InfraRed Spectrum of Polyatomic Molecules XVI. Methyld 3Chloride and Methyld 3 Bromide

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Infra-Red Spectrum of Polyatomic Molecules

XVI. Methyl-d_3-Chloride and Methyl-d_3-Bromide

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Methyl-d_3-chloride and methyl-d_3-bromide have been synthesized, their infra-red spectrum in the range from 2.8 to 18μ measured, and a complete assignment of the fundamental frequencies has been given. A modified valence-type potential function including two interaction terms fits the fundamental frequencies of the four molecules CH_3Cl, CD_3Cl, CH_3Br, and CD_3Br to within one percent.

IN connection with the synthesis of methyl-d_3-alcohol-d the deutero-methyl halides were prepared. The ordinary halides and related compounds have been previously thoroughly investigated experimentally as well as theoretically. It was therefore considered of interest to see what agreement could be obtained between theory and experiment for the isotopic molecules.

EXPERIMENTAL PART

The infra-red spectrometer used has been described previously.[1] Fluorite, rocksalt, and potassium bromide prisms were used in the appropriate spectral regions. Glass tubes 30 cm long and 4.4 cm or 2.5 cm in diameter with cleaved rocksalt windows, sealed on with Duco cement or Apiezon wax, were used as absorption cells. For some of the experiments the rocksalt windows had been polished, thus increasing their transmission considerably (*ca.* 25 percent). Blanks were recorded over the whole spectral range.

Preparation of Sample

The methyl-d_3-halides were synthesized from CD_3NO_2 which was prepared from CH_3NO_2 by exchange.[2] CD_3NO_2 was reduced to CD_3NH_2HCl as described by H. Krause.[3] The reduction takes place nearly quantitatively at about 70°C with hydrochloric acid and iron filings, if air is excluded, and the medium is kept acidic to completion of the reaction. By removing CO_2 and O_2 from the water used in the reaction and replacing the air in the reaction vessel by H_2 a yield of CD_3NH_2 of 90 percent and better was obtained. CD_3NH_2 is distilled from the strongly basic solution and collected in HCl. The CD_3NH_2HCl solution was evaporated nearly to dryness and then the benzoyl derivative of the amine was prepared in the usual manner. It was dissolved in ether and reprecipitated with ligroin.[4] The benzoyl methyl amide on heating with PCl_5 (PBr_5) decomposes[5] forming the methyl halides, C_6H_5CN, HCl (HBr), and $POCl_3$ ($POBr_3$). The methyl halide was driven over with a slow stream of N_2, and purified by leading it through 30 and 50 percent KOH solutions and over fused KOH and $CaCl_2$ to remove water, finally freezing it out with a dry-ice mixture. Since the decomposition temperature of the benzoylchlorimid, formed as an intermediate, is higher than the boiling point of $POCl_3$ the latter has to be removed first. For the bromine compound which decomposes below the boiling point of $POBr_3$, this is not necessary. The CD_3-group is stable against exchange, therefore no special precautions for storage need to be taken.

Purity of the Product

From the density measurements of the D_2O before and after the exchange with nitromethane and the distribution coefficient[2] the deuterium content could be calculated. This calculation gave a 95 percent pure CD_3NO_2 assuming only CD_3NO_2 and CH_3NO_2 to be present. Mass-spectrograph analysis by Dr. W. Kennedy,

[1] H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. **6**, 197 (1938).
[2] O. Reitz, Zeits. f. physik. Chemie **A176**, 363 (1936). For details, see T. P. Wilson, to be published.
[3] H. Krause, Chem. Zeitung **40**, 810 (1916).
[4] P. van Romburgh, Rec. Trav. Chim. **4**, 388 (1885). F. E. Dunlap, J. Am. Chem. Soc. **24**, 763 (1902).
[5] H. v. Pechmann, Ber. **28**, 2367 (1895); **33**, 611 (1900); **44**, 1465 (1911).

