O_2 selected by Kelley,[24] is $\Delta S^\circ_{25} = -26.27 \pm 0.16$ e.u. These two values agree to just within the limits of error, and should confirm the applicability of the Third Law to the entropy of red HgO.

The values of ΔS derived from the dissociation pressures and from e.m.f. measurements are in good agreement, although it may easily be possible that they are both wrong. A part of Randall's calculations was based on doubtful data, *e.g.*, for the heat capacity of HgO he used a value at 600° derived from the measurements of Guenther between 25 and 75°K.; also, the probable error in ΔH derived from the cell measurements is large enough to account for the discrepancy.

Giving the two values of ΔF equal weight, the best value of ΔH is derived from these values, and from the calorimetric entropy of HgO

$$\mathrm{Hg(liq)} + {}^1/_2\mathrm{O_2(g)} = \mathrm{HgO(red)}$$
$$\Delta F^\circ_{25} = -13{,}965 \pm 35 \text{ cal.}$$
$$\Delta S^\circ_{25} = -26.27 \pm 0.16 \text{ e.u.}$$
$$\Delta H^\circ_{25} = -21{,}708 \pm 82 \text{ cal.}$$

COLUMBUS, OHIO

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(24) K. K. Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

Methylchloroform: The Infrared Spectrum from 130–430 cm.$^{-1}$, the Energy Levels and Potential for Internal Rotation and the Thermodynamic Properties[1]

BY KENNETH S. PITZER AND J. L. HOLLENBERG

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The infrared spectrum of gaseous methylchloroform has been measured in the range 130–430 cm.$^{-1}$. In addition to bands showing PQR structures at 239 and 344 cm.$^{-1}$, there is a series of absorption peaks in the range 130–180 cm.$^{-1}$. This series is interpreted as a sequence of difference bands involving internal rotation and yields values for the first three energy level separations associated with that motion. These energy levels are interpreted with a two term expansion of the potential function for internal rotation. Other vibration frequencies are discussed and the thermodynamic functions are calculated for methylchloroform.

The molecule CH_3–CCl_3, methylchloroform, has been the subject of several recent spectroscopic investigations. The most recent publications are those of Venkateswarlu,[2] El-Sabban, Meister and Cleveland,[3] and Smith, Brown, Nielsen, Smith and Liang.[4] These authors give references to earlier work. These various investigations cover both the Raman and infrared spectra except for the region of the infrared below about 250 cm.$^{-1}$. It is the purpose of this paper to present the infrared spectrum of methylchloroform in the range 130–430 cm.$^{-1}$ and to discuss the implication of our additional results with respect to the vibration frequency assignment and in particular the torsional vibration.

Experimental Method and Results

The spectrum was measured in a grating spectrometer described recently by Bohn, Freeman, Gwinn, Hollenberg and Pitzer.[5] The experimental procedures were the same as those described previously. The sample of methylchloroform was from the Eastman Kodak Co. The spectrum is shown in Fig. 1.

In the region from 300 to 400 cm.$^{-1}$ which overlaps previous investigations, we agree completely with the most recent work—that of Venkateswarlu.[2] He found the weak band at 382 cm.$^{-1}$ and the strong one at 344 cm.$^{-1}$. In each case the frequency value agrees within 1 cm.$^{-1}$.

We find no trace of a band in the gas at 411 cm.$^{-1}$, where Smith, *et al.*, found one in the liquid. Similarly we find nothing near 300 cm.$^{-1}$ where a weak Raman band has been observed. However, the fundamental at 239 cm.$^{-1}$ appears clearly with a PQR structure. The shoulder near 283 cm.$^{-1}$ is probably real but not certain. The most interesting feature of the spectrum is the series of three decreasing absorption peaks in the region 130–180 cm.$^{-1}$. While our experimental signal in this region is very small, we believe these peaks to be real. However, the exact frequency of the first peak is uncertain.

