Pure Rotation Spectrum of the HCl Flame

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Pure rotation lines for $j = 17$ to 33 of the emission spectrum of the HCl flame are measured with a KBr prism. The following empirical formulae are determined to represent two series of lines measured corresponding to pure rotation in the two lowest oscillation states,

$$N=0, \quad \nu = 20.9j - 0.00185j^3; \qquad N=1, \quad \nu = 20.2j - 0.00163j^3.$$

The linear coefficients agree satisfactorily with values calculated from the empirical oscillation-rotation formula. Theoretically the two cubic coefficients should be equal. The frequency is strongly influenced by the cubic term for high values of j so that the observed difference between these coefficients is regarded as real.

INTRODUCTION

A STUDY of a prism spectrometer in the far infrared, where available energy, rather than interference effects, limits the resolving power, led to the conclusion that the spectrometer should be able to resolve the rotation structure of absorption bands as well as it is possible to resolve them in the near infrared. In fact the resolving power should be as great or greater than that obtainable with a grating.[1]

Recently synthetic crystals, useful as prism materials (KCl, KBr and KI), have become available. These materials are transparent to greater than 30μ making possible a prism spectrometer for the study of far infrared spectra heretofore studied by reststrahlen technique and gratings.[2] Previously, the transmission limit of NaCl at 15–17μ determined the boundary for prism investigations into the infrared.

A prism spectrometer was constructed in this laboratory for the detailed study of spectra in this new region from 15–30μ. Recent developments in infrared technique were incorporated in this instrument such as high sensitivity thermocouple, large aperture optics, vacuum optical path, preliminary spectral purification by residual ray mirrors and Rubens selectively transparent shutters. These added to the possibilities of obtaining high resolving power in the far infrared. Further details of the features of this spectrometer are given in a previous paper.[3]

The first studies in this new spectral region should naturally be devoted to the problems which are of greatest general interest. The two problems studied and herein reported are the emission spectra of HCl and H_2O and also the atmospheric absorption.

A preliminary calculation shows that HCl molecules are excited by moderate temperatures $(T > 500°C)$ to quantum states $(j > 17)$ which would give rise to a pure rotation spectrum, $\lambda < 29\mu$. It is easier to get pure rotation spectra of a flame in emission than in the absorption of a heated gas, because of the weakness in total radiation. For this reason the emission spectrum of a hydrogen flame burning in an atmosphere of chlorine was chosen for study. Since this molecule has already been extensively studied in both the near and the far infrared, further contribution to its spectrum is of interest. The first study of the HCl emission spectrum was carried out by Julius in 1888.[4] He determined the position of the fundamental oscillation band. The author is not aware of any subsequent publications on the HCl flame. Recent studies under high dispersion of the emission of CO_2 and H_2O flames in the near infrared have been made by Neunhoeffer.[5]

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[1] John Strong, Phys. Rev. **37**, 1661 (1931).
[2] John Strong, Phys. Rev. **36**, 1663 (1930).
[3] John Strong, R. S. I. **3**, 810 (1932).
[4] W. H. Julius, Arch. Neerl. **22**, 310 (1888).
[5] M. Neunhoeffer, Ann. d. Physik **2**, 334 (1929); **4**, 352 (1930).

His resolution was sufficient to show that it was possible to get the rotation structure from a flame.

The Bunsen flame emission is of interest as a calibration source for this region ($15-30\mu$).

The absorption of water vapor in this region is of importance to meteorology because of the rôle it may play in the transfer of heat by radiation at temperatures from 200 to 300°K.

APPARATUS

A lamp wherein hydrogen was burned in an atmosphere of chlorine was designed and constructed by Dr. George C. Munro. This lamp consisted of three parallel fish tail burners, mounted in a vertical tube. A window opposite the fish tail burners was covered with a 1μ lacquer film. The radiations, passing out through the lacquer window, were focussed on the spectrometer slit by a $3''$ focus concave silvered mirror. With the exception of about $12''$ the entire optical path of the pure rotation radiation of the flame from flame to thermopile was in vacuum. A vertical stream of chlorine completely surrounded the burners. In order to prevent the delicate lacquer film from breaking due to the weight of the chlorine gas an air aspirator created a slightly reduced pressure at the top of the tube. The exhaust gases from the lamp were drawn through a flue by a fan. Here they were much diluted by air and discharged into the atmosphere from the top of the laboratory.

The current generated by the pure rotation spectrum falling on the thermopile[6] was measured with a Leeds and Northrup type H. S. galvanometer. The galvanometer was placed on a vibrationless support.[7] A galvanometer scale at 8 meters distance was read to 1/10 mm with a telescope. No amplifier was used.

