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## Substituted Methanes. IV. Vibrational Spectra and Calculated Thermodynamic Properties of Deuterotrichloromethane\*

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(Received April 20, 1950)

Raman displacements, semiquantitative relative intensities, quantitative depolarization factors, and wave numbers and percent transmission for the infra-red bands in the region 400–5000  $\text{cm}^{-1}$  have been obtained for  $\text{CCl}_3\text{D}$ . Thermodynamic properties—heat content, free energy, entropy, and heat capacity—have been calculated from the spectroscopic and molecular structure data, to a rigid rotator, harmonic oscillator approximation, for nine temperatures from 298.16° to 1000°K.

**R**AMAN displacements and visual estimates of the relative intensities of the Raman lines for deuterotrichloromethane (deuteriochloroform) have been obtained previously<sup>1–3</sup> in three investigations, but only one report<sup>3</sup> has been made regarding the polarization state of the lines and that gave only qualitative information. No previous infra-red spectral data could be found for this molecule.

As a part of the work on substituted methanes and ethanes that is being carried out in this laboratory, Raman and infra-red spectral data have been obtained for this compound, and thermodynamic properties for the ideal gaseous state have been calculated to a rigid rotator, harmonic oscillator approximation. No previous observed or calculated thermodynamic properties were found in the literature for this molecule.

### EXPERIMENTAL

The Raman displacements, semiquantitative relative intensities, and quantitative depolarization factors were obtained with previously described instruments and methods<sup>4</sup> at 30°C. Eastman 103-J plates were used and excitation was by Hg 4358Å. The relative intensities are only semiquantitative, since no correction was made for variation of the sensitivity of the plate with wavelength, and since calibration marks were not placed upon each plate but only upon a master calibration plate with the same type of emulsion. The depolarization factors were obtained by the well-tested single exposure method.

The infra-red absorption spectra were obtained both with a Beckman IR-2 spectrophotometer (KBr optics) and with a Perkin-Elmer 12-C spectrometer (NaCl optics). A continuous slit drive was used with both

instruments to maintain the deflection of the recorder as constant as possible. Records were obtained for the vapor, liquid, and  $\text{CS}_2$  solutions at 30°C. The gas and liquid cells were 10 cm and 0.11 mm in length, respectively, for the Beckman instrument and the liquid cell was 0.027 mm thick for the Perkin-Elmer records. The thickness for the liquid cells was determined by the method of interference fringes.<sup>5,6</sup> The spectrum was scanned from 400–10000  $\text{cm}^{-1}$ , but bands were found only in the region 600–2300  $\text{cm}^{-1}$ .

The  $\text{CCl}_3\text{D}$  was prepared by the reaction of sodium deuterioxide with chloral in  $\text{D}_2\text{O}$  solution. The product thus obtained was dried with anhydrous  $\text{CaSO}_4$ , then distilled in vacuum into the Raman tube. A mass spectrometric analysis showed it to contain approximately 10 percent  $\text{CCl}_3\text{H}$ , but probably less than 0.1 percent of other impurities.

### SPECTRAL DATA AND ASSIGNMENTS

The present Raman data are compared with the previous data in Table I, columns 1–8. As indicated in column 2,  $\Delta\nu$  values have been obtained in 4 separate investigations; however, values from only 3 of these were averaged to obtain the “probable values” in column 3, since Truchet’s values<sup>3</sup> seem to be generally too large.

The infra-red data obtained in the present investigation also are given in Table I, columns 9–14. Only two bands were observed for the vapor since the vapor pressure at 30°C was rather small. The percent transmission curve is shown in Fig. 1. The bands at 3.31, 8.22, and 13.16 $\mu$  for the liquid and the band at 12.94 $\mu$  for the gas are caused by the 10 percent  $\text{CCl}_3\text{H}$  present in the sample, as indicated in the figure.

In column 15 of Table I are given—in **bold face type**—the wave numbers for the fundamentals calculated in paper III<sup>7</sup> of this series, and—in *italics*—the combina-

\* Presented at the Chicago meeting of the American Physical Society (November, 1949); abstract in Phys. Rev. **77**, 740 (1950).

† Based upon investigations carried out in partial fulfillment of the requirements for the degree of Master of Science.