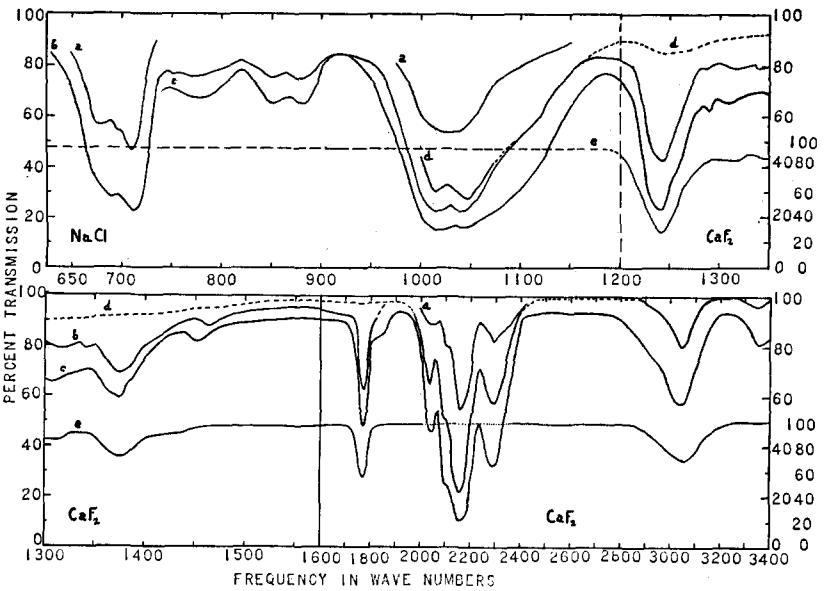

FIG. 1. Absorption spectrum of CD_3Cl. Curves: (*a*) 26 mm Hg; (*b*) ~90 mm Hg; (*c*) 216 mm Hg; (*d*) bands of the purified CD_3Cl (~80 mm Hg) coincide in the C−D and C−H stretch ranges with the 90 mm Hg bands of (*b*) – – – – – visually from records. (*e*) bands of the impurity at ~5 mm Hg (transmission scale ½ normal scale).

who determined the CD_2HNO_2 content to be about 12 percent, checks the above calculation. The nitromethane had been provided specially by the Commercial Solvents Corporation and was distilled through a fractionating column, retaining only the middle fraction.

TABLE I. Frequencies, intensities, and assignment of CD_3Cl bands.

Frequency in cm^{-1}	Int.	Assignment	Frequency in cm^{-1}	Int.	Assignment
680, 695, 711	S	P, Q, R $\nu C-Cl(\pi)$	1240	S	impurity
775	W	$2\tau(\sigma)$	1310	V. W.	imp.
855	W	? CD_2HCl	1373	M	imp.
881	W	? CD_2HCl	1452	V. W.	CD_2HCl
1016, 1029, 1043	S	P, Q, R $\delta(\pi)$	1764	M	imp.
1050–1060	M	$2\delta(\sigma)$	2040	M	$2\delta(\pi)$
			2104	M	$2^2\delta(\sigma), \nu(\pi)$
			2162	V. S.	
			2287	S	$2\nu(\sigma)$
			3043	M	CD_2HCl +imp.
			3368	W	$2\nu(\sigma)+2\delta(\sigma)$

TABLE II. Frequencies, intensities, and assignment of CD_3Br bands.

Frequency in cm^{-1}	Int.	Assignment	Frequency in cm^{-1}	Int.	Assignment
566, 577, 588	S	P, Q, R $\nu C-Br(\pi)$	1239	S	imp.
717	M	$2\tau(\sigma)$	1308	V. W.	imp.
790	W	CD_2HBr?	1377	M	imp.
978, 987, 999	S	P, Q, R $\delta(\pi)$	1455	W	CD_2HBr
1053	S	$2\delta(\sigma)$	1762	S	imp.
~1200	W	?	2089	S	$2^2\delta(\sigma), \nu(\pi)$
			2152	V. S.	
			2294	M	$2\nu(\sigma)$
			3035	M	CD_2HBr +imp.
			3350	W	$2\nu(\sigma)+2\delta(\sigma)$