CALIBRATION

Calibration wave-lengths were determined by the transmissions of atmospheric CO_2[8] (13.95μ) and CS_2[9] (25.2μ). (See Table I.) For CS_2 radi-

[6] John Strong, R. S. I. **3**, 65 (1932).
[7] John Strong, Phys. Rev. **37**, 1565 (1931).
[8] Louis Russell Weber and H. M. Randall, Phys. Rev. **40**, 835 (1932).
[9] D. M. Dennison and Norman Wright, Phys. Rev. **38**, 2077 (1931).

TABLE I. *Calibration data.*

λ in μ	M ×10,000	$n_{38°C}$	Gas	λ in μ	M ×10,000
14	4206	1.5141	CO_2	13.95	4190
15	4440	——	CS_2	25.20	7960
16	4692				
17	4963				
18	5254				
19	5564				
20	5895				
21	6248				
22	6620				
23	7015				
24	7432				
25	7871				
26	8332				
27	8820				
28	9340				
29	9890				

ations from $20-30\mu$ were separated from the total radiation of a globar by two reflections from fluorite. The purity of the spectrum dispersed by the HB_2 prism was further insured by the use of a NaCl shutter. The saturated vapor of CS_2 was retained in a thin cell equipped with 1μ lacquer windows. The cell was removable and the transmission was given by the ratio of "cell in" to "cell out" energies. (See Fig. 1.)

The prism was cut from a synthetic crystal grown by a method described in a former paper. It was cut and polished and figured by J. W. Fecker and Company. The prism, property of the University of Michigan, was kindly loaned to me by Professor Randall for this investigation.

The prism angle was measured on a "student" spectrometer as $28° 20' 10''$. The calibration curve was defined by this datum, the index of KBr at 13.95μ as determined from the smoothed
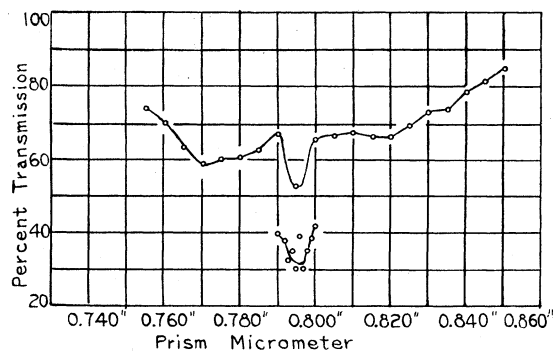

FIG. 1. CS_2 transmission curve for the 25.2μ band.

data of Korth,[10] the prism micrometer readings at 13.95 and 25.20μ, the fact that 1° prism rotation equals 0.1817″ on the micrometer screw, and the assumption that the ultraviolet terms do not contribute to the dispersion of KBr in this interval.

From these data the following dispersion equation for KBr is obtained in which ultraviolet terms appear in the constant term.

$$n^2 = 4.90435 - 19,858(\lambda_0^2 - \lambda^2)^{-1},$$

where $\lambda_0 = 88.3\mu$ as determined by Barnes.[11]

The relationship between prism micrometer readings, M, and λ is given by the relation:

Fig. 2. Emission spectra of Bunsen flame, A, of gas-oxygen flame B and C, and oxy-hydrogen flame, D and E.

[10] K. Korth, Zeits. f. Physik 84, 677 (1933).
[11] R. Bowling Barnes, Zeits. f. Physik 75, 723 (1932).

$$\frac{\sin^2 (48° \ 14' \ 52'' - M/.1817)}{\sin^2 (28° \ 20' \ 10'')} = 4.90435$$

$$- 19,858(7797 - \lambda^2)^{-1}.$$

This relationship is open to criticisms on the ground that the assumption that the ultraviolet terms are essentially constant may not be valid. Furthermore the index for 13.95μ is for 38°C whereas the prism was used at 23°C. It is contended that the errors arising from these sources are insignificant. The data used, with the exception of the index at 13.95μ, were all taken at 23°C. The temperature coefficient of the index of refraction of all known prism materials decreases to very low values at their extreme infrared limit of transmission. In any event the errors introduced would be of second order and should appear only midway between 13.95μ and 25.20μ as well as considerably beyond 25.20μ.

