of methane, its chlorine derivatives, and methyl bromide were investigated. With the exception of methane which was taken directly from the gas cylinder, the substances were introduced into the Raman tube by a two-stage distillation. The quantity introduced was sufficient to give a maximum saturated vapor pressure of about seven atmospheres. During an exposure the Raman tube was kept at a temperature high enough to vaporize the substance completely. Thirty-two of the thirty-five fundamental bands of the molecules were recorded on Eastman 103a-O and 103a-J plates, with exposure times ranging from 1 to 24 hr.

The experimental results are listed in Tables I to VI. The Raman shift given for each band is that of the main maximum. When it is certain that a Fermi resonance is present, the maxima of both bands are given, and the resonance is indicated by a bracket. For frequencies or intensities determined from two or more plates the mean deviation is given. The related integrated intensities, i_{λ} , listed in the tables are reduced values. For the fundamentals they are the measured relative integrated intensities divided by the molar density of the vapor and multiplied by the factor $\{1 - \exp(-h\nu_{\lambda}c/kT)\}(\nu - \nu_{\lambda})^4$, where ν_{λ}

is the Raman shift, ν the frequency of the exciting light, and the other symbols have their usual meanings. Thus these values are independent of the conditions of the experiment; they are the squares of the matrix elements of the polarizability for the $v = 0$ to $v = 1$ transitions in a common arbitrary unit chosen so that the value for ν_3 of methane is 1000. For overtones and combination tones the listed values were obtained by applying the density and frequency reduction factors, but not the temperature factor.

VIBRATIONAL ANALYSIS

Since rotation must be practically unhindered at the gas pressures used the rotational structure of the rotation vibrational bands should be fully developed. For methane, some of the rotational lines were resolved; for the other compounds only the intensity distribution in the envelope of the rotational structure was measured. However, the intensity contours of the unresolved bands are very useful in the assignment of the bands to the vibrational modes of the molecule. For a totally symmetric (a_1) vibration of a symmetric top molecule the band consists of a strong sharp Q branch with rotational wings (O , P , R , and S branches). The intensity of the wings relative to the Q branch depends on the depolarization factor, and is zero for cubic symmetry. For a nontotally symmetric or a degenerate vibration all the branches have nearly equal intensities; hence the Q branch is less pronounced than for totally symmetric vibrations and, with low resolution, appears merged with the wings. For a degenerate vibration Coriolis interaction between the vibration and the free rotation can lead to a broadening of the band and a decrease in the intensity of the central maximum. For asymmetric top molecules the contours of the bands can be more complicated, but are characteristic of the modes of vibration.

The vibrational assignments, given in Tables I to VI, are based on the band contours, reproduced in Figs. 3-8. These assignments confirm in all cases those listed by Herzberg (8). A detailed discussion of each spectrum follows.

Methane (Table I, Fig. 3)

In addition to the strong bands, $\nu_1(a_1)$ and $\nu_3(f_2)$, observed by Dickinson, Dillon, and Rasetti(6) and by MacWood and Urey (10), a band was found

TABLE I
THE RAMAN SPECTRUM OF GASEOUS METHANE

Observed Raman shifts, cm^{-1}	Assignment	Reduced relative intensity, i_λ
1300 (liquid) (5)	$\nu_4(f_2)$	8
1535.4 ± 0.6	$\nu_2(e)$	160 ± 6
2582 ± 2	$2\nu_4(A_1 + E + F_2)$	—
2915.0 ± 0.6	$\nu_1(a_1)$	990 ± 20
3017.0 ± 0.6	$\nu_3(f_2)$	1000 ± 20

at $\Delta\nu = 1535 \text{ cm}^{-1}$ from Hg4358A, when Hg4047A and its companion lines were removed from the exciting light by a filter. This band, which has a

sharp Q branch with approximately one-fifth of the intensity of the band, must be assigned to the fundamental $\nu_2(e)$. Burgess (3) has recently shown that this vibration is weakly active in the infrared and that the frequency of the Q branch

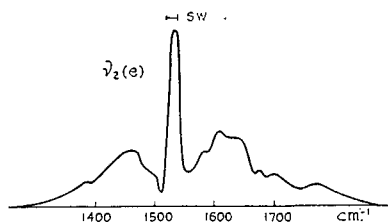


FIG. 3. The ν_2 Raman band of methane.

is 1533.6 cm^{-1} . The wings of the Raman band show features characteristic of discrete rotational structure but the resolution obtained does not warrant a detailed analysis, particularly as the structure is being reinvestigated at higher dispersion. The resolution of the individual rotation lines of $\nu_3(f_2)$ was somewhat better than that obtained by earlier workers, but the frequencies will not be given here since the band structure has recently been measured at much higher dispersion (17). The faint diffuse band with its center at 2670 cm^{-1} is probably the overtone of $2\nu_4$.

Carbon Tetrachloride (Table II, Fig. 4)

The doubly degenerate vibration ν_2 gives rise to a Raman band with a maximum at 221 cm^{-1} corresponding to the Q branch. The partially resolved

TABLE II
THE RAMAN SPECTRUM OF GASEOUS CARBON TETRACHLORIDE

Observed Raman shifts, cm^{-1}	Assignment	Reduced integrated intensity, i_λ
221 ± 2	$\nu_2(e)$	154 ± 10
310.0 ± 0.6	$\nu_4(f_2)$	214 ± 10
434 ± 1	$\left\{ \begin{array}{l} 2\nu_2(A_1) \\ \nu_1(a_1) \\ \nu_1 + \nu_4(F_2) \end{array} \right.$	—
459.0 ± 0.6		291 ± 4
756 ± 2		316 ± 6
794.3 ± 0.8	$\left\{ \begin{array}{l} \nu_3(f_2) \\ \nu_1 + \nu_4 + \nu_3(A_1 + E + F_2) \\ 2\nu_3(A_1 + E + F_2) \end{array} \right.$	34 ± 6
1557.0 ± 0.6		
1585 ± 2		

maxima at 211 and 230 cm^{-1} are at the calculated positions of the maxima in the O and S branches respectively. The maximum at 230 cm^{-1} is more intense than that at 211 cm^{-1} , showing that an underlying component is present which can be classified as the $2\nu_2(E) - \nu_2$ transition if a negative anharmonicity is assumed. The frequency of the transition, $2\nu_2(A_1) - \nu_2$, calculated from the observed frequency of $2\nu_2(A_1)$ (see below), is $434 - 221 = 213 \text{ cm}^{-1}$; thus, this component falls on the maximum in the O branch and, as expected, is weaker than $2\nu_2(E) - \nu_2$.