TABLE I

FUNDAMENTAL FREQUENCIES OF METHYLCHLOROFORM

Symmetry	Designation	Frequency (gas)	Symmetry	Designation	Frequency (gas)
A_1	ν_1	2954	E	ν_7	3017
	ν_2	1383		ν_8	1456
	ν_3	1075		ν_9	1089
	ν_4	526		ν_{10}	725
	ν_5	344		ν_{11}	351
A_2	ν_6	214		ν_{12}	239

Spectral Assignment.—Previous workers have come to agree on all of the fundamental frequencies shown in Table I except for numbers 3, 6 and 11. We have little new information to contribute with respect to ν_3, which is principally a C–C stretching motion. We are strongly influenced by the fact that almost all observers of the Raman spectrum have resolved a band at about 1070 cm.$^{-1}$ from the ν_9 band at 1084 cm.$^{-1}$, and by the observation of Smith, *et al.*, that the lower frequency component is moderately polarized while the higher one is fully depolarized. This pair cannot be a resonance doublet if the polarization is different for the two components, and it is then difficult to understand the intensity of the 1070 cm.$^{-1}$ band except as a fundamental. Thus we have selected this band for ν_3, the gas phase frequency being 1075 cm.$^{-1}$.

The unsymmetrical C–Cl bending motion, ν_{11}, is expected to have a frequency near that of the symmetrical bending motion, ν_5, at 344 cm.$^{-1}$. Previ-

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(1) This work was assisted by the American Petroleum Institute through Research Project 50.

(2) P. Venkateswarlu, *J. Chem. Phys.*, **20**, 1810 (1952); **19**, 298 (1951).

(3) M. Z. El-Sabban, A. G. Meister and F. F. Cleveland, *ibid.*, **20**, 1810 (1952); **19**, 885 (1951).

(4) D. C. Smith, G. M. Brown, J. R. Nielsen, R. M. Smith and C. Y. Liang, *ibid.*, **20**, 473 (1952).

(5) C. R. Bohn, N. K. Freeman, W. D. Gwinn, J. L. Hollenberg and K. S. Pitzer, *ibid.*, in press.

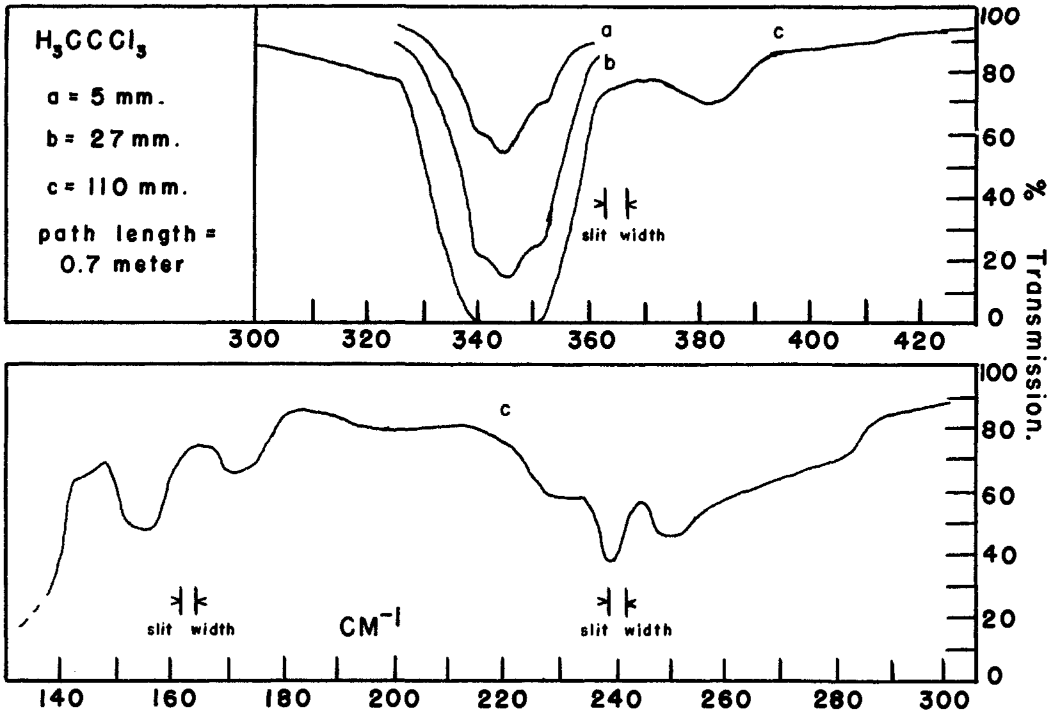

Fig. 1.—The infrared absorption spectrum of methylchloroform.