<sup>1</sup> R. W. Wood and D. H. Rank, Phys. Rev. **48**, 63 (1935).

<sup>2</sup> O. Redlich and F. Pordes, Sitz. Akad. Wiss. Wien IIb, **145**, 67 (1936).

<sup>3</sup> M. Rene Truchet, Comptes Rendus **202**, 1997 (1936).

<sup>4</sup> F. F. Cleveland, J. Chem. Phys. **11**, 1, 227 (1943); **13**, 101 (1945).

<sup>5</sup> D. C. Smith and E. C. Miller, J. Opt. Soc. Am. **34**, 130 (1944).

<sup>6</sup> G. B. M. Sutherland and H. A. Willis, Trans. Faraday Soc. **41**, 181 (1945).

<sup>7</sup> Zietlow, Cleveland, and Meister, J. Chem. Phys. **18**, 1076 (1950).

tion and overtone wave numbers calculated from the probable values of the fundamentals listed in column 3. The calculated values of the fundamentals are of course much more reliable than for the overtones and combinations. The numbering of the fundamentals in column 16 follows the procedure given in Paper I.<sup>8</sup>

#### THERMODYNAMIC PROPERTIES FOR CCl<sub>3</sub>D

The heat content, free energy, entropy, and heat capacity of CCl<sub>3</sub>D were calculated for temperatures

from 298.16° to 1000°K, to a rigid rotator, harmonic oscillator approximation. Nuclear spins and the effect of isotopic mixing were neglected. The calculated values are for the ideal gaseous state at one atmosphere pressure.

The bond distances and interbond angles required for the calculation of the moments of inertia were taken from the microwave data<sup>9</sup> for CCl<sub>3</sub>H; they were: C—H=C—D=1.090±0.005Å, C—Cl=1.761±0.004Å, and Cl—C—Cl=112° 0'±40'. From these, the moments

TABLE I. Raman and infra-red spectral data and assignments for deuterotrichloromethane (CCl<sub>3</sub>D).<sup>a</sup>

PR	N	$\Delta\nu$	PV	Raman				$\nu$	$I_e$	Infra-red		$\nu$	$I_e$	$\nu$	$I_e$	$\nu_c$	Assignments	Type
				AD	I <sub>PR</sub>	T	$\rho$	PS	vapor		CS <sub>2</sub> soln.			liquid				
262	3(4)	261.7	0.3		100	D	0.87	D								257.5	$\nu_6$	E
365	3(4)	365.5	0.5		90	P	0.10	P								368.1	$\nu_8$	A <sub>1</sub>
649	3(4)	650.1	0.8		69	P	0.03	P								641.1	$\nu_2$	A <sub>1</sub>
735	3(4)	736.9	1.5		12	D	0.84	D	747	VS	648	M				734.1	$\nu_8$	E
											743	(VS)				731	2 $\nu_8$	A <sub>1</sub>
908	3(4)	908.4	0.4		3	D	0.87	D	909	VS	904	VS		910	VS	914.7	$\nu_4$	E
														(1095)	W, b	1102	$\nu_8 + \nu_6$	E
											1400	M				1387	$\nu_2 + \nu_8$	E
1463	1	1463		VW												1474	2 $\nu_6$	A <sub>1</sub> +E
1642	1	1642		VW												1645	$\nu_4 + \nu_6$	A <sub>1</sub> +A <sub>2</sub> +E
1796	1	1796		VW												1817	2 $\nu_4$	A <sub>1</sub> +E
2255	3(4)	2254.7	1.0		15	P	0.26	P			b		2245	M		2259.0	$\nu_1$	A <sub>1</sub>

<sup>a</sup>  $\Delta\nu$  is the Raman displacement in cm<sup>-1</sup>;  $I$  is the semiquantitative relative intensity;  $\rho$  is the depolarization factor;  $\nu$  is the wave number of the infra-red absorption band in cm<sup>-1</sup>;  $I_e$  is the estimated intensity of absorption (W=weak, M=medium, S=strong, V=very); b=broad; PR=present results; N=number of times  $\Delta\nu$  has been measured in separate investigations; PV=probable value (mean of the N values, including the present value); AD is the average deviation of the individual values from the mean; T=Truchet, reference 3; PS=polarization state of the line (P=polarized, D=depolarized);  $\nu_c$ =calculated frequencies (see reference 7); and uncertain data are enclosed in parentheses.