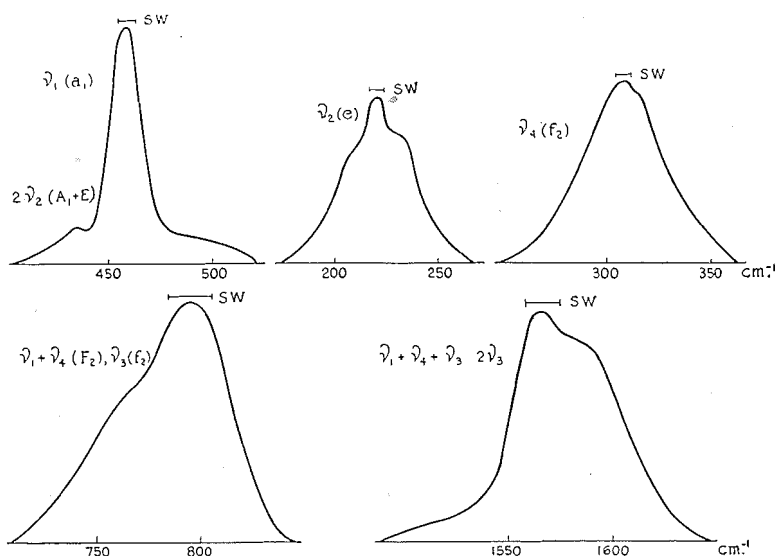


FIG. 4. Raman bands of carbon tetrachloride.*

The triply degenerate frequency ν_4 shows only a central maximum. Since there is a Coriolis interaction between the mutually degenerate modes, the resultant splitting of the rotational branches leads to an almost symmetrical contour without maxima in the wings.

The triply degenerate fundamental ν_3 has two components of unequal intensities, in agreement with the observations of Morino, Watanabe, and Mizushima (11). The positions and relative intensities of the components are qualitatively consistent with an inexact Fermi resonance between $\nu_3(f_2)$ and $\nu_1 + \nu_4(F_2)$. The small changes in frequency, chiefly in ν_3 and ν_4 , in passing from the gas to the liquid are sufficient to make the resonance almost exact in the liquid where two components of equal intensity are observed (22). The difference in the relative intensities of the two components, in the gas and the liquid confirms that a Fermi resonance is involved rather than a departure of the molecule from tetrahedral symmetry. The abnormally intense overtone of ν_3 has two components which can be classified as $\nu_1 + \nu_3 + \nu_4$ and $2\nu_3$. A third component, which was observed in the liquid (22) at 1524 cm.^{-1} and which can be assigned to $2\nu_1 + 2\nu_4$, is not prominent in the gas, because the resonance is less exact.

The totally symmetric frequency ν_1 gives a band accompanied by wings which cannot be interpreted as due to rotation. The definite maximum at 434 cm.^{-1} is undoubtedly caused by a Fermi resonance of the A_1 part of $2\nu_2$ with ν_1 . The broad wing on the high frequency side of ν_1 must be due to the transition $\nu_3 - \nu_4$ with a calculated position $794 - 310 = 484 \text{ cm.}^{-1}$. Such a component has been noted in the liquid by Rank and Van Horn (15) confirming the

*In these diagrams a common intensity scale has not been used since there is an intensity ratio of over 100 between the weakest and strongest bands.

theoretical prediction of Horiuti (9). The stronger component $(\nu_1 + \nu_4) - \nu_4$ should occur at $756 - 310 = 446 \text{ cm.}^{-1}$, but is obscured by the isotopic broadening of the main component of ν_1 . The diffuseness of $\nu_3 - \nu_4$ arises from the rotational structure characteristic of this type of vibration; also, weaker components due to transitions between higher levels in Fermi resonance may be present.

Methyl Chloride (Table III, Fig. 5)

Symmetric top molecules such as methyl chloride, methyl bromide, and chloroform have three totally symmetric (a_1) and three doubly degenerate (e) vibrations.

TABLE III
THE RAMAN SPECTRUM OF GASEOUS METHYL CHLORIDE

Observed Raman shifts, cm.^{-1}	Assignment	Reduced integrated intensity, i_λ
725.3 ± 0.6	$\nu_3(a_1)$	126 ± 4
1012 ± 2	$\nu_6(e)$	11 ± 4
1370 (liquid) (20)	$\nu_2(a_1)$	
1473 ± 2	$\nu_5(e)$	55 ± 4
2874 ± 2	$\{ 2\nu_5(A_1)$	28 ± 3
2965.5 ± 0.6	$\nu_1(a_1)$	221 ± 4
3043 ± 1	$\nu_4(e)$	189 ± 6

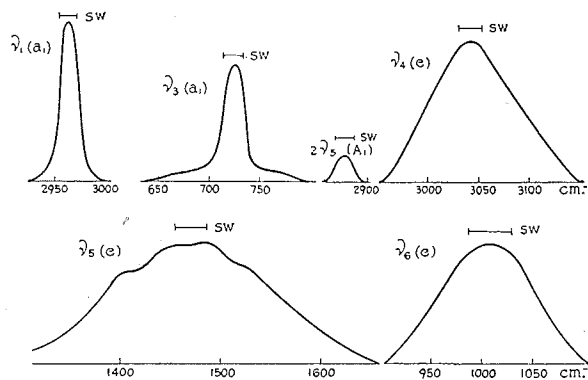


FIG. 5. Raman bands of methyl chloride.

Five fundamentals and one overtone ($2\nu_5$) were observed for methyl chloride. Two of the totally symmetric vibrations, ν_1 and ν_3 , are immediately identified by the strong Q branch and the weak rotational wings characteristic of such vibrations. The low intensity of the wings for ν_1 indicates that the line is highly polarized. The frequency, 725.3 cm.^{-1} , of ν_3 differs from the infrared value, 732 cm.^{-1} (2), by more than experimental error, but agrees with the value given by Nielsen and Ward (12), who observed the ν_1 and ν_3 bands in the Raman

spectrum of the gas. The third totally symmetric vibration ν_3 , at 1355 cm.^{-1} according to infrared data, must have a very low intensity since it was not observed.