MEASUREMENTS ON H_2O

The new results obtained from measurements of the emission of a Bunsen flame are shown in Fig. 2, curve A and are tabulated in Table II. That these maxima are due to H_2O is indicated by the curves B and C for the emission of H_2 burning from two fish tail burners of the HCl
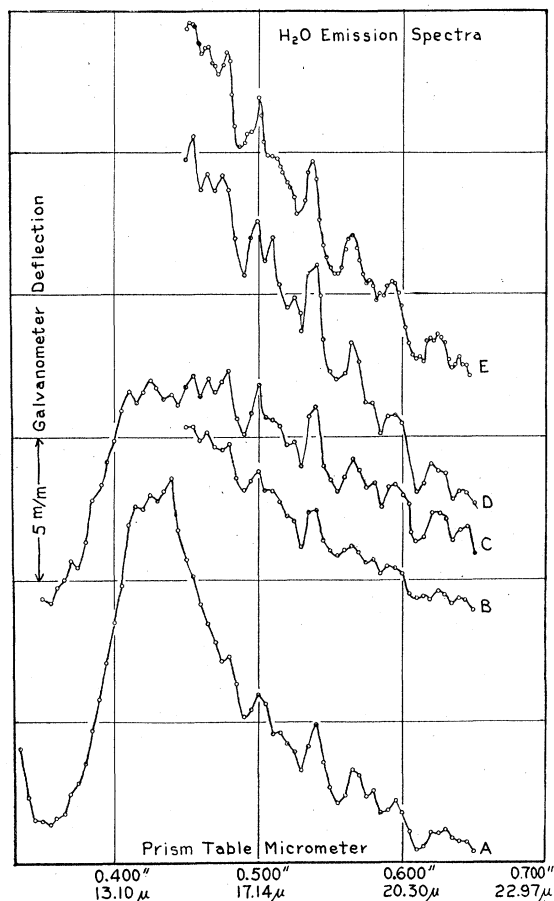
TABLE II.

H_2O emission lines

M $\times 1000$	λ in μ	M $\times 1000$	λ in μ	M $\times 1000$	λ in μ
413	13.54	500	17.14	578	19.65
425	14.19	510	17.49	593	20.09
440	14.84	525	18.00	616	20.75
452	15.33	538	18.42	620	20.86
464	15.81	565	19.25	630	21.13
478	16.34			642	21.46

Atmospheric absorption lines

$M \times 1000$	735	791	830	862	883
λ in μ	23.81	25.09	25.93	26.61	27.03

lamp in an atmosphere of air. Curves D and E are for one burner of the lamp with an atmosphere of pure oxygen instead of air as in the above case.

Unfortunately the emission of the H_2O flame was never extended beyond 20μ.

The "cell out" measurements on CS_2 give the absorption lines given in Table II. These atmospheric lines are presumably due to H_2O.
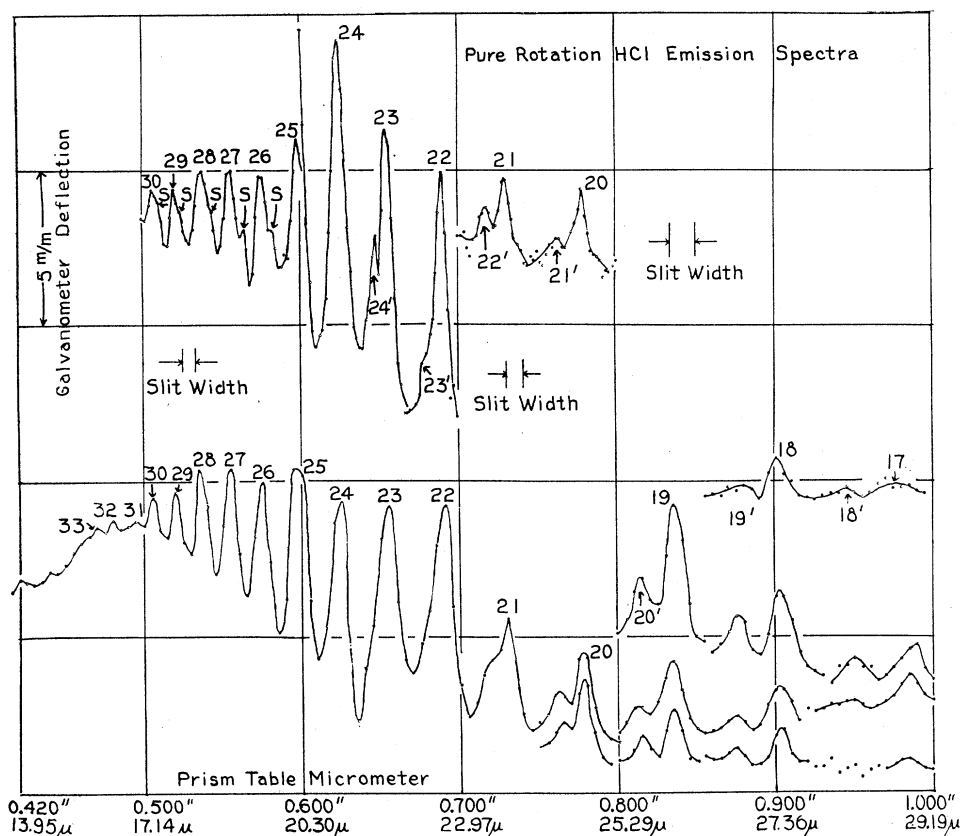
FIG. 3. Pure rotation HCl emission spectra.

