Millimeter- and Submillimeter-Wave Spectra and Molecular Constants of Silver Chloride*

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A new type of high-temperature spectrometer for operation in the millimeter- and submillimeter-wave regions has been constructed and used for measurements of numerous rotational transitions of AgCl at 750°C. Significant improvement in sensitivity over other high-temperature spectrometers operating in the submillimeter region has been achieved. With it, rotational lines of AgCl up to a frequency of 366 858.51 Mc/sec ($\lambda=0.8$ mm) have been measured with high precision. The molecular constants obtained are. For $Ag^{107}Cl^{35}$, $B_e=3686.9639$ Mc/sec, $\alpha_e=17.8498$ Mc/sec, $\gamma_e=0.01883$ Mc/sec, $D_e=1.8903$ kc/sec, $\omega_e=343.52$ cm^{-1}, $\omega_e x_e=1.169$ cm^{-1}, $r_e=2.28078$ Å; for $Ag^{109}Cl^{35}$, $B_e=3670.2777$ Mc/sec, $\alpha_e=17.7284$ Mc/sec, $\gamma_e=0.01859$ Mc/sec, $D_e=1.8739$ kc/sec, $\omega_e=342.68$ cm^{-1}, $\omega_e x_e=1.163$ cm^{-1}, $r_e=2.280779$ Å; for $Ag^{107}Cl^{37}$, $B_e=3536.8734$, $\alpha_e=16.7705$ Mc/sec, $\gamma_e=0.01708$ Mc/sec, $D_e=1.7383$ kc/sec, $\omega_e=336.58$ cm^{-1}, $\omega_e x_e=1.118$ cm^{-1}, $r_e=2.280781$ Å; for $Ag^{109}Cl^{37}$, $B_e=3520.1846$ Mc/sec, $\alpha_e=16.6520$ Mc/sec, $\gamma_e=0.01710$ Mc/sec, $D_e=1.7192$ kc/sec, $\omega_e=336.04$ cm^{-1}, $\omega_e x_e=1.121$ cm^{-1}, $r_e=2.280782$.

INTRODUCTION

RECENTLY Krisher and Norris[1] reported centimeter wave measurements of two rotational transitions of AgCl. From measurements of these centimeter-wave transitions alone, the centrifugal distortion constants and vibrational constants could not be obtained with meaningful accuracy. For example, these observers report the centrifugal stretching constant D_e for $Ag^{107}Sl^{35}$ with an error limit as large as the constant itself. The ω_e and $\omega_e x_e$ values they list are taken from infrared data. Since evaluation of the other molecular parameters such as the B_0 values and potential constants depends to some extent on the unmeasured centrifugal distortion, we seemed justified in completing our initially planned work on the millimeter-wave spectrum of the various isotopic species of this substance. However, the high-J transitions are not sensitive to the Stark effect, nor to nuclear quadrupole splitting. Therefore the molecular dipole moment and the Cl nuclear quadrupole coupling constants which Krisher and Norris[1] give are more accurate than we can obtain. Thus there are advantages to be gained from microwave measurements at both low and high frequencies.

SPECTROMETER

Numerous measurements on millimeter and submillimeter wave rotational spectra have been made in this laboratory with high-temperature, molecular-beam absorption techniques.[2–4] In the molecular-beam absorption spectrometer employed, the molecules were simply sprayed across the path of the microwave power. Because the absorption coefficients of linear molecules are strong in the shorter millimeter-wave region, it was possible to detect the power absorption directly without the more complicated techniques of molecular beam resonance. Some increase in sensitivity was needed, however, for observation of less abundant isotopes.