The doubly degenerate bands ν_4 and ν_6 have contours resembling Gaussian error curves as predicted by Teller (18) from the theory of Coriolis interaction. The ν_6 band is extremely weak and the contour given in Fig. 5 cannot be considered very accurate. The ν_5 band is broader and shows four maxima; these features are probably due to the larger value of ζ for this vibration. The center of the band, taken midway between the two central maxima, is about 18 cm.^{-1} higher than the origin of the infrared band. This illustrates the fact that, unless at least partial resolution of the band is achieved, the vibrational frequency corresponding to such broad bands cannot be found accurately.

Methyl Bromide (Table IV, Fig. 6)

All six fundamental frequencies and one overtone ($2\nu_5$) were observed. The doubly degenerate band, ν_6 , is broad and extremely weak. The totally symmetric

TABLE IV
THE RAMAN SPECTRUM OF GASEOUS METHYL BROMIDE

Observed Raman shifts, cm.^{-1}	Assignment	Reduced integrated intensity, i_λ
609 ± 1	$\nu_3(a_1)$	188 ± 2
956 ± 5	$\nu_6(e)$	~ 0.4
1309 ± 1	$\nu_2(a_1)$	11 ± 2
1456 ± 4	$\nu_5(e)$	57 ± 2
2862 ± 2	$\{ 2\nu_5(A_1)$	27 ± 4
2972 ± 1	$\nu_1(a_1)$	172 ± 4
3068 ± 4	$\nu_4(e)$	133 ± 9

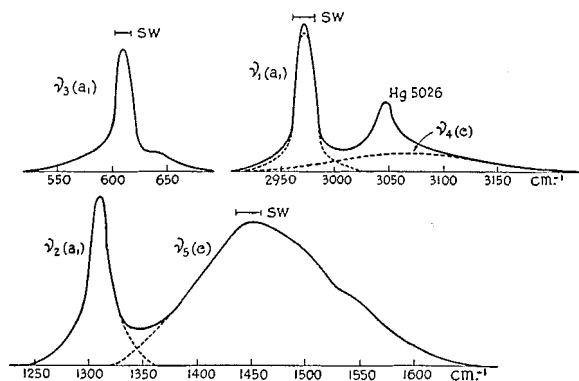


FIG. 6. Raman bands of methyl bromide.

and doubly degenerate bands can be distinguished immediately by their contours. The frequencies of the totally symmetric bands are in good agreement with

infrared values, but the frequencies of the central maxima of the degenerate bands are all somewhat higher than the infrared values.

Chloroform (Table V, Fig. 7)

All six fundamental bands and one overtone ($2\nu_5$) band were observed in chloroform. Except for ν_3 and ν_6 the frequencies agree well with those obtained

TABLE V
THE RAMAN SPECTRUM OF GASEOUS CHLOROFORM

Observed Raman shifts, cm.^{-1}	Assignment	Reduced integrated intensity, i_λ
255.5 ± 0.5	$\nu_6(e)$	225 ± 8
364.8 ± 0.5	$\nu_3(a_1)$	168 ± 6
671.1 ± 0.6	$\nu_2(a_1)$	174 ± 2
767.7 ± 0.6	$\nu_5(e)$	155 ± 2
1218 ± 3	$\nu_4(e)$	46 ± 2
1527 ± 2	$2\nu_5(A_1 + E)$	15 ± 2
3032.0 ± 0.5	$\nu_1(a_1)$	157 ± 6

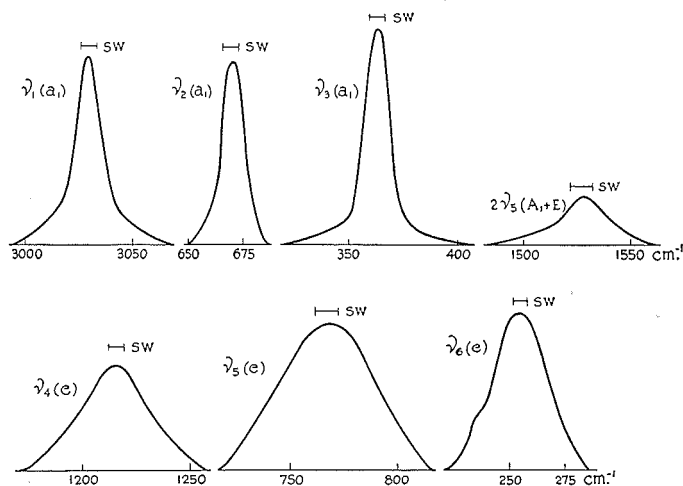


FIG. 7. Raman bands of chloroform.

by Nielsen and Ward (12), who measured all the fundamentals in the vapor. The assignment of the bands is immediately evident from the intensity contours and the frequencies. The low frequency bands, ν_2 and ν_6 , are asymmetric; the low frequency component of ν_6 is unquestionably real, and is possibly $3\nu_6 - 2\nu_5$ shifted to lower frequency as a consequence of resonance degeneracy with ν_5 .

Methylene Chloride (Table VI, Fig. 8) -

If methylene chloride has a tetrahedral structure of point group C_{2v} there should be nine fundamentals, of which four are A_1 species, one A_2 , two B_1 , and two B_2 . The contours of the totally symmetric bands for the asymmetric top

TABLE VI
 THE RAMAN SPECTRUM OF GASEOUS METHYLENE CHLORIDE

Observed Raman shifts, cm.^{-1}	Assignment	Reduced integrated intensity, i_λ
281.5 ± 0.6	$\nu_4(a_1)$	69 ± 2
712.9 ± 0.6	$\nu_3(a_1)$	137 ± 4
748 ± 2	$\nu_9(b_2)$	38 ± 6
~ 893	$\nu_7(b_1)$	—
1153 ± 2	$\nu_5(a_2)$	7 ± 2
1255 (liquid) (21)	$\nu_8(b_2)$	—
1430.1 ± 0.8	$\nu_2(a_1)$	22 ± 2
1493 ± 2	$2\nu_9(A_1)$	—
2854 ± 2	$2\nu_2(A_1)$	5 ± 2
2995.7 ± 0.4	$\nu_1(a_1)$	108 ± 4
3040 ± 2	$\nu_6(b_1)$	98 ± 6