MEASUREMENTS ON HCl

Measurements of the HCl rotation spectrum were made with an NaCl shutter beyond 24μ and metallic shutter below 24μ. As previously stated, the total emission of the flame was small (not perceptible to the hand) so the two fluorite reflections, used before with a Globar source, were unnecessary.

Results of all measures on HCl are plotted in Fig. 3 and given in Table III; about 50 lbs. of chlorine were boiled away to make these measures. The level of liquid chlorine was indicated by the frost which formed on the outside of the tank.

It is noticed that there are three series of lines. Those lines represented by the quantum numbers 17 to 33, those represented by the primed quantum numbers 18′ to 24′ and those represented as satellites of the lines 26S to 30S.

CLASSIFICATION OF HCl LINES

The difference between two energy states of rotation in the zero oscillation state is given by the relationship

$$W_0(j+1) - W_0(j-1) = \nu^+{}_{osc}(j-1)$$
$$- \nu^-{}_{osc}(j+1) = \nu_{rot}(j-1) + \nu_{rot}(j).$$

Using the oscillation-rotation data of Colby, Meyer and Bronk[12] we can make the following comparison between the values of this energy difference with that obtained from the data for the first series of pure rotation lines given in Table II. This comparison follows:

j	$\nu^+{}_{osc}(j-1) - \nu^-{}_{osc}(j+1)$	$\nu_{rot}(j-1) + \nu_{rot}(j)$	Δ
18	$3138.8 - 2429.9 = 708.9$	$345.6 + 364.6 = 710.2$	$-1.3 \sim$ /cm
19	$3148.1 - 2401.2 = 746.9$	$364.6 + 384.2 = 748.8$	$-1.9 \sim$ /cm

[12] Colby, Meyer and Bronk, Astrophys. J. **57**, 7 (1923).

The agreement to $1.3\sim/$cm for $j=18$ and to $1.9\sim/$cm for $j=19$ confirms the classification of the lines $j=17$ to $j=33$ as pure rotation lines of HCl in the ground oscillation state.

The corresponding relationship for the first oscillation state, $N=1$, is

$$W_1(j+1) - W_1(j-1) = \nu^+_{osc}(j) - \nu^-_{osc}(j)$$
$$= \nu_{rot}(j-1) + \nu_{rot}(j).$$

The comparison of the data of Colby, Meyer and Bronk with the second series of HCl lines is as follows:

j	$\nu^+_{osc}(j) - \nu^-_{osc}(j)$	$\nu_{rot}(j-1) + \nu_{rot}(i)$	Δ
18	$3155.4 - 2429.9 = 725.5$	$354.0 + 371.9 = 725.9$	$0.4\sim/$cm
19	$3161.5 - 2401.2 = 760.3$	$371.9 + 391.1 = 763.0$	$2.7\sim/$cm

The agreement to $0.4\sim/$cm for $j'=18$ and to $2.7\sim/$cm for $j'=19$ confirms a classification of the lines $j'=18$ to $j'=24$ as pure rotation lines of HCl in the state of oscillation $N=1$.

The five satellites designated by S, are unexplained. They are not due to pure rotation in the state $N=1$ since they do not agree with the positions predicted by an empirical equation representing the lines $j'=18$ to $j'=24$. They are not due to rotation isotope effect. This effect is very small for pure rotation as the chlorine atom is very near the center of rotation and the moment of inertia is consequently insensitive to small changes of its mass. For $j=27$ the distance between HCl_{37} and HCl_{35} is about $1\sim/$cm whereas the displacement of the satellite from the line $j=27$ is about $8\sim/$cm.

It would be inconsistent with the expected distribution in the energy states to classify these lines as pure rotation for the state $N=2$. One would expect more than only these five lines to appear.