ous workers have suggested three possibilities for ν_{11}: the very weak Raman band at about 305 cm.$^{-1}$, the very weak infrared band at 382 cm.$^{-1}$, or a location so close as to be unresolved from the strong infrared band at 344 cm.$^{-1}$. Since we found nothing near 305 cm.$^{-1}$, we do not favor that selection. Concerning the other two possibilities we may note that the band at 382 is extremely weak; a considerably stronger band would be unnoticed in the range 340–352 cm.$^{-1}$. Also El-Sabban, *et al.*, carried out a normal coördinate calculation for methylchloroform and predicted for ν_{11} a value of 363 cm.$^{-1}$, which is exactly midway between 344 and 382 cm.$^{-1}$. We shall see that the interpretation of the spectrum in the 130–180 cm.$^{-1}$ range and the thermodynamic data favor strongly the selection of the value 351 cm.$^{-1}$ for ν_{11}. Thus we shall assume that it is buried in the strong band centered at 344 cm.$^{-1}$, and that the 382 cm.$^{-1}$ band is to be explained as $\nu_9 - \nu_4 = 725 - 344 = 381$ cm.$^{-1}$. The shoulder near 283 cm.$^{-1}$, if real, can be interpreted as $\nu_4 - \nu_{12} = 526 - 239 = 287$. The corresponding sum combination is observed with moderate intensity in the infrared.

The internal rotational or torsional vibration, ν_6, is inactive as a fundamental in either the Raman or the infrared spectra. However, combinations of this frequency with any of the fundamentals of E symmetry are allowed. A characteristic feature of the torsional vibration will be its large anharmonicity. Thus with its low frequency the molecules will be distributed over several quantum states and the successive transitions (0 → 1, 1 → 2, 2 → 3, etc.) will be appreciably separated by the anharmonicity. The observed features of the spectrum which invite attention in this regard are the succession of peaks we found at approximately 135, 154 and 172 cm.$^{-1}$ and the series 565, 548 and 533 cm.$^{-1}$ found by Smith, *et al.*, and by Venkateswarlu. The probable interpretation of these two series is $\nu_{11}(E) \pm \nu_6$. Then the extreme components (138 and 565) correspond to the 0–1 energy separation for ν_6, the middle components to the 1–2 separation and the inner components to the 2–3 separation. The middle components serve best for precise calculation of ν_{11}. We find

$$548 = \nu_{11} + \nu_6(1\text{–}2)$$
$$154 = \nu_{11} - \nu_6(1\text{–}2)$$
$$\nu_{11} = 351 \text{ cm.}^{-1}$$
$$\nu_6(1\text{–}2) = 198 \text{ cm.}^{-1}$$

Then we may solve for the other energy separations in the ν_6 sequence as

$$\nu_6(0\text{–}1) = 565 - 351 = 214 \text{ cm.}^{-1}$$
$$\nu_6(2\text{–}3) = 351 - 172 = 179 \text{ cm.}^{-1}$$

These frequencies indicate peaks at 137 cm.$^{-1}$ and at 530 cm.$^{-1}$ which are in satisfactory agreement with the less precise observations at these points.

The intensity of a sum combination should be higher than that of the corresponding difference combination by the Boltzmann factor giving the relative population of the respective initial states. Similarly, the bands arising from 1–2 and 2–3 transitions should have decreased intensity for the same reason. The Boltzmann factor for a 200 cm.$^{-1}$ energy difference at room temperature is about 0.4. The intensities of the various bands in this series are in reasonable agreement on this basis, although the measurements of intensity are only qualitative in most cases.

It is also interesting to note that the permitted 0–2 transition for internal rotation is calculated to be at 412 cm.$^{-1}$ while Smith, *et al.*,[4] found a band for the liquid at 411 cm.$^{-1}$. While we find no band for the gas at that frequency it is possible that the intermolecular forces in the liquid enhance its intensity.

We shall see below that the thermodynamic data offer an excellent confirmation of this general interpretation of the frequencies related to ν_6 and ν_{11}.

Potential Barrier to Internal Rotation.—With a succession of three accurately defined energy intervals we are in a position to investigate not only the height but also the shape of the potential barrier to internal rotation in methylchloroform. Let us take a series expansion for this potential, $V(\varphi)$, as

$$V(\varphi) = {}^1/_2V_3(1 - \cos 3\varphi) + {}^1/_2V_6(1 - \cos 6\varphi) + \dots$$

where φ is the angle of rotation and V_3, V_6 . . . are constants.