Spectral evidence showed the presence of an identical impurity in CD_3Cl and CD_3Br. In the case of CD_3Cl it was possible to remove the impurity by absorbing it on active charcoal at dry-ice temperature and distilling CD_3Cl off at room temperature. After this treatment the CD_3Cl did not show any of the suspected impurity bands (see Fig. 1). On heating the charcoal with the blowpipe a substance was collected in the trap of the absorption cell which gave the spectrum of the impurity. This substance has a very strong absorption even at a pressure of 5 mm Hg. In the plots of the absorption curves for CD_3Cl the absorption curve of the impurity and the pure CD_3Cl are given with the curves for the mixture of the two. The bands of the impurity at 5 mm Hg are given at reduced scale. CD_3Br could be purified in the same manner. The spectrum of the CD_3Br impurity showed the same bands as that in CD_3Cl. The separation on charcoal is not as complete as in the CD_3Cl case.

INFRA-RED ABSORPTION BANDS AND ASSIGNMENT

The bands of CD_3Cl and CD_3Br, observed at different pressures are given in Figs. 1 and 2.

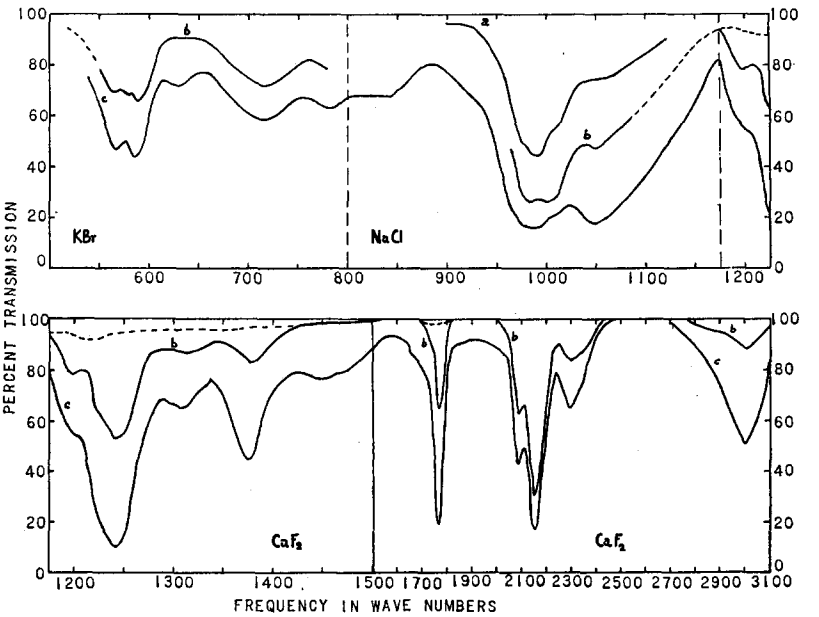

FIG. 2. Absorption spectrum of CD_3Br. Curves: (*a*) 35 mm Hg; (*b*) 89 mm Hg, – – – – – visually from records of pure CD_3Br, solid lines in 1200–1400 cm^{-1} range: CD_3Br+impurity. (*c*) 144 mm Hg.

The frequencies, their estimated intensities, and their assignments are given in Tables I and II.

Comparison of the shape and intensities of these bands with those of the ordinary methyl halides measured by Bennett and Meyer[6] leads to this assignment. We expected three parallel type bands (eventually four, if there is resonance between the first harmonic of $^2\delta(\sigma)$ and $\nu(\pi)$) and three perpendicular type bands (doubly degenerate). The intensities of these bands for the methyl halides are as follows: The higher frequency branch of $2^2\delta(\sigma)$, $\nu(\pi)$ is about twice as strong as the lower, which is about equal to $^2\nu(\sigma)$, $\delta(\pi)$ is stronger than $^2\delta(\sigma)$, $^2\tau(\sigma)$ is usually quite weak, $\nu_{C-X}(\pi)$ medium strong. This agrees with the bands observed for CD_3Cl and CD_3Br. The $P-R$ branch spacings could only be measured for two bands $\delta(\pi)$ and $\nu_{C-X}(\pi)$. They are given in Table III. The calculated values,[7] with 1.72A for C–Cl, 1.88 for C–Br, 1.09 for C–H and tetrahedral angles, compare well with the measured ones. The values for CH_3Cl and CH_3Br are from Bennett and Meyer's paper:[6]