Our new spectrometer is essentially of the hot-cell type, but it uses the principles of the free-space cell as developed in this laboratory. The disadvantage of increased Doppler broadening in this instrument is more than offset by the greatly inproved signal-to-noise ratio resulting from a fivefold increase in the absorption path. This spectrometer is simpler to operate and easier to construct than any other microwave spectrometer described in the literature.[5–8]

Figure 1 is a sketch of the absorption cell. The silver chloride, or other substance to be investigated, is placed along the bottom side in the central region of a round, cylindrical sleeve of a nonreactive metal which fits closely inside a stainless steel pipe with a 2.5 in. diam and a 60 in. length. The pipe, sealed at opposite ends with Teflon windows, is evacuated and then heated over a 30 in. portion of the central region. The ends of the cell in the region of the Teflon windows are cooled by coils containing flowing water. Conical focusing horns electroformed from copper were used with Teflon lenses to focus the millimeter waves through the cylindrical absorption cell. It is remarkable that the losses of this system are so low that we have been able to measure submillimeter wave rotational lines of Li^7F^{19} to wavelengths as short as 0.6 mm. Figure 2 shows a display on the cathode-ray oscilloscope of AgCl lines in the millimeter- and submillimeter-wave regions.

The harmonic generator earlier designed[9] in this laboratory was used for generation and detection of the millimeter- and submillimeter-wave radiation. A klys-

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[1] L. C. Krisher and W. G. Norris, J. Chem. Phys. **44**, 391 (1966).
[2] J. R. Rusk and W. Gordy, Phys. Rev. **127**, 817 (1962).
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[5] A. Honig, M. Mandel, M. L. Stitch, and C. H. Townes, Phys. Rev. **96**, 629 (1954).
[6] D. R. Lide, Jr., J. Chem. Phys. **42**, 1013 (1965).
[7] J. Hoeft, Z. Naturforsch. **19a**, 1134 (1964).
[8] T. Törring, Z. Naturforsch. **19a**, 1428 (1964).
[9] W. C. King and W. Gordy, Phys. Rev. **93**, 407 (1954).

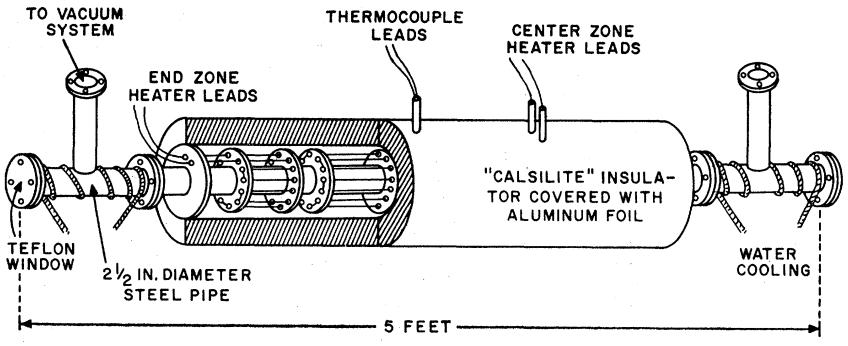


FIG. 1. Diagram of the absorption cell for high-temperature operation. Focusing horns and Teflon lenses (not shown) are employed to direct the microwave energy through the cell.

tron (manufactured by OKI Electric Industry, Ltd. (Japan)) operating in the region of 8–9 mm was used to drive the harmonic generator. Frequency measurements were made in the usual way, with a frequency standard monitored by station WWV.

With this spectrometer, linewidths as small as 150 kc/sec were readily obtainable on these AgCl lines at the operating temperature of 750°C. These lines are sharper than would be expected for a normal hot cell operating at this temperature. We therefore conclude that the effective line broadening temperature in the cell is appreciably less than the temperature required to vaporize the molecules.