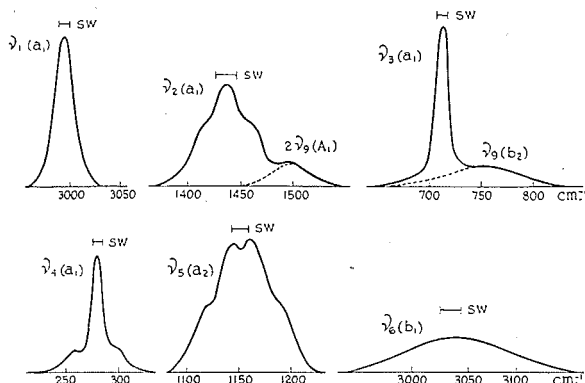


FIG. 8. Raman bands of methylene chloride.

should show a strong Q branch with rotational wings, just as for the symmetric top. There is therefore no doubt that the Raman bands at 2996, 1430, 713, and 281 cm.^{-1} correspond to the A_1 type vibrations. Of particular interest is the contour of $\nu_2(a_1)$ at 1430 cm.^{-1} . In the liquid this line has a depolarization factor of $6/7$ (4), which has led to some doubt as to the assignment of the band. In the gas, however, the band has the characteristic appearance of an a_1 vibration; the comparatively high intensity in the wings shows that the depolarization factor is in fact large.

The contour of the band at 1153 cm.^{-1} is remarkable in that there are four maxima with a central minimum; the intensity distribution resembles that of a type B infrared band, the envelope of which has been calculated by Badger and Zumwalt (1); the Q lines form two maxima on either side and fairly close to the band origin. A consideration of the structure of Raman bands for the asymmetric top shows that this distribution of intensity should occur for the torsional oscillation (type A_2) for the C_{2v} point group. The band can therefore be unambiguously assigned to $\nu_5(a_2)$.

The bands at 3040 and 748 cm^{-1} are broad and flat with a single maximum. It is clear that they correspond to the antisymmetric species B_1 or B_2 ; they are assigned to the frequencies $\nu_6(b_1)$ and $\nu_9(b_2)$ respectively. A very weak band at 893 cm^{-1} is assigned to $\nu_7(b_1)$. The band found in the liquid at 1255 cm^{-1} (21) and interpreted as $\nu_8(b_2)$ was not observed in the vapor.

DISCUSSION OF THE RELATIVE INTENSITIES

The polarizability theory of the Raman effect, as developed by Placzek (13), shows that the intensity of a fundamental Raman band can be expressed:

$$I_\lambda \propto N(\nu - \nu_\lambda)^4 (45\alpha'^2 + 13\gamma'^2) (Q_\lambda)_0^2 / \{1 - \exp(-h\nu_\lambda c/kT)\},$$

where α' and γ'^2 are, respectively, the average value and the anisotropy of the derivative of the polarizability with respect to the normal coordinate Q , $(Q)_0 = \sqrt{h/8\pi^2c\nu_\lambda}$, and N is the number of scattering molecules. It is assumed that the incident light is unpolarized and confined to directions perpendicular to the direction of observation. The frequency factor $(\nu - \nu_\lambda)^4$ and the temperature factor depend on the conditions of the experiment and can be eliminated from the experimental intensities. Furthermore, when intensities from different compounds are compared using the same experimental arrangement, they can be reduced to *relative intensities of scattering per molecule*, i_λ , by dividing the experimental intensities by a factor proportional to the number of molecules per unit volume. Then one can write

$$i_\lambda = C(45\alpha'^2 + 13\gamma'^2)$$

where C is a constant for all bands. The relative intensities for the fundamental bands in Tables I to VI have been reduced in this way.

From considerations of symmetry it is possible to state whether the constants α' and γ'^2 have values different from zero for a vibration of a given symmetry species; and thus to make predictions concerning the activity of the vibration in Raman effect and the depolarization of the band. In general, however, it is not possible to evaluate α' or γ'^2 in terms of more fundamental quantities without the use of an oversimplified model. Therefore, the only expedient is a semi-empirical approach such as that of Wolkenstein (23), based on bond polarizabilities.

Experimental Test of the Bond Polarizability Theory of Raman Intensities

In Wolkenstein's theory, it is assumed that (a) one of the principal axes of the polarizability of the bond coincides with the direction of the bond and the other two principal polarizabilities are equal for a bond of the single type, (b) the bond polarizabilities change when the bond length changes, and (c) the bond polarizabilities are independent of changes in the bond angles. The polarizability of a single bond XY can therefore be characterized by four constants—the principal polarizabilities $(\alpha_{XY})_1$ along the bond and $(\alpha_{XY})_2$ perpendicular to the bond, and the rates of change of these, $(\alpha'_{XY})_1$ and $(\alpha'_{XY})_2$, with respect to the bond length. When the geometrical and dynamic problem of calculating the intensities of the Raman bands of a given molecule is solved, it is

found that only certain combinations of the bond polarizabilities and their derivatives occur in the expressions for the intensities. These are:

$\gamma^2_{XY} \equiv (a_1 - a_2)^2_{XY}$, the anisotropy of the bond polarizability,

$a'_{XY} \equiv (1/3)(a'_1 + 2a'_2)_{XY}$, the mean rate of change of the bond polarizability, and

$\gamma'^2_{XY} \equiv (a'_1 - a'_2)^2_{XY}$, the anisotropy of the rate of change of the bond polarizability.

A fourth constant, $a_{XY} \equiv (1/3)(a_1 + 2a_2)$, the mean bond polarizability, is not involved in Raman intensities.

Wolkenstein, using this concept of bond polarizabilities and assuming valence force fields, derived formulae for the relative intensities and depolarizations of the Raman bands of the linear and the bent symmetrical molecule, XY_2 , and the tetrahedral molecule, XY_4 . However, the intensity data available were insufficient for an adequate test of the theory.