The position of $^2\delta(\sigma)$ in CD_3Cl cannot be determined very accurately since it forms the shoulder of the very strong $\delta(\pi)$ band. There are two indirect methods of determining it quite accurately. In the methyl halides the $^2\delta(\sigma)$ band remains nearly constant, changing from 1445 cm^{-1} in CH_3I to 1476 cm^{-1} in CH_3F. Then from the $^2\delta(\sigma)$ value of CD_3Br the lower limit would be 1053 cm^{-1}. The upper limit can be obtained from a consideration of the first harmonic. The

TABLE III. Doublet spacings in the isotopic methyl chlorides and bromides.

Frequency	CH_3Cl	CD_3Cl	CH_3Br	CD_3Br
exp $\delta(\pi)$	28 cm^{-1}	27 cm^{-1}	25 cm^{-1}	21 cm^{-1}
$\nu_{C-X}(\pi)$	35 cm^{-1}	31 cm^{-1}	28 cm^{-1}	22 cm^{-1}
Mean value	31.5 cm^{-1}	29.0 cm^{-1}	26.5 cm^{-1}	21.5 cm^{-1}
Calculated	31.1 cm^{-1}	29.8 cm^{-1}	25.5 cm^{-1}	23.9 cm^{-1}

TABLE IV. The resonance frequencies $2^2\delta(\sigma)$, $\nu(\pi)$.

Frequency	CH_3Br	CD_3Br	CH_3Cl	CD_3Cl
$2^2\delta(\sigma)$, $\nu(\pi)$	2860 cm^{-1}	2089	2880	2104
	2972	2152	2967	2162
Mean value	2916	2121	2924	2133
$2^2\delta(\sigma)$	2900	2106	2920	?
Δ	+16	+15	+4	+3 to +4

[6] W. H. Bennett and C. F. Meyer, Phys. Rev. **32**, 888 (1928).
[7] S. L. Gerhard and D. M. Dennison, Phys. Rev. **43**, 197 (1933).

TABLE V. Force constants of the isotopic methyl chlorides and bromides.

Constant	Type	Chlorides	Bromides	Dimensions
f_r	C−H stretch	5.01×10^{5}	5.03×10^{5}	Dynes/cm
f_α	H−C−H bending	0.5346×10^{-11}	0.5334×10^{-11}	Dynes/radian
f_β	H−C−X bending	0.6885×10^{-11}	0.6079×10^{-11}	Dynes/radian
$f_{\beta\beta}$	H−C−X interaction	-0.0288×10^{-11}	-0.0296×10^{-11}	Dynes/radian
f_R	C−X stretch	3.368×10^{5}	2.88×10^{5}	Dynes/cm
$f_{R\beta}$	H−C−X, C−X interaction	0.607×10^{-3}	0.59×10^{-3}	Dynes/cm$^{\frac{1}{2}}$ radian$^{\frac{1}{2}}$

difference between the mean value of the two bands $2^2\delta(\sigma)$, $\nu(\pi)$ and $2^2\delta(\sigma)$ seems to be constant for CH_3Br and CD_3Br and allows us to fix the upper limit of $^2\delta(\sigma)$. From Table IV the upper limit of $^2\delta(\sigma)$ is 1065 cm^{-1}. Thus $^2\delta(\sigma)$ equal to 1058 cm^{-1} should probably be correct within our limits of error.

THEORETICAL PART

The methyl group has been assumed to have the tetrahedral shape of methane, the C−H distance[8] being 1.093A. The length of the carbon-halogen bond was assumed to be 1.72A for the C−Cl and 1.88A for the C−Br bonds, respectively.[9]

TABLE VI. Calculated and observed frequencies of CH_3Cl and CD_3Cl.