OBSERVED FREQUENCIES AND SPECTRAL CONSTANTS

Dunham's theory[10] was used in analysis of the data. Comparisons of final results show, however, that the more familiar formula derived from the simple Morse potential function[11] leads to molecular constants which are not distinguishably different from those derived from Dunham's theory. In his solution of the Schrödinger equation for the diatomic vibrating rotor Dunham employed a potential function in the form of the power series:

$$V(\xi)=hca_0\xi^2(1+a_1\xi+a_2\xi^2+a_3\xi^3+\cdots), \quad (1)$$

where $\xi=(r-r_e)/r_e$ and where the a_0, a_1, a_2, $\cdots$ represent the potential constants. His solution led to the formula:

$$F_{vJ}=\sum_{lm} Y_{lm}(v+\tfrac{1}{2})^l J(J+1)^m \quad (2)$$

for the energy levels. The Y's represent spectral constants to be evaluated from observed frequencies; v and J are the vibrational and rotational quantum numbers. Only six of the spectral constants are required for fitting the theory to the present observations within the accuracy of the measurements. Applications of the selection rules for pure rotational absorption having $\Delta v=0$ and $\Delta J=+1$ leads to the expression:

$$\begin{aligned}\nu=&2Y_{01}(J+1)+2Y_{11}(v+1/2)(J+1)\\&+2Y_{21}(v+1/2)^2(J+1)+4Y_{02}(J+1)^3\\&+4Y_{12}(v+1/2)(J+1)^3\\&+Y_{03}(J+1)^3[(J+2)^3-J^3], \quad (3)\end{aligned}$$

which was applied to the observed frequencies.

Equation (3) was fitted by least squares methods to the observed frequencies with the aid of a digital computer (IBM 7072). Many more frequencies were measured than were necessary for evaluation of the six constants. Therefore the agreement between observed and calculated frequencies gives a check on the consistency and accuracy of the observations as well as a check on the adequacy of the theory. Table I gives comparisons of all observed frequencies with those calculated from the fitted constants for the four different isotopic species. The greatest discrepancy between observed and calculated frequency is only 0.08 Mc/sec, well within the accuracy of the measurement, only 0.1 Mc/sec for the highest frequencies. The six Dunham constants Y thus derived for the different isotopic species are listed in Table II.

In the present work the Dunham constants of Eq. (3) were found to correspond numerically within the

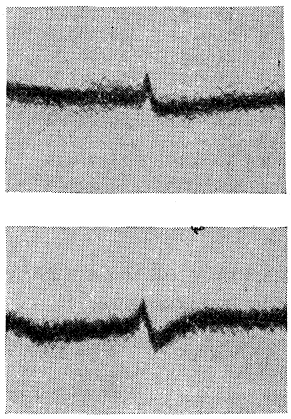


FIG. 2. Illustrations of the signal-to-noise ratio obtained with oscilloscope presentation at a high submillimeter-wave frequency (upper curve) and on molecules in a high vibrational state (lower curve).

[10] J. L. Dunham, Phys. Rev. **41**, 721 (1932).
[11] P. M. Morse, Phys. Rev. **34**, 57 (1929).

TABLE I. Observed frequencies of silver chloride.