The energy levels are readily obtained if V_6, etc., are zero because the Schrödinger equation then reduces[6] to the Mathieu equation whose characteristic values have been tabulated. While an exact expression can be obtained in the form of an infinite determinant[7] for the case where V_6, etc., are not zero, the evaluation of this determinant has not proven to be practical. We have chosen to regard the potential terms beyond V_3 as a perturbation and to apply first-order perturbation theory. This requires the wave functions for the zeroth approximation, but the Mathieu functions are now available.[8] Since these functions are expressed in Fourier series, the necessary integrals are all of the well known type

$$\int_0^\pi \cos l \times \cos m \times \cos n \times dx$$

with l, m and n integers.

It was found that the two term series written above was sufficient with the values $V_3 = 1017$ cm.$^{-1}$ or 2910 cal./mole and $V_6 = 19.9$ cm.$^{-1}$ or 57 cal./mole. These constants yield energy intervals of 214.0, 197.4 and 179.0 cm.$^{-1}$ as compared to the observed values of 214, 197 and 179 cm.$^{-1}$. The effect of V_6 is to make the potential minima narrower and the maxima broader than would be given by the one term formula. This effect of V_6 is to increase the anharmonicity. It is evident from the small size of V_6 as compared to V_3 that the potential curve is only slightly different from the simple one-term cosine curve which has been generally applied to internal rotation problems. It was recently shown[9] that all of the available data on ethane are consistent with the simple one-term cosine formula for the potential barrier.

Thermodynamic Properties.—The entropy of gaseous methylchloroform was calculated by Rubin, Levedahl and Yost[10] from their low temperature heat capacity measurements. Their value is compared in Table II with the value given by the molecular data with the usual statistical formulas. We used the same bond distances, bond angles and moments of inertia as Smith, *et al.*,[4] and the frequencies listed in Table I.

The contribution of internal rotation was calculated for the precise spectroscopic energy levels as listed above. Since only the first three energy intervals were observed, values were calculated for a sufficient number of additional levels to complete the thermal range required.

TABLE II

THE ENTROPY OF METHYLCHLOROFORM AT 286.53°K.

Transl. + rotation	65.98 cal./deg. mole
Vibration	8.07
Internal rotation	2.15
Total, calcd.	76.20
Experimental	76.22 ± 0.16

TABLE III

CALCULATED THERMODYNAMIC FUNCTIONS FOR METHYLCHLOROFORM

T	C_p^0	$(H^0 - H_0^0)/T$	$-(F^0 - H_0^0)/T$	S^0
100	11.65	8.92	49.94	58.86
150	15.00	10.44	53.84	64.28
200	18.01	12.00	57.06	69.07
250	20.38	13.44	59.88	73.32
286.53	21.88	14.42	61.80	76.21
298.16	22.17	14.71	62.37	77.09
300	22.40	14.76	62.45	77.22
400	25.74	17.12	67.04	84.15
500	28.32	19.11	71.05	90.17
600	30.27	20.81	74.58	95.53
700	31.92	22.29	78.03	100.34
800	33.26	23.58	81.09	104.67
900	34.38	24.62	83.93	108.66
1000	35.33	25.74	86.58	112.34
1100	36.16	26.65	89.09	115.74
1200	36.86	27.48	91.44	118.92
1300	37.47	28.22	93.68	121.90
1400	38.01	28.90	95.79	124.68
1500	38.47	29.52	97.80	127.33

It is evident that the entropy values in Table II agree well within the experimental error. It is to be emphasized that this is a real check in that the thermal data were not used in evaluating any of the molecular constants. Also the still somewhat uncertain frequency, 1075 cm.$^{-1}$, for ν_3 contributes only 0.06 cal./deg.; consequently any moderate change here would not affect the agreement in Table II.

Table III contains the thermodynamic properties of methylchloroform as calculated for a series of temperatures. Since V_6 is small and has the same effect as V_3 on the average potential energy for internal rotation, we chose a simple barrier with $V_0 = V_3 + V_6 = 2967$ cal./mole for further calculations. On this basis the entropy contribution of internal rotation at 286.53°K. is 2.16 as compared to the 2.15 value from the exact calculation. The other features of the calculation followed the standard formulas.

We wish to acknowledge with thanks the assistance of Dr. Edward Gelles in the calculations presented in Table III.

BERKELEY, CALIFORNIA

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