	CH_3Cl			CD_3Cl		
	Non-degenerate class (A_1)					
Freq.	Calc.	Obs.	Δ %	Calc.	Obs.	Δ %
$\nu(\pi)$	2948	*ca.* 2928	+0.7	2119	*ca.* 2136	−0.8
$\delta(\pi)$	1358	1355	+0.2	1034	1029	+0.5
$\nu_{C-X}(\pi)$	730	732	−0.3	691	695	−0.6
	Degenerate class (E_1)					
$^2\nu(\sigma)$	3063	3047	+0.5	2280	2287	−0.8
$^2\delta(\sigma)$	1460	1460	—	1053	1058	−0.5
$^2\tau(\sigma)$	1020	1020	—	776	775	−0.15

TABLE VII. Calculated and observed frequencies of CH_3Br and CD_3Br.

	CH_3Br			CD_3Br		
	Non-degenerate class (A_1)					
Freq.	Calc.	Obs.	Δ %	Calc.	Obs.	Δ %
$\nu(\pi)$	2954	*ca.* 2932	+0.8	2123	*ca.* 2134	− 0.5
$\delta(\pi)$	1302	1305	−0.2	983	987	− 0.4
$\nu_{C-Br}(\pi)$	613	610	+0.5	576	577	− 0.2
	Degenerate class (E_1)					
$^2\nu(\sigma)$	3074	3061	+0.4	2297	2294	+ 0.1
$^2\delta(\sigma)$	1452	1450	+0.1	1048	1053	− 0.5
$^2\tau(\sigma)$	953	957	−0.4	717	717	—

[8] E. F. Barker and N. Ginsburg, J. Chem. Phys. **3**, 668 (1935).

The following modified valence-force type potential function* was used for the calculation:

$$2V=f_r\sum^{3}(\Delta CH)^2+f_\alpha\sum^{3}(\Delta HCH)^2+f_\beta\sum^{3}(\Delta HCX)^2+f_{\beta\beta}\sum^{6}(\Delta HCX)(\Delta HCX)+f_R(\Delta CX)^2+f_{R\beta}\sum^{6}(\Delta CX)(\Delta HCX).$$

With six force constants, it was possible to account for the 12 frequencies of the isotopic molecules to within 1 percent. The values of the force constants do not differ much from those calculated by Linnett[10] which were based on the light molecules only. The frequencies calculated and observed are given in Tables VI and VII.

Due to resonance between $\nu(\pi)$ and $2^2\delta(\sigma)$ the exact frequency of $\nu(\pi)$ cannot be obtained in the halides, thus making it impossible to determine the necessity for an interaction constant in the C−H stretches. $\nu(\pi)$ for this calculation was found by adding Δ to the mean value of the

[9] These values are rather arbitrarily chosen from electron diffraction and spectroscopic measurements by G. B. B. M. Sutherland, Nature **140**, 239 (1937); J. Chem. Phys. **7**, 1066 (1939).

* Note: This is not the most general potential function which can be written for the methyl halides. It has been found possible to represent the frequencies of the E_1 factor by a diagonal potential function: $F_\alpha'=(f_\alpha-f_{\alpha\alpha})$; $F_\beta'=(f_\beta-f_{\beta\beta})$ and $F_r'=(f_r-f_{rr})$. The A_1 frequencies can be reproduced by a diagonal potential function with one interaction term, involving $f_{R\alpha}$ and $f_{R\beta}$. The A_1 force constants in terms of internal displacement coordinates are: $F_r=(f_r+2f_{rr})$; $F_R=f_R$; $F_\alpha=[(f_\alpha+2f_{\alpha\alpha})+(f_\beta+2f_{\beta\beta})-2(f_{\alpha\beta}+2f_{\alpha\beta'})]$ and $F_{\alpha R}=\sqrt{3}(f_{R\alpha}-f_{R\beta})$. It is found experimentally that $F_r=F_r'$ which makes $f_{rr}=0$. Since $f_{\alpha\alpha}$, $f_{\beta\beta}$, $f_{\alpha\beta}$, $f_{\alpha\beta'}$ cannot be determined separately $f_{\alpha\alpha}=f_{\alpha\beta}=f_{\alpha\beta'}=0$ has been assumed conditionally and the difference $F_\alpha-2(F_\alpha'+F_\beta')$ expressed in terms of $f_{\beta\beta}$. The same has been done in the case of $(f_{R\alpha}-f_{R\beta})$; i.e., $f_{R\alpha}$ set equal to zero. The correctness of these assumptions can only be proven by obtaining the frequencies of other isotopic compounds of different symmetry with this set of force constants and comparing with experiment.