		$Ag^{107}Cl^{35}$		$Ag^{109}Cl^{35}$		$Ag^{107}Cl^{37}$		$Ag^{109}Cl^{37}$	
v	$J \rightarrow J'$	Measured frequencies (Mc/sec)	Difference from calculated frequencies (Mc/sec)	Measured frequencies (Mc/sec)	Difference from calculated frequencies (Mc/sec)	Measured frequencies (Mc/sec)	Difference from calculated frequencies (Mc/sec)	Measured frequencies (Mc/sec)	Difference from calculated frequencies (Mc/sec)
0	14 → 15	110 315.79	−0.00	109 817.19	0.05	105 831.31	−0.01	105 332.67	−0.01
0	19 → 20	147 061.26	−0.02	146 396.80	−0.05	141 084.05	0.00	140 419.39	0.07
0	22 → 23	169 097.96	0.03	168 334.02	−0.00	169 271.48	−0.01	168 474.24	0.01
0	23 → 24	176 441.53	0.01	175 644.44	−0.01	176 315.96	−0.03	175 485.62	−0.04
0	24 → 25	183 783.97	0.04	182 953.76	0.00	183 359.37	−0.03	182 495.87	−0.01
0	27 → 26	205 804.43	−0.02	204 874.81	0.03	204 482.84	0.04	203 520.08	0.02
0	28 → 29	213 142.04	0.02	212 179.42	−0.02	211 521.68	0.01	210 525.86	−0.03
0	29 → 30	220 478.36	0.03	219 482.66	−0.00	218 559.22	0.03	217 530.34	−0.02
0	32 → 33	242 479.03	0.01	241 384.12	0.04	239 664.03	−0.04	238 535.95	−0.04
0	33 → 34	249 809.72	−0.06	248 681.74	0.01	246 696.13	−0.02	245 534.95	0.06
0	34 → 35	257 138.71	0.02	255 977.83	−0.02	253 726.76	0.01	252 532.67	−0.02
0	39 → 40	293 759.30	0.02	292 433.57	0.02	281 833.92	0.01		
0	44 → 45	330 334.49	−0.02			105 329.18	0.03	104 834.10	0.02
0	49 → 50	366 858.51	−0.01	365 204.52	−0.01	140 414.55	0.04	139 754.73	−0.01
1	14 → 15	109 781.45	−0.03	109 286.47	0.03	168 468.11	0.00	167 676.58	−0.01
1	19 → 20	146 348.79	−0.05	145 689.08	0.00	175 479.13	−0.04	174 654.61	0.04
1	22 → 23	168 278.58	0.02	167 520.18	0.01	182 489.02	0.01	181 631.72	−0.03
1	23 → 24	175 586.52	0.01	174 795.21	0.01	203 512.10	0.04	202 556.19	0.01
1	24 → 25	182 893.42	−0.06	182 069.22	−0.05	210 517.47	0.01	209 528.71	−0.02
1	27 → 28	204 806.89	−0.01	203 884.07	0.01	217 521.55	0.01	216 499.93	0.01
1	28 → 29	212 108.91	−0.01	211 153.27	−0.01	238 525.88	−0.01	237 405.74	0.06
1	29 → 30	219 409.65	−0.04	218 421.16	−0.03	245 524.49	0.02	244 371.66	−0.01
1	32 → 33	241 303.36	0.00	240 216.45	0.01	252 521.72	−0.02	251 336.02	0.03
1	33 → 34	248 598.35	−0.00	247 478.67	−0.01	104 828.15	−0.01	104 336.62	−0.01
1	34 → 35	255 891.74	0.04	254 739.38	−0.05	139 746.53	−0.03	139 091.40	−0.04
1	44 → 45	328 731.15	0.03	...	...	167 666.40	−0.01	166 880.56	−0.04
2	14 → 15	109 248.16	0.01	108 756.87	−0.00	174 643.94	0.03	173 825.37	0.06
2	19 → 20	145 637.71	0.03	144 982.95	−0.05	181 620.52	−0.03	180 769.34	−0.04
2	22 → 23	167 460.89	0.06	166 708.06	0.02	202 543.39	−0.00	201 594.29	0.00
2	23 → 24	174 733.32	0.00	173 947.77	0.03	209 515.31	0.01	208 533.58	0.03
2	24 → 25	182 004.61	−0.00	181 186.46	−0.03	216 485.99	0.00	215 471.69	−0.01
2	27 → 28	203 811.47	−0.01	202 895.42	−0.02	237 390.12	−0.05	236 277.97	0.04
2	28 → 29	211 077.92	0.01	210 129.26	0.01	244 355.34	−0.03	243 210.76	−0.07
2	29 → 30	218 343.11	−0.03	217 361.82	0.01	251 319.05	0.03	250 141.95	−0.03
2	32 → 33	240 130.11	0.06	239 051.24	−0.02	173 810.56	−0.01	172 997.93	−0.01
2	33 → 34	247 389.65	−0.05	246 278.06	0.04			179 908.66	0.03
2	34 → 35	254 647.51	−0.03	253 503.45	0.01	208 515.20	0.01	207 540.58	−0.00
3	14 → 15	108 716.04	0.02	108 228.30	0.05	215 452.51	0.03	214 445.51	0.03
3	19 → 20	144 928.29	−0.04	144 278.20	0.01	243 188.50	−0.00	242 052.15	−0.02
3	22 → 23	166 645.01	0.02	165 897.70	−0.02			248 950.23	0.01
3	23 → 24	173 881.92	0.01	173 102.12	0.03				
3	24 → 25	181 117.74	−0.01	180 305.56	−0.01				
3	27 → 28	202 818.20	−0.05	201 908.87	−0.06				
3	28 → 29	210 049.15	−0.01	209 107.39	0.05				
3	29 → 30	217 278.81	0.00	216 304.73	0.03				
3	32 → 33	238 959.48	−0.02	237 888.44	−0.01				
3	33 → 34	246 183.36	0.05	245 080.04	0.03				
3	34 → 35	253 405.78	0.03	252 270.19	−0.00				
4	23 → 24	173 032.33	0.01	172 258.28	0.02				
4	24 → 25	180 232.72	0.02	179 426.56	−0.03				
4	28 → 29	209 022.53	0.01	208 087.75	0.01				
4	29 → 30	216 216.80	0.00	215 249.96	−0.05				
4	33 → 34	244 979.79	−0.01	243 884.56	0.01				
4	34 → 35	252 166.80	−0.03	251 039.52	−0.00				