<sup>b</sup> Unresolved from solvent band.

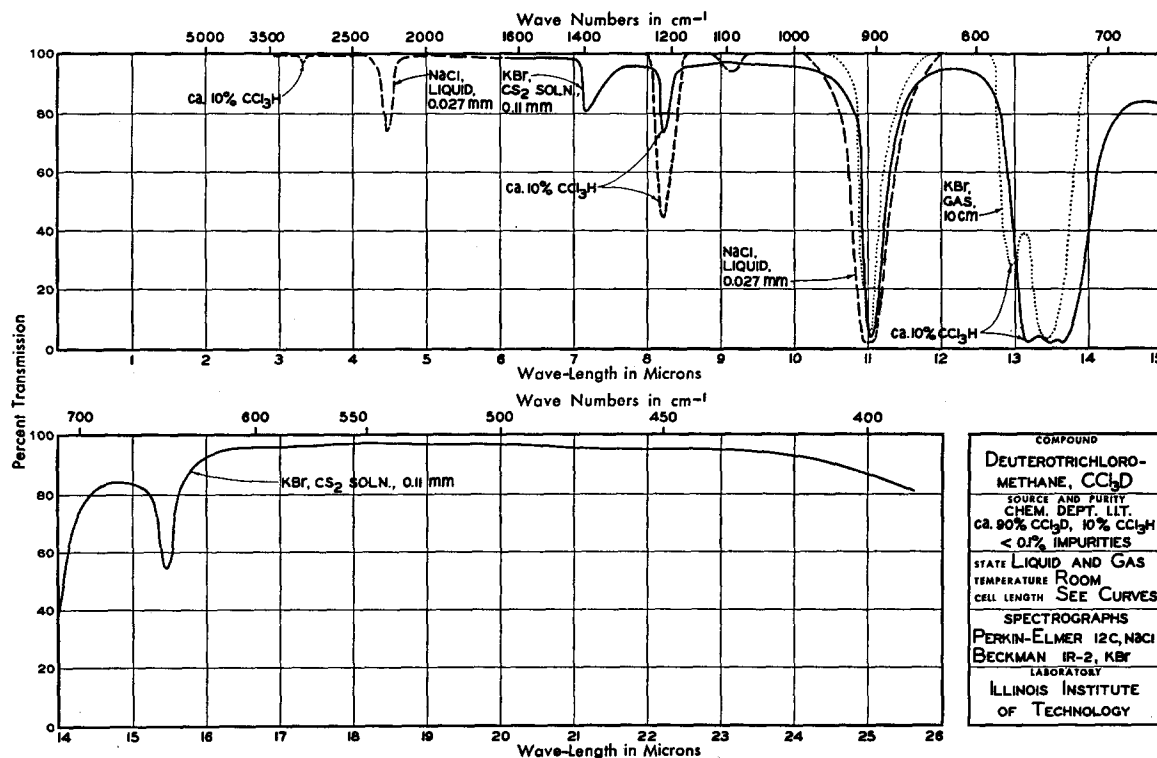


FIG. 1. Infra-red absorption bands for deuterotrichloromethane.

<sup>8</sup> Meister, Rosser, and Cleveland, J. Chem. Phys. 18, 346 (1950).

<sup>9</sup> Unterberger, Trambarulo, and Smith, J. Chem. Phys. 18, 565 (1950).

TABLE II. Wave numbers and degeneracies corresponding to the fundamental frequencies of  $\text{CCl}_3\text{D}$ .

Designation	Wave number ( $\text{cm}^{-1}$ )	Degeneracy
$\nu_1$	2255	1
$\nu_2$	650	1
$\nu_3$	365	1
$\nu_4$	*909	2
$\nu_5$	*747	2
$\nu_6$	262	2

\* Gaseous state.

of inertia were found to be:  $I_{zz} = 302 \text{ Awu. } A^2 (501 \cdot 10^{-40} \text{ g cm}^2)$ , and  $I_{xx} = I_{yy} = 159 \text{ Awu. } A^2 (264 \cdot 10^{-40} \text{ g cm}^2)$ . The symmetry number was 3 and Birge's 1941 values<sup>10</sup> of the physical constants were used throughout the calculations. The values used for the fundamentals and their degeneracies are given in Table II.