[10] J. W. Linnett, J. Chem. Phys. **8**, 91 (1940).

two observed frequencies, Δ being the difference between this value and $2^2\delta(\sigma)$. This gave for the force constants of the C−H and C−D stretches in the degenerate and non-degenerate classes nearly the same value. It is also found that the force constant for the C−D stretch is always a little (*ca.* 0.1 unit) higher than the corresponding constant for C−H. This apparent difference is due to different anharmonicity effects for the protium and deuterium stretching vibrations. The observed and calculated product rule ratios for the isotopic methyl halides differ as predicted by O. Redlich[11] in accordance with the theory.

In conclusion I should like to thank Professor E. Bright Wilson, Jr. for suggesting the study of these molecules and for his continued interest during the course of this work.

[11] O. Redlich, J. Chem. Phys. **7**, 865 (1939).

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The Near Infra-Red Absorption Spectrum of Methyl Iodide

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(Received August 31, 1942)

The infra-red absorption spectrum of methyl iodide vapor has been reexamined under improved conditions at 3.3, 6.9, 8, and 11.3 microns with the result that each region reveals new detail. Near 3.36 microns some regular structure of mean separation 4.8 cm^{-1} overlaps the parallel band. The *Q* branches of the 6.9 mu band show a definite fine structure. The *Q* branch of the 8 mu band converges toward lower frequencies. In the 11.3 mu band the lines composing the *Q* branches converge toward higher frequencies.

INTRODUCTION

THE methyl halides have long been of interest in molecular spectroscopy. Of these, methyl iodide is of present interest, both because iodine has no known isotopes to complicate the spectrum, and because none of the parallel bands have ever been resolved. Bennett and Meyer,[1] and others[2–5] also, have located and examined the absorption bands in the near infra-red as well as their instruments permitted. In view, however, of the advances in experimental technique it was felt a reexamination was warranted. This has resulted in the finding of additional detail in each region examined as well as the revealing of several interesting convergence features.

The grating spectrometer, equipped with rocksalt foreprism, used in this work has been described in earlier publications[6] from this laboratory. While measuring the absorption, appropriate echelette gratings were rotated at intervals of five seconds of arc, and at each setting a measure of the transmitted light intensity was observed with the cell of CH_3I gas in and out of the light beam. The cells were made of cylindrical glass tubing closed off at the ends with carefully prepared rocksalt windows. The cells and gratings were maintained at about 30°C. The methyl iodide was secured from the Eastman Kodak Company.

In regions where atmospheric water vapor might obscure the absorption of the CH_3I, the air in the spectrometer case was dried by means of trays of phosphoric pentoxide. Both original and replica gratings by R. W. Wood were employed. Table I lists the gratings and spectrometer constants used for each of the regions measured.

THE 3.3-MICRON REGION

Figure 1 shows the observations near 3.3 microns plotted with ordinates in percent

* Now at Emory University.

[1] W. H. Bennett and C. F. Meyer, Phys. Rev. **32**, 888 (1928).

[2] W. W. Coblentz, Publication No. 35, Carnegie Institution of Washington, 1905, p. 61.

[3] W. W. Sleator, Phys. Rev. **38**, 147 (1931).

[4] J. G. Moorhead, Phys. Rev. **39**, 788 (1932).

[5] E. F. Barker and E. K. Plyler, J. Chem. Phys. **3**, 367 (1935).

[6] W. B. Steward and H. H. Nielsen, Phys. Rev. **47**, 828 (1935).