

Substituted Methanes. II. Vibrational Spectra and Calculated Thermodynamic Properties of Deuterotribromomethane

Salvador M. Ferigle, Forrest F. Cleveland, William M. Boyer, and Richard B. Bernstein

Citation: *The Journal of Chemical Physics* **18**, 1073 (1950); doi: 10.1063/1.1747861

View online: <http://dx.doi.org/10.1063/1.1747861>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/18/8?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

Substituted Methanes. XXIX. Vibrational Spectra, Potential Constants, and Calculated Thermodynamic Properties for Dibromochlorofluoromethane and Bromodichlorofluoromethane

J. Chem. Phys. **31**, 1633 (1959); 10.1063/1.1730665

Substituted Methanes. XVI. Vibrational Spectra, Potential Constants, and Calculated Thermodynamic Properties of Dibromodifluoromethane

J. Chem. Phys. **21**, 1781 (1953); 10.1063/1.1698663

Substituted Methanes. XIV. Vibrational Spectra, Potential Constants, and Calculated Thermodynamic Properties of Bromochloromethane

J. Chem. Phys. **21**, 930 (1953); 10.1063/1.1699063

Substituted Methanes. VIII. Vibrational Spectra, Potential Constants, and Calculated Thermodynamic Properties for Dibromodichloromethane

J. Chem. Phys. **20**, 454 (1952); 10.1063/1.1700441

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

J. Chem. Phys. **18**, 1081 (1950); 10.1063/1.1747864



Substituted Methanes. II. Vibrational Spectra and Calculated Thermodynamic Properties of Deuterotribromomethane*

SALVADOR M. FERIGLE** AND FORREST F. CLEVELAND
Spectroscopy Laboratory, Department of Physics

AND

WILLIAM M. BOYER*** AND RICHARD B. BERNSTEIN
Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois
(Received April 11, 1950)

Raman displacements, semiquantitative relative intensities, quantitative depolarization factors, and wave numbers and percent transmission for the infra-red bands in the region $400\text{--}5000\text{ cm}^{-1}$ have been obtained for CBr_3D . Details about the measurement of the depolarization factors are given. Thermodynamic properties—heat content, free energy, heat capacity, and entropy—have been calculated from the spectroscopic and molecular structure data for eight temperatures from 298.16° to 1000°K .

RAMAN displacements and relative intensities of deuterotribromomethane (deuterobromoform) have been published by Redlich and Stricks,¹ but no depolarization factors nor infra-red spectral data have been found in the literature. 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.

The deuterotribromomethane was prepared by the reaction of sodium deuteroxide with bromal in D_2O solution. The CBr_3D thus obtained was dried with anhydrous CaSO_4 and distilled in vacuum. A mass-spectrometric analysis showed it to contain approximately 4 percent CBr_3H .

RAMAN SPECTRUM OF CBr_3D

The Raman spectrum of CBr_3D has been redetermined and quantitative polarization data obtained. The spectrograms were obtained on Eastman 103-J plates with a Hilger E-518 spectrograph having a dispersion of $320\text{ cm}^{-1}/\text{mm}$ ($64\text{A}/\text{mm}$) at 4500A , and with a two-prism spectrograph having a dispersion of $144\text{ cm}^{-1}/\text{mm}$ ($29\text{A}/\text{mm}$) at 4500A , with Hg 4358A as the exciting line, by the experimental methods previously described.² The depolarization factors have been obtained by the single-exposure method given by Cleveland,³ the densities of the two components have been measured with a Leeds and Northrup microphotometer equipped with a Speedomax pen recorder, instead of the Gaertner microdensitometer previously

used. The depolarization factors have been measured as the ratio of the peak intensities for the weak and strong components. The correction for background has been made by taking the reading of the background density at the wave-length corresponding to the peak, on a smooth background curve drawn on the microphotometer tracing, transforming it into intensity from the calibration curve, and subtracting this background intensity value from the line intensity. Crawford and Horwitz⁴ suggested taking the background minimum just in front of the line, but it seems that this "minimum adjacent background" correction is not adequate in all cases⁵ and, as Lyons states,⁶ "the method of taking background readings need not be necessarily arbitrary." Corrections for real or apparent polarization of the scattered beam in its optical path, for reciprocity failure of the plates, and for convergence errors have been made.³ The present results are given in Table I, columns 2-4; the first column gives the Raman displacements reported by Redlich and Stricks.¹ The Raman displacements are, in general, in good agreement; however, some of the present values appear somewhat greater, in better agreement with our infra-red data.