accuracy of the measurements to the more familiar spectral constants[12]:

$$B_e = Y_{01}, \quad \alpha_e = -Y_{11},$$
$$D_e = -Y_{02}, \quad \gamma_e = Y_{21},$$
$$H_e = Y_{03}, \quad \beta_e = Y_{12}.$$

[12] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York. 1950), Chap. 3.

The constants ω_e and $\omega_e x_e$ are not directly measured since no vibrational transitions were observed. However, these constants were indirectly obtained to a high degree of accuracy from the rotational constants (see later discussion). In some diatomic molecules where many transitions are measured with high precision, as in the present work, a difference in B_e and Y_{01} can be detected. For the AgCl, however, the difference was so small as to produce effects only in the eighth figure

TABLE II. Measured rotational constants.

Molecule	$Y_{01}(B_e)$ (Mc/sec)	$Y_{11}(-\alpha_e)$ (Mc/sec)	$Y_{21}(\gamma_e)$ (Mc/sec)	$Y_{02}(-D_e)$ (kc/sec)	$Y_{12}(\beta_e)$ (kc/sec)	$Y_{03}(H_e)$ (cps$\times 10^{-3}$)
$Ag^{107}Cl^{35}$	3686.9639	−17.8498	0.01883	−1.8903	−0.00054	−0.29
	±0.0006	±0.0003	±0.00005	±0.0004	±0.00009	±0.08
$Ag^{109}Cl^{35}$	3670.2777	−17.7284	0.01859	−1.8739	−0.00051	−0.10
	±0.0006	±0.0003	±0.00005	±0.0005	±0.00009	±0.08
$Ag^{107}Cl^{37}$	3536.8734	−16.7705	0.01708	−1.7383	−0.00032	
	±0.0008	±0.0004	±0.00008	±0.0008	±0.00013	
$Ag^{109}Cl^{37}$	3520.1846	−16.6520	0.01710	−1.7192	−0.00064	
	±0.0010	±0.0005	±0.00010	±0.0011	±0.00017	

of Y_{01} and to be within the limits of error in the measurements of Y_{01}.

From the B_e values, the equilibrium internuclear distance was calculated for each isotopic species. These distances are given in Table III. The absolute values of r_e are limited by the error in h to six significant figures, but the relative values of r_e are measured more accurately.