Since in methane and its chlorine derivatives only CH and CCl bonds occur, the relative intensities and depolarizations of the Raman bands depend on only six constants γ^2_{CH} , a'_{CH} , γ'^2_{CH} , γ^2_{CCl} , a'_{CCl} , and γ'^2_{CCl} . In principle, these constants can be evaluated (apart from ambiguities regarding sign) from six of the 28 measured intensities for this series of compounds, and the validity of the theory tested by calculating the remaining intensities and depolarization factors. In practice, however, the problem is not simple since force constants enter into the intensity formulae for those vibrations of the molecule for which there are other vibrations of the same symmetry species. It has been stressed recently by various authors (e.g. Glockler and Tung (7), Torkington (19)) that a unique set of force constants cannot be obtained from the observed vibrational frequencies of a molecule, because the most general force field, even when a high degree of symmetry is present, involves more constants than there are frequencies. Consequently, if the calculated intensities for such vibrations do not agree with the observed, one does not know whether the theory is invalid or the force field is inadequate. It is found, moreover, that the calculated intensities are very sensitive to the force constants. However, when a vibration is the only one of its symmetry species present in the molecule, the force constants do not appear explicitly in the expression for the intensity; they enter implicitly through the frequency, ν_λ , which can be measured experimentally. Thus, these vibrations can be used to check the validity of the theory without a detailed knowledge of the force field.

A direct test of the theory can be carried out by considering $\nu_2(e)$ of CH_4 and $\nu_5(a_2)$ of CH_2Cl_2 . The normal mode $\nu_2(e)$ of CH_4 is the superposition of two modes, ν_{2a} and ν_{2b} , where ν_{2b} is the torsional oscillation of the two CH_2 groups relative to one another and ν_{2a} is the deformation vibration orthogonal to this. Since there appear to be errors in some of the formulae given by Wolkenstein for tetrahedral molecules, we have calculated the intensity of $\nu_2(e)$ from first principles. The calculation gives

$$i(\nu_{2a}, \text{CH}_4) = i(\nu_{2b}, \text{CH}_4) = 104\gamma_{\text{CH}}^2/m_1l_1^2\nu_2;$$

thus,

$$i(\nu_2, \text{CH}_4) = 208\gamma_{\text{CH}}^2/m_1l_1^2\nu_2,$$

in which m_1 is the mass of the H-atom and l_1 is the length of the CH bond.

The intensity of $\nu_5(a_2)$, the torsional vibration of CH_2Cl_2 , can also be calculated easily. The result is

$$i(\nu_5, \text{CH}_2\text{Cl}_2) = 52(\gamma_{\text{CH}} + K\gamma_{\text{Cl}})^2/(m_1l_1^2 + K^2m_2l_2^2)\nu_5,$$

in which m_2 is the mass of the Cl atom, l_2 the length of the CCl bond, and $K = m_1l_1^2/m_2l_2^2$. Since K is very small (~ 0.01), the expression reduces to

$$i(\nu_5, \text{CH}_2\text{Cl}_2) = 52\gamma_{\text{CH}}^2/m_1l_1^2\nu_5.$$

The calculated intensity ratio of these two bands is

$$I(\nu_2, \text{CH}_4)/I(\nu_5, \text{CH}_2\text{Cl}_2) = 4(\nu_5/\nu_2) = 3.0.$$

The measured ratio is 23 (from Tables I and VI). Although the measured ratio has a large percentage error arising mainly from the error in the intensity of the very faint ν_5 band of CH_2Cl_2 , there is no doubt that it is greater than the calculated value by a factor of 5 to 10. It is therefore concluded that the anisotropy of the bond polarizability is not a constant of the bond.

A second simple test of the bond polarizability theory can be carried out for both CH and CCl bonds by considering the relative intensities of the a_1 vibration of XY_4 , the b vibration of the XY_2 group in Z_2XY_2 , and the XY stretching vibration in Z_3XY . For the CH bond the series used is CH_4 , CH_2Cl_2 , and CHCl_3 ; for the CCl bond, CCl_4 , CH_2Cl_2 , and CH_3Cl . The intensity formulae are (23):

$$i(\nu_{a_1}, \text{XY}_4) = (180/\nu_{a_1})(1/m_Y)\alpha_{\text{XY}}'^2,$$

$$i(\nu_b, \text{YX}_2 \text{ in } \text{Z}_2\text{XY}_2) = (14/\nu_b)(1/m_Y + 4/3m_{\text{XZ}})\gamma_{\text{XY}}'^2,$$

$$i(\nu_{a_1}, \text{XY in } \text{Z}_3\text{XY}) = (1/\nu_{a_1})(1/m_Y + 1/m_{\text{XZ}})(45\alpha_{\text{XY}}'^2 + 13\gamma_{\text{XY}}'^2).$$

The depolarization factor of ν_{a_1} (XY in Z_3XY) is given by:

$$\rho = \frac{6\gamma_{\text{XY}}'^2}{45\alpha_{\text{XY}}'^2 + 7\gamma_{\text{XY}}'^2}.$$

For the CH bond, $\nu_1(a_1)$ of CH_4 and $\nu_6(b_1)$ of CH_2Cl_2 were used for the calculation of the constants $\alpha_{\text{CH}}'^2$ and $\gamma_{\text{CH}}'^2$, and $\nu_1(a_1)$ of CHCl_3 as the check. The results are given in Table VII. The agreement is seen to be poor, and the conclusion is reached that the rate of change of polarizability is strongly

TABLE VII

	Calculated	Experimental
$i(\nu_1, \text{CHCl}_3)$ $\rho(\nu_1, \text{CHCl}_3)$	314 0.12	157 0.24(4)

dependent on the nature of the neighboring bonds. To reproduce the experimental values above α'^2_{CH} , calculated from ν_1 of CH_4 , would have to be reduced by a factor of two.

A similar calculation for the CCl bond was made using $\nu_1(a_1)$ of CCl_4 and $\nu_9(b_2)$ of CH_2Cl_2 to determine α'^2_{CCl} and γ'^2_{CCl} , and using $\nu_3(a_1)$ of CH_3Cl as a check (Table VIII). In this case the agreement for i is better than for the CH bond,

TABLE VIII

	Calculated	Experimental
$i(\nu_3, \text{CH}_3\text{Cl})$ $\rho(\nu_3, \text{CH}_3\text{Cl})$	177 0.062	126 0.15(4)

but is nevertheless not good. Agreement can be obtained by assuming that α'^2_{CCl} in CH_3Cl is smaller than α'^2_{CCl} in CCl_4 by a factor of 0.72. This also gives a slight improvement in the agreement for ρ .