INFRA-RED SPECTRUM OF CBr_3D

Infra-red absorption spectra have been obtained with both sodium chloride (12C Perkin-Elmer recording spectrometer) and potassium bromide (IR-2 Beckman spectrophotometer) optics. A continuous slit drive was used in both instruments to maintain the incident energy as constant as possible. The cell thicknesses were measured by the method of interference fringes.^{7,8}

The results are given in Table I, columns 5 and 6, and the percent transmission curve is shown in Fig. 1.

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

** One of the investigations carried out in partial fulfillment of the requirements for the Ph.D. Degree.

*** The preparation of the CBr_3D was part of a Master's thesis (1950).

¹ O. Redlich and W. Stricks, *Sitz. Akad. Wiss. Wien, IIb*, **145**, 192 (1936).

² F. F. Cleveland, *J. Chem. Phys.* **11**, 1, 227 (1943).

³ F. F. Cleveland, *J. Chem. Phys.* **13**, 101 (1945).

⁴ B. L. Crawford, Jr. and W. Horwitz, *J. Chem. Phys.* **15**, 268 (1947).

⁵ B. L. Crawford, Jr. and W. Horwitz, *J. Chem. Phys.* **16**, 147 (1948).

⁶ P. A. Lyons, Thesis, University of Wisconsin, 1948.

⁷ D. C. Smith and E. C. Miller, *J. Opt. Soc. Am.* **34**, 130 (1944).

⁸ G. B. B. M. Sutherland and H. A. Willis, *Trans. Faraday Soc.* **41**, 181 (1945).

All the infra-red bands can be interpreted as fundamentals or combination bands, allowed by the selection rules for the C_{3v} structure. The assignments are given at the right in Table I. In the numbering of the fundamentals, we have followed the procedure of the first paper of this series.⁹ The broad infra-red band at 848 cm^{-1} was resolved in the gas into two components at 846 and 866 cm^{-1} . In carbon disulfide solution, this band also was resolved, the maxima of absorption appearing at 845 and 861 cm^{-1} ; in chloroform solution the maxima exist at 848 and 866 cm^{-1} ; this small difference can probably be accounted for in terms of a solvent effect. This doublet corresponds to a Fermi resonance between the fundamental ν_4 and the combination band $\nu_3 + \nu_5 = 855\text{ cm}^{-1}$, both of symmetry E . The two components of the Fermi resonance doublet have been designated in Table I as ν_4' and ν_4'' . The 1144 cm^{-1} band could be partly due to the small amount of CBr_3H present in the sample; however, since the other frequencies of this compound (especially the very strong C—H band) have not been observed, it seems reasonable to deduce that this band is due mainly to the combination $\nu_2 + \nu_5$ of CBr_3D . All the bands for the gaseous state are weak because the vapor pressure was rather small.

THERMODYNAMIC PROPERTIES OF CBr_3D

The heat content, free energy, entropy, and heat capacity of CBr_3D have been calculated for temperatures from 298.16° to 1000°K , to a rigid rotator, harmonic oscillator approximation. Nuclear spins and the effect of the isotopic mixing have been neglected. The calculated values are for the ideal gaseous state at one atmosphere pressure. The moments of inertia have been calculated with C—Br = 1.91 \AA and with a Br—C—Br angle of 111° , as given by Lévy and Brockway,¹⁰ and assuming C—D = 1.09 \AA , as in CD_4 . The values obtained were $I_{zz} = 792$ and $I_{xx} = I_{yy} = 405\text{ Awv. \AA}^2$. The C—D distance is probably somewhat different in CBr_3D than in CD_4 , but even if this is the case the error thus introduced would be quite small, since the contribution of the D atom to the moment of inertia is already only a fraction of the total. No microwave data are as yet available.