They are not easily described to instrumental causes (as they might be if they were measured with a grating rather than a prism). The data are not sufficient to allow a precise determination of their wave-lengths on account of their nearness to the lines $j=26-j=31$.

Empirical Equations

The fourteen lines $j=17$ to $j=33$ were fitted to an equation of the form

$$\nu = Aj - Bj^3.$$

TABLE III. *Pure rotation HCl emission lines.*

j	M $\times1000$	λ in μ	ν observed in $\sim/$cm	ν calculated in $\sim/$cm	$\Delta\nu$ in $\sim/$cm
$N=0$					
17	985	28.93	345.6	346.2	-0.6
18	904	27.43	364.6	365.4	-0.8
19	835	26.03	384.2	384.4	-0.2
20	778	24.79	403.4	403.2	0.1
21	730	23.69	422.1	421.8	0.3
22	690	22.72	440.1	440.3	-0.2
23	655	21.82	458.3	458.2	0.1
24	624	21.08	474.4	476.0	1.6
25	598	20.23	494.3	493.6	0.7
26	575	19.56	511.2	510.9	0.3
27	555	18.95	527.7	527.9	-0.2
28	538	18.42	542.9	544.6	-1.7
29	520	17.82	561.1	561.0	0.1
30	506	17.35	576.4	577.1	-0.7
31	495	16.96	589.6	592.8	-3.2
32	480	16.41	609.4	608.2	1.2
33	470	16.04	623.4	623.2	0.2
$N=1$					
18'	949	28.27	354.0	354.1	-0.1
19'	876	26.89	371.9	372.6	-0.7
20'	813	25.57	391.1	391.0	0.1
21'	763	24.45	409.0	409.1	-0.1
22'	718	23.41	427.2	427.2	0
23'	680	22.48	444.8	444.8	0
24'	648	21.62	462.5	462.1	0.4
Satellites					
26S	582	19.76	506.1		
27S	564	19.23	520.0		
28S	544	18.61	537.3		
29S	524	17.95	557.1		
30S	510	17.49	571.7		

This was easily done by plotting ν/j versus j^2 and drawing a straight line through the points. A is determined by the intercept of this line and B is determined by its slope.

A similar procedure was followed for the lines $j'=18$ to $j'=24$. The equations obtained were

for $N=0$ $\quad \nu = 20.9j - 0.00185j^3$ and
for $N=1$ $\quad \nu' = 20.2j' - 0.00163j'^3$.

The data for lines $j=24$, 28 and 31 were not used in this determination. The calculated and observed frequencies are given in Table III together with discrepancies. Discarding the three lines just mentioned the average deviation for a single line from the calculated values is $0.4\sim/$cm. This is a measure of the accuracy of the determination of a single line.

Discussion

The blend $\frac{3}{4}HCl_{35} + \frac{1}{4}HCl_{37}$ gives a line for $j=27$ about $0.2\sim/$cm displaced from the line of pure HCl_{35}. Since this is small compared to

the $0.4\sim$/cm accuracy no analysis was carried out to determine two formulae (for $N=0$) for the two important isotopic constituents of the chlorine. More precise measures of this spectrum should, however, give data which would allow this isotope effect to be determined because the half-line breadth is calculated to be of the order of $1\sim$/cm.

From the formula representing the lines of the oscillation-rotation spectrum it is possible to calculate the coefficient of the pure rotation spectrum from the relationship (Linear coefficient+Square coefficient)$_{oscillation}$=(Linear coefficient)$_{pure\ rotation}$. From the data of Colby, Meyer and Bronk, we get good agreement with the pure rotation coefficient.

$$20.598+0.301=20.899$$

(from oscillation-rotation lines).

This value, 20.899, agrees better with the empiri-cal value 20.9 than with Czernys' value 20.794.[13]

The difference between the linear coefficient, A, for $N=0$ and A for $N=1$ should be twice the square coefficient of the oscillation-rotation formula. Here we have

$$20.9-20.2=0.7 \text{ (observed) and}$$

$$2\times.3=0.6 \text{ (calculated).}$$

The cubic term from the Colby, Meyer and Bronk data is 0.002056 as compared to 0.00185 for $N=0$ and 0.00163 for $N=1$ and 0.00164 from Czerny's measurements. Since the determination of the cubic term is more accurate when determined for larger values of j the value 0.00185 for $N=0$ and 0.00163 for $N=1$ are therefore to be considered most reliable.

In conclusion I wish to acknowledge my appreciation of· the help I have obtained from Professor R. A. Millikan and Professor W. V. Houston.

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[13] M. Czerny, Zeits. f. Physik **53**, 317 (1929).