TABLE III. Internuclear distances.[a]

Molecule	r_e (Å)
$Ag^{107}Cl^{35}$	2.280781±0.000031
$Ag^{109}Cl^{35}$	2.280779±0.000031
$Ag^{107}Cl^{37}$	2.280781±0.000031
$Ag^{109}Cl^{37}$	2.280782±0.000031

[a] The value 505534.9 Mc/sec amu Å^2 was used to convert the rotational constant B_e to r_e.

VIBRATIONAL CONSTANTS

The vibrational constants ω_e and $\omega_e x_e$ correspond to the Dunham constants Y_{10} and $-Y_{20}$, respectively. While the constants are not measured directly because only $\Delta v=0$ transitions are observed in the millimeter region, they can be obtained from our measurements with the Dunham theory.[10] The values which we obtained for these constants are listed in Table IV. These could not be found from the earlier centimeter wave measurements,[1] but they have been previously measured with optical spectroscopy. In Table IV we list Bryce's values[13] from optical spectroscopy for comparison with ours. It is of interest that we can measure these vibrational constants indirectly in the millimeter and submillimeter region with higher precision than they have been obtained by more direct measurements in the optical region. The constant ω_e represents the fundamental vibrational frequency; $\omega_e x_e$, the first anharmonicity constant.

TABLE IV. Vibrational constants.

Molecule	Present ω_e (cm^{-1})	Optical[a] spectroscopy ω_e	Present $\omega_e x_e$ (cm^{-1})	Optical[a] spectroscopy $\omega_e x_e$
$Ag^{107}Cl^{35}$	343.52±0.04	343.6	1.169±0.003	1.163
$Ag^{109}Cl^{35}$	342.68±0.04	342.4	1.163±0.003	
$Ag^{107}Cl^{37}$	336.58±0.08	336.0	1.118±0.005	
$Ag^{109}Cl^{37}$	336.04±0.11		1.121±0.006	

[a] Reference 13.

POTENTIAL CONSTANTS

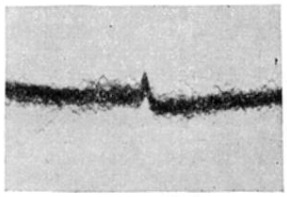
The first four potential constants in the Dunham expression Eq. (1) were obtained from the observed Y values with the relation given by Dunham.[10] The resulting values are listed in Table V. Values of these constants could not be obtained from the earlier centimeter wave measurements alone, but Krisher and Norris[1] combined their data with the vibrational constants from optical spectroscopy[13] to obtain values which are in good agreement with the constants obtained from microwave measurements only.

TABLE V. Potential coefficients.

Molecule	a_0 (cm^{-1})	a_1	a_2	a_3
$Ag^{107}Cl^{35}$	239 881±57	−3.2538±0.0003	6.898±0.013	−11.58±0.14
$Ag^{109}Cl^{35}$	239 788±58	−3.2533±0.0003	6.898±0.014	−11.61±0.14
$Ag^{107}Cl^{37}$	240 052±107	−3.2545±0.0006	6.924±0.023	−11.80±0.24
$Ag^{109}Cl^{37}$	240 423±159	−3.2563±0.0008	6.889±0.030	−11.47±0.32

[13] B. A. Bryce, Phys. Rev. 35, 960 (1930).

$Ag^{109}Cl^{35}$
$v=0$
$J=49 \rightarrow 50$
$\nu=365\ 204.52$ Mc/sec
$\lambda=0.82$ mm



$Ag^{107}Cl^{35}$
$v=4$
$J=29 \rightarrow 30$
$\nu=216\ 216.80$ Mc/sec
$\lambda=1.39$ mm

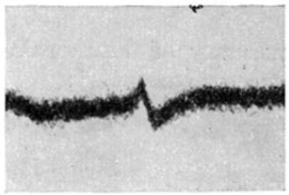


FIG. 2. Illustrations of the signal-to-noise ratio obtained with oscilloscope presentation at a high submillimeter-wave frequency (upper curve) and on molecules in a high vibrational state (lower curve).