The results obtained for the thermodynamic properties are given in Table III.

Since 5 of the 9 fundamentals are liquid state frequencies, the values of the thermodynamic properties listed in the table may be slightly larger than the values for the ideal gaseous state. However, even if one assumes that the gaseous frequencies are  $6 \text{ cm}^{-1}$  higher than the liquid values—which is the mean of the two observed shifts—the values listed in the first row of Table III for  $298.16^\circ\text{K}$  would decrease only by 0.07, 0.06, 0.13, and 0.09 cal. deg.<sup>-1</sup> mole<sup>-1</sup>, respectively. These are probably greater than the actual errors, since the greatest contributions to the thermodynamic properties are made by

<sup>10</sup> R. T. Birge, *Rev. Mod. Phys.* **13**, 233 (1941).

TABLE III. Heat content, free energy, entropy, and heat capacity of  $\text{CCl}_3\text{D}$  for the ideal gaseous state at one atmosphere pressure.<sup>a</sup>

$T$	$(H^\circ - H_0^\circ)/T$	$-(F^\circ - H_0^\circ)/T$	$S^\circ$	$C_p^\circ$
298.16	11.55	59.40	70.95	16.37
300	11.58	59.47	71.05	16.42
400	13.09	63.02	76.11	18.68
500	14.37	66.08	80.45	20.22
600	15.44	68.79	84.23	21.32
700	16.34	71.25	87.59	22.13
800	17.11	73.49	90.60	22.75
900	17.76	75.54	93.30	23.23
1000	18.33	77.44	95.77	23.61

<sup>a</sup>  $T$  is in degrees Kelvin and the other quantities are in cal. deg.<sup>-1</sup> mole<sup>-1</sup>.

the low frequencies which are expected to have a smaller shift.

#### ACKNOWLEDGMENTS

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## The Conductance of Potassium Chloride, Potassium Bromide and Potassium Iodide in Aqueous Solutions from 5 to $55^\circ$ \*

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(Received May 3, 1950)

The equivalent conductivities of dilute solutions of potassium chloride, potassium bromide, and potassium iodide have been measured at various temperatures, and extrapolated to infinite dilution. These results, when combined with those of A. R. Gordon and others, yield limiting equivalent conductivities of each of the three potassium salts at  $10^\circ$  intervals between 5 and  $55^\circ\text{C}$ .

#### INTRODUCTION

IN recent years accurate values of the conductivities<sup>1,2</sup> and transport numbers<sup>3,4</sup> of some simple salts have been reported at temperatures between 15 and  $45^\circ$ ,

\* This communication embodies part of the thesis presented by Henry Zeldes to the Graduate School of Yale University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy (1947).

† Present address: Oak Ridge National Laboratory, Oak Ridge, Tennessee.

<sup>1</sup> G. C. Benson and A. R. Gordon, *J. Chem. Phys.* **13**, 473 (1945); **13**, 470 (1945).

<sup>2</sup> H. E. Gunning and A. R. Gordon, *J. Chem. Phys.* **11**, 18 (1943); **10**, 126 (1942).

and of hydrochloric acid<sup>5,6</sup> from 0 to  $60^\circ$ . The work reported in this paper extends the range of these results by conductivity measurements at 5 ( $25$ ) and  $55^\circ$  on potassium chloride and bromide solutions, and at  $10^\circ$  intervals from 5 to  $55^\circ$  on solutions of potassium iodide.

In subsequent papers from this laboratory, measure-

<sup>3</sup> R. W. Allgood and A. R. Gordon, *J. Chem. Phys.* **10**, 124 (1942).

<sup>4</sup> Allgood, LeRoy, and Gordon, *J. Chem. Phys.* **8**, 418 (1940).

<sup>5</sup> B. B. Owen and F. H. Sweeton, *J. Am. Chem. Soc.* **63**, 2811 (1941).

<sup>6</sup> H. S. Harned and E. C. Dreby, *J. Am. Chem. Soc.* **61**, 3113 (1939).