The values used for the fundamentals and their degeneracies are given in Table II; wave numbers for the gaseous state have been used when available. ν_4 has been taken as the mean value of the two components of the Fermi resonance doublet, so that the value 856 cm^{-1} is not very accurate, but it seems that this is the best possible choice with the available information. The symmetry number has been taken equal to 3 and Birge's 1941 values of the physical constants¹¹ have

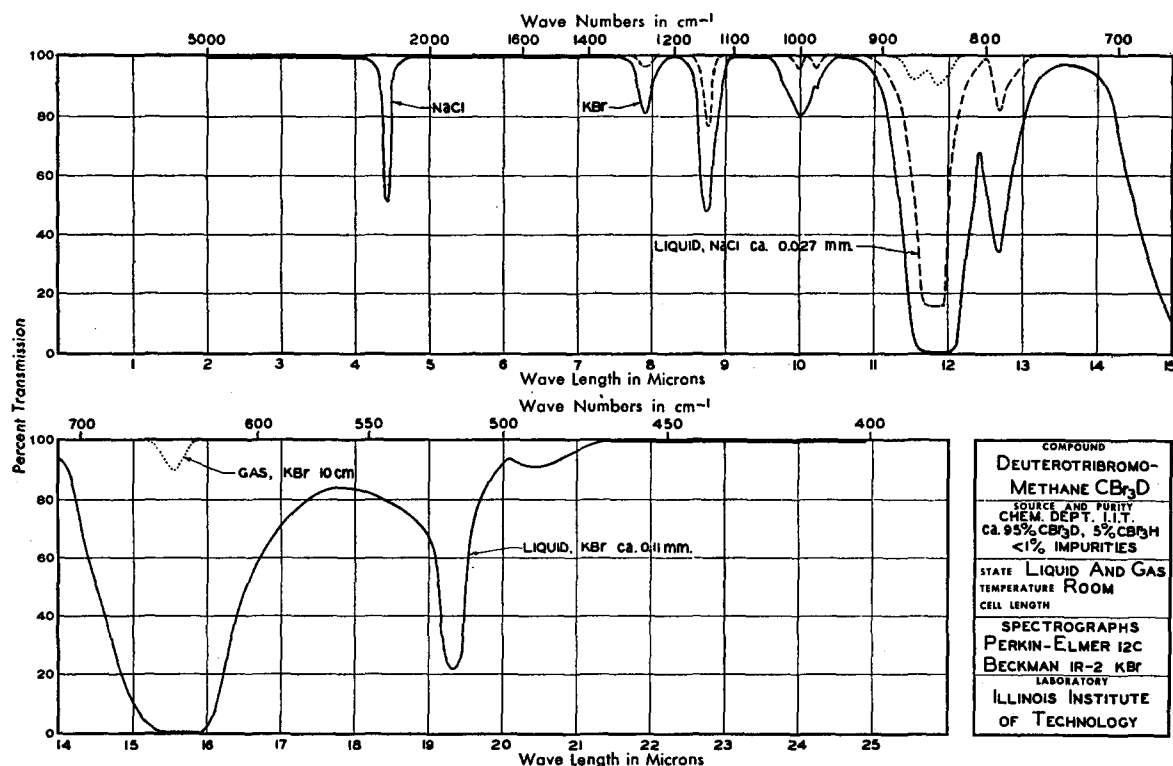


FIG. 1. Infra-red absorption bands for deuterotribromomethane.

⁹ Meister, Rosser, and Cleveland, *J. Chem. Phys.* **18**, 346 (1950).

¹⁰ H. A. Lévy and L. O. Brockway, *J. Am. Chem. Soc.* **59**, 1662 (1937).