The inadequacy of the bond polarizability theory is also apparent from a comparison of the intensities of the bands characteristic of the CH_3 group in methyl chloride and methyl bromide. Although the intensities of the deformation frequency, $\nu_5(e)$, are almost the same in the two compounds, those of the stretching frequencies, $\nu_1(a_1)$ and $\nu_4(e)$, in CH_3Cl are 28% and 42% higher, respectively, than in CH_3Br . The frequencies, on the other hand, show changes of less than 1%. Even more striking is the difference in the intensities of the symmetrical deformation vibration, $\nu_2(a_1)$, of the CH_3 group in these two molecules; in gaseous methyl chloride the band could not be detected, whereas in methyl bromide it was easily recorded. In these cases, the intensity of the band is therefore much more dependent on the types of the neighboring bonds than is the frequency. If a comprehensive theory of Raman intensities can be developed, experimental intensities can perhaps be used along with the frequencies in determining a unique set of force constants for molecules.

Total Intensities of Vibrational Raman Scattering

The total intensity of the vibrational Raman scattering, $\sum i_\lambda$, is plotted in Fig. 9 for each molecule of the series. The high value of the total intensity in methane is noteworthy; this intensity is concentrated in the ν_1 and ν_3 bands, which are more than three times as intense as any other band in this group of compounds. In proceeding along the series from methane to carbon tetrachloride, the total intensity falls to a minimum for methylene chloride and then rises

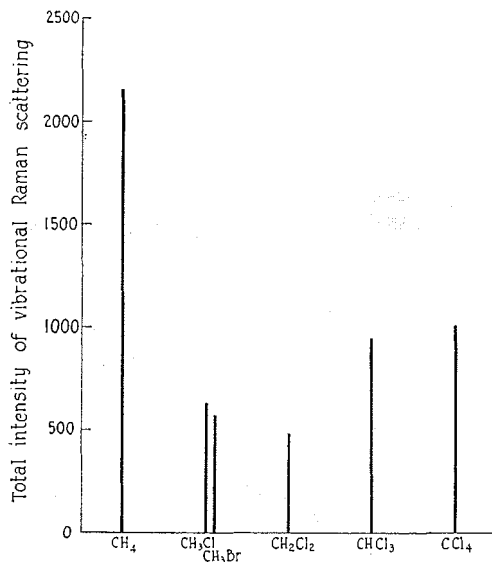


FIG. 9. Comparison of total intensities of vibrational Raman scattering.

again. There is therefore a correlation of the total intensity with the degree of symmetry of the molecule; with decreasing symmetry the total intensity decreases.

INTENSITY DISTRIBUTION IN TOTALLY SYMMETRIC RAMAN BANDS OF SYMMETRICAL TOP MOLECULES

For totally symmetrical vibrations of freely rotating molecules the division of intensity between the five branches of the band is related to the value of α'^2/γ'^2 and hence to the value of ρ . The isotropic (polarized) scattering which depends on α'^2 is all contained in the Q branch, whereas the anisotropic (depolarized) scattering which depends on γ'^2 is distributed throughout all five branches. For transverse observation the division of intensity is as follows:

$$i_Q \propto (45\alpha'^2 + 13x\gamma'^2),$$

$$i_{OPRS} \propto 13(1-x)\gamma'^2,$$

$$i_{total} \propto (45\alpha'^2 + 13\gamma'^2),$$

where x depends on the ratio of the moments of inertia and can be found from curves, valid for $B \ll kT$, given by Placzek and Teller (14). If I_Q/I_{OPRS} has been obtained experimentally, α'^2/γ'^2 and ρ can be evaluated.

The intensity distributions in the ν_3 bands of CH_3Cl and CH_3Br were carefully measured and used to determine α'^2/γ'^2 . The theoretical distribution in the wings was obtained from curves of Placzek and Teller, using the appropriate values of B and kT . The theoretical distribution was then modified for the finite slit width and matched to the experiment contour by adjusting the intensity

scale factor. The extent and general shape of the wings agreed very well with the theoretical curve, as shown for CH_3Br in Fig. 10. The contour of the Q branch

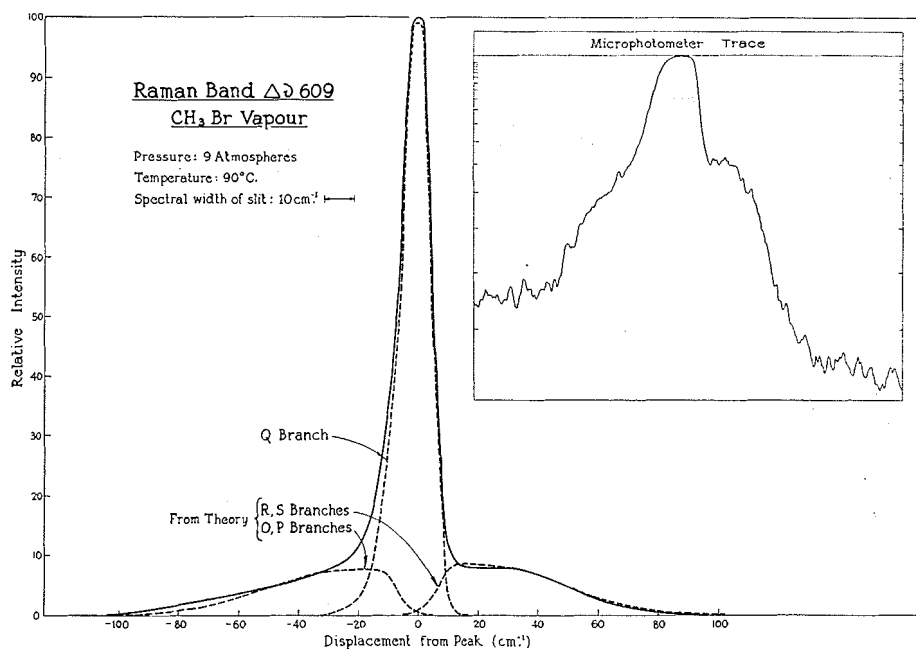


FIG. 10. Intensity distribution in a totally symmetric Raman band (ν_3 band of methyl bromide).

was obtained by subtracting the theoretical curves for the wings from the experimental contour. The values of α'^2/γ'^2 and ρ , calculated by the method outlined, are given in Table IX.