¹¹ R. T. Birge, *Rev. Mod. Phys.* **13**, 233 (1941).

TABLE I. Raman and infra-red spectral data and assignments for deuterotribromomethane (CBr₃D).^a

Raman (liquid)				Infra-red			
Redlich and Stricks	$\Delta\nu$ Present	I	ρ	$\nu_a I_a$ gas	$\nu_a I_a$ liquid	Assign- ments	Type
153.4	155	70	0.78			ν_6	E
221.6	222	100	0.26			ν_2	A_1
519.3	519	41	0.18		517 S	ν_2	A_1
628.5	633	16	0.77	644 W	634 VS	ν_6	E
					786 S	$\nu_6 + \nu_6$	$A_1 + A_2 + E$
840	844			846 W	848 VS	ν_4'	E
856.5	858	9	0.83	866 W		ν_4''	E
					978 W	$\nu_4' + \nu_6$	$A_1 + A_2 + E$
					1003 W	$\nu_4'' + \nu_6$	$A_1 + A_2 + E$
					1144 S	$\nu_2 + \nu_6$	E
					1267 M	$2\nu_6$	$A_1 + E$
2247	2251	11	0.28		2256 S	ν_1	A_1

^a $\Delta\nu$ is the Raman displacement in cm^{-1} ; I is the semiquantitative relative intensity; ρ is the depolarization factor of the Raman line; ν_a is the wave number of the infra-red absorption band in cm^{-1} ; and I_a is the qualitative intensity of absorption (W =weak, M =medium, S =strong, V =very).

been used throughout the calculations. 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 8 cm^{-1} higher than the liquid values—which is the mean of the two shifts which were observed—the thermodynamic properties listed in the first row of Table III for 298.16°K would decrease only by 0.09, 0.20, 0.29, and 0.05 cal. $\text{deg}^{-1} \text{ mole}^{-1}$, respectively. These values are probably greater than the actual errors, since the greatest contributions to the thermodynamic properties are made by the low frequencies which are expected to have a smaller shift.

ACKNOWLEDGMENTS

The Hilger E-518 spectrograph used in this investigation was obtained, in part, with a grant from the

TABLE II. Wave numbers and degeneracies corresponding to the fundamental frequencies of CBr₃D.

Designation	Wave number (cm^{-1})	Degeneracy
ν_1	2251	1
ν_2	519	1
ν_3	222	1
ν_4	*856	2
ν_5	*644	2
ν_6	154	2

* Gaseous state.

TABLE III. Heat content, free energy, entropy, and heat capacity of CBr₃D for the ideal gaseous state at one atmosphere pressure.^a

T	$(H^0 - H_0^0)/T$	$-(F^0 - H_0^0)/T$	S^0	C_p^0
298.16	13.02	66.32	79.34	17.77
400	14.50	70.36	84.86	19.74
500	15.68	73.73	89.41	21.02
600	16.65	76.68	93.33	21.93
700	17.46	79.30	96.76	22.60
800	18.14	81.68	99.82	23.12
900	18.72	83.86	102.58	23.53
1000	19.21	85.85	105.06	23.86

^a T is in degrees Kelvin and the other quantities in cal. $\text{deg}^{-1} \text{ mole}^{-1}$.

Permanent Science Fund of the American Academy of Arts and Sciences; and the optical parts for the two-prism spectrograph were obtained with a grant from The Society of the Sigma Xi. The authors are grateful for this assistance. One of us (S. M. F.) wishes to thank the *Junta de Relaciones Culturales* of Spain for a scholarship that made it possible for him to carry out his part of this research. Thanks also are due to Dr. V. H. Dibelier of the National Bureau of Standards, who performed the mass-spectrometric analysis, and to Dr. Sidney Katz of the Institute of Gas Technology on our campus who kindly made available the Perkin-Elmer infra-red spectrometer. The D₂O was obtained through the courtesy of Dr. Martin Kilpatrick and the AEC.