TABLE IX
DEPOLARIZATION FACTORS FOR TOTALLY SYMMETRICAL RAMAN BANDS

Raman band	I_Q/I_{OPRS} , experimental	α'^2/γ'^2	ρ (vapor), calculated from I_Q/I_{OPRS}	ρ (liquid), experimental (4)
ν_3 of CH_3Br	1.6	0.33	0.28	0.20
ν_3 of CH_3Cl	2.2	0.48	0.21	0.15

The formulae used for the evaluation of ρ are strictly valid only for transverse observation, but in our experiments no attempt was made to prevent oblique rays from entering the scattering medium. Oblique rays increase the observed isotropic intensity over the anisotropic, since the scattering in the forward or backward direction is proportional to $90\alpha'^2 + 14\gamma'^2$ compared with $45\alpha'^2 + 13\gamma'^2$ in the transverse direction. The ρ values obtained by the above procedure are therefore lower than the actual values. It is noteworthy that the ρ values measured by Cabannes and Rousset (4) for the liquid are still lower. The

probable explanation is that the ρ values of Cabannes and Rousset refer essentially to the Q branch. Even though molecular rotation in the liquid is hindered to a large extent, some of the anisotropic scattering falls in the wings of the line and is not included in the depolarization measurement unless a very wide slit is used.

The effect of oblique rays on the ρ values cannot be large, since their intensity is greatly reduced by the inverse square law and reflection losses. This conclusion is substantiated by the fact that the ρ values, representing lower limits of the actual values for the vapor, are nevertheless higher than the values for the liquid. Thus the use of the formulae for transverse observation in the calculations given in the discussion of relative intensities is justified.

STRUCTURE OF THE Q BRANCHES OF THE ν_3 BANDS OF CH_2Cl AND CH_3Br

Even with a comparatively wide slit the Q branch of the ν_3 bands in CH_3Br and CH_2Cl show distinct asymmetry. Accurate intensity contours for the Q branches of these bands, obtained by using a narrow slit (3 cm.^{-1}) and the fine-grained Ilford Special Lantern plates, are reproduced in Figs. 11 and 12. The rotational wings are suppressed because of the small slit width.

The obvious causes of a marked asymmetry of the Q branch are: (a) transitions from excited vibration levels giving rise to components shifted by anharmonicity,

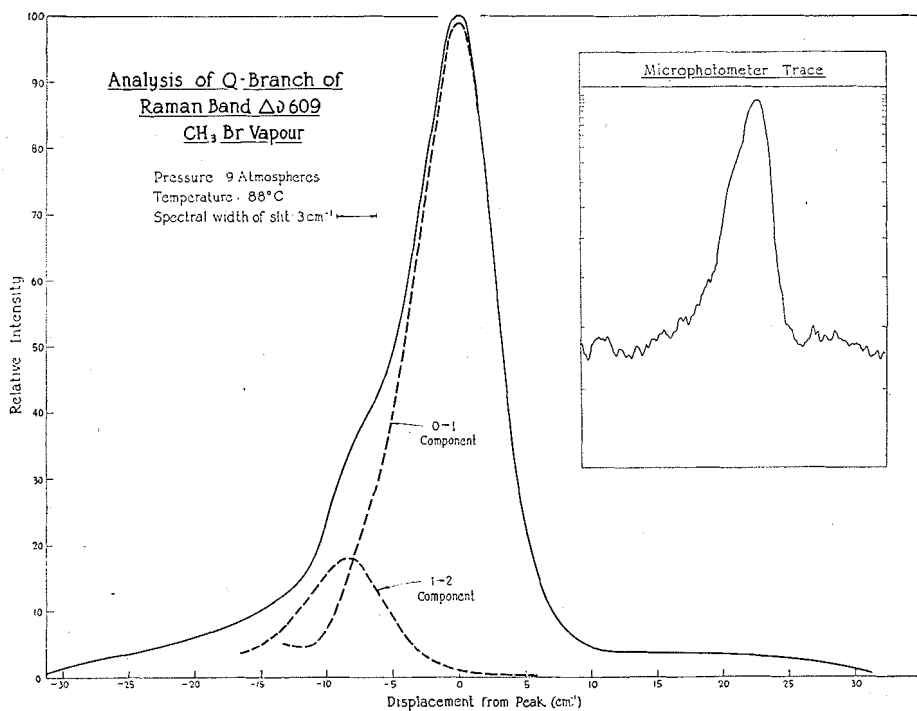


FIG. 11. Intensity contour of the Q branch of the ν_3 band of methyl bromide.

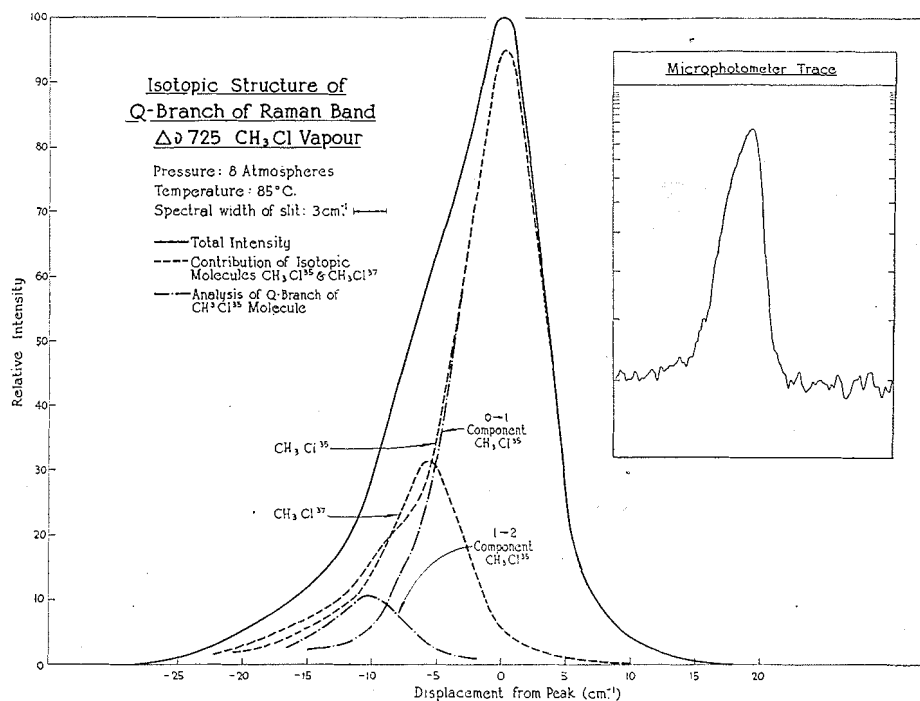


FIG. 12. Intensity contour of the Q branch of the ν_3 band of methyl chloride.

and (b) the presence of two or more isotopic forms of the molecule. Both effects can be calculated approximately for the ν_3 vibration since it is the characteristic vibration of the substituted bond and can be treated in a diatomic approximation.

For CH_3Br the effect of anharmonicity alone needs to be considered. The only transition from an excited vibrational state having an appreciable intensity is the $2 \leftarrow 1$ transition; it gives a component shifted towards lower frequencies by $2x_e\nu_3$ from the $1 \leftarrow 0$ component. The anharmonicity constant, x_e , can be calculated approximately from the dissociation energy, D , of the C Br bond by the formula $x_e = \nu_3/4D$. The ratio of the intensities of the two components is given by $I_{2 \leftarrow 1}/I_{1 \leftarrow 0} = 2 \exp(-h\nu_3/kT)$. The shift calculated from $D = 2.63$ ev. (16) is 8.3 cm^{-1} , and the intensity ratio for the temperature of the vapor in the experiment is 0.2.

The experimental contour was analyzed by a graphical method. The high frequency side of the band contains a negligible intensity contribution from the $2 \leftarrow 1$ transition. Therefore, by taking the ordinates of the $1 \leftarrow 0$ component beginning at the high frequency side, and plotting a corresponding ordinate reduced by the factor 0.18 and shifted 8.3 cm^{-1} towards lower frequencies, the intensity contour was separated into two parts. The components resulting from this analysis are approximately symmetrical, showing that the asymmetry of the Q branch in this case is due mainly to anharmonicity.

For CH_3Cl the chlorine isotope effect must also be considered. The line of the molecule containing the heavier isotope is shifted towards lower frequencies by the amount, $\nu_3(1 - \mu/\mu_i)$, where μ and μ_i are respectively the reduced masses in a diatomic approximation of $\text{CH}_3 - \text{Cl}^{35}$ and $\text{CH}_3 - \text{Cl}^{37}$. The calculated shift is 5.8 cm.^{-1} , and the intensity ratio of the components is 3.06:1, the relative abundance of the chlorine isotopes. The analyses of the experimental intensity curve gave two components, still quite asymmetric, as shown in Fig. 12. Calculations for the anharmonicity predict a shift of 10.5 cm.^{-1} and an intensity of 0.11 for the $2 \leftarrow 1$ component relative to the $1 \leftarrow 0$ component. An analysis of the $\text{CH}_3\text{Cl}^{35}$ component with these data gave two symmetrical components. The asymmetry of the ν_3 band in CH_3Cl is thus explained.

For both molecules the contour of the Q branch after correction for anharmonicity and isotope effect still shows a half width of 7 cm.^{-1} . Since the exciting line is very narrow and the spectral slit width was only 3 cm.^{-1} , the Q branch must have an intrinsic half width of 5 to 6 cm.^{-1} . This half width is probably due to interaction between vibration and rotation, since it has been shown recently that isotropic Raman scattering is not broadened to any extent by collisions (5).

REFERENCES

1. BADGER, R. M. and ZUMWALT, L. R. *J. Chem. Phys.* 6: 711. 1938.
2. BENNETT, W. H. and MEYER, C. F. *Phys. Rev.* 32: 888. 1928.
3. BURGESS, J. S. *Phys. Rev.* 76: 302. 1949.
4. CABANNES, J. and ROUSSET, A. *Ann. phys.* 19: 229. 1933.
5. CRAWFORD, M. F., WELSH, H. L., and HARROLD, J. H. *Can. J. Phys.* 30: 81. 1952.
6. DICKINSON, R. G., DILLON, R. T., and RASETTI, F. *Phys. Rev.* 34: 582. 1929.
7. GLOCKLER, G. and TUNG, J. *J. Chem. Phys.* 13: 388. 1945.
8. HERZBERG, G. *Molecular spectra and molecular structure. II. Infrared and Raman spectra of polyatomic molecules.* D. Van Nostrand Company, Inc., New York. 1945.
9. HORIUTI, J. *Z. Physik* 84: 380. 1933.
10. MACWOOD, G. E. and UREY, H. C. *J. Chem. Phys.* 4: 402. 1936.
11. MORINO, V., WATANABE, I., and MIZUSHIMA, S. *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, 39: 348. 1942.
12. NIELSEN, J. R. and WARD, N. E. *J. Chem. Phys.* 5: 201. 1937.
13. PLACZEK, G. *Marx, Handb. d. Radiologie VI(2).* (Akademische Verlagsgesellschaft m.b.H., Leipzig, 1934).
14. PLACZEK, G. and TELLER, E. *Z. Physik* 81: 209. 1933.
15. RANK, D. H. and VAN HORN, J. A. *J. Optical Soc. Am.* 36: 454. 1946.
16. SAMUEL, R. *Revs. Modern Phys.* 18: 103. 1946.
17. STOICHEFF, B. P., CUMMING, C., ST. JOHN, G. E., and WELSH, H. L. *Phys. Rev.* 84: 592. 1951.
18. TELLER, E. *Hand- und Jahrb. d. chem. phys.* 9, II: 43. 1934.
19. TORKINGTON, P. *J. Chem. Phys.* 17: 357. 1949.
20. WAGNER, J. *Z. physik. Chem., B*, 40: 36. 1938.
21. WAGNER, J. *Z. physik. Chem., B*, 45: 69. 1939.
22. WELSH, H. L., CRAWFORD, M. F., and SCOTT, G. D. *J. Chem. Phys.* 16: 97. 1948.
23. WOLKENSTEIN, M. W. *J. Phys. (U.S.S.R.)*, 5: 185. 1941.