über den Erwartungswerten für $m=0$ modifiziert. Da die Quadrupolkopplungskonstanten sich in 1. Näherung für angeregte interne Rotationszustände nicht ändern [21], ist die Hyperfeinstruktur mit Kenntnis der χ_{gg} (aus $m=0$) für $m \neq 0$ im voraus berechenbar und kann als Zuordnungshilfe verwendet werden. Die Passung der berechneten zu den gemessenen Frequenzaufspaltungen wird allerdings schlechter als für $m=0$, was vermutlich seinen Grund in den Vereinfachungen des zugrunde liegenden Modells hat.

$\chi_{aa} = -(0{,}33 \pm 0{,}02)$ MHz, $\chi_{bb} = -(2{,}86 \pm 0{,}02)$ MHz,
$\chi_{cc} = +(3{,}19 \pm 0{,}02)$ MHz,
$|\mu_a| = (0{,}72 \pm 0{,}01)$ D, $|\mu_b| = (1{,}71 \pm 0{,}02)$ D.

Tab. 4. Quadrupolkopplungskonstanten und Dipolmomentkomponenten mit Standardfehlern aus Linien $m=0$.

Neben den Quadrupolkopplungskonstanten wurden dem $m=0$-Spektrum die Information über die Dipolmomentkomponenten entnommen. Sie wurden nach dem Schema des starren Kreisels an die Frequenzablagen der Stark-Satelliten von drei $m=0$-Linien bei verschiedenen Feldstärken angepaßt, und zwar:

$$3_{2,1} - 3_{1,2} \quad (M=3);$$
$$4_{2,2} - 4_{1,3} \quad (M=4);$$
$$5_{2,3} - 5_{1,4} \quad (M=5).$$

Es wurde bei möglichst hohen Feldstärken gemessen, da sich dann der Einfluß der Quadrupolwechselwirkung vernachlässigen läßt.

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[21] R. LETT u. H. FLYGARE, J. Chem. Phys. **47**, 4730 [1967].

The Rotational Spectra and Dipole Moments of AgF and CuF by Microwave Absorption

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The rotational transitions $J=1 \rightarrow 2$ and $2 \rightarrow 3$ were measured for $^{107}Ag^{19}F$ and $^{109}Ag^{19}F$ by microwave absorption. These spectra allowed the determination of the Dunham-coefficients Y_{01}, Y_{11}, Y_{21}, and Y_{02} and from these the potential coefficients a_0 and a_1 and internuclear distance r_e were derived. For $^{63}Cu^{19}F$ and $^{65}Cu^{19}F$ the hyperfine structure was observed in the $J=0 \rightarrow 1$ and $1 \rightarrow 2$ rotational spectra. In addition to the Dunham coefficients the quadrupole coupling constants, $e\,q\,Q$, and spin-rotation coupling constant, c, for the Cu nucleus were obtained. Stark effect measurements on both AgF and CuF resulted in the determination of the electric dipole moment for the ground vibrational state.

Since the advent of high temperature microwave spectroscopy, the alkali halides, or the group I_a-VII diatomic molecules, have been studied in great detail. However, the first MW rotational study of a member of the I_b-VII sub-group appeared only recently. That study of AgCl [1] was followed quickly with a similar investigation of AgBr [2], but no new studies have since appeared. Rotational investigations and especially Stark effect measurements on this sub-family of the alkali halides are highly desirable from a theoretical view point; however, this group presents experimental difficulties since many of these monohalides are thermally unstable or chemically reactive when in contact with hot surfaces. The silver and copper monofluorides appear more reactive and unstable than their other monohalides and have required some special techniques for spectral observation.

Our initial observations were made in the molecular beam spectrometer which was employed in earlier measurements [3]. About 5 grams of AgF (80% pure material) were place in the tantalum oven. The

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[1] L. C. KRISHER and W. G. NORRIS, J. Chem. Phys. **44**, 391 [1966]. — E. PEARSON and W. GORDY, Phys. Rev. **152**, 42 [1966].

[2] L. C. KRISHER and W. G. NORRIS, J. Chem. Phys. **44**, 974 [1966].

[3] T. TÖRRING, Z. Naturforsch. **23 a**, 777 [1968].

search region was significantly reduced because the rotational constant of ^{107}AgF was available from absorption band spectra [4]. This proved to be quite fortunate since we subsequently found that the $J=1 \rightarrow 2$, $v=0$ resonance could be observed at 750 °C for no more than 5 minutes before the AgF was completely decomposed and the Ta oven rendered useless due to chemical attack. Later, attempts were made to observe the $J=0 \rightarrow 1$ transitions in a hot-cell spectrometer, but these met complete failure. Since AgF is liquid above 450 °C and is thus in close contact with the hot metal oven surfaces, several attempts to observe this resonance were made by first coating the Ta oven with a non-reactive substance with the hope that less decomposition and reaction would result. An alcoholic paste of ZrO_2 and MgO was applied to the inside oven surface and baked at 1000 °C. Upon heating AgF to 750 °C in this oven, complete decomposition occurred and no resonance was observed. Since there was no apparent reaction with the Ta oven, reaction with the oxides was assumed. Next, CaF_2 was tried as coating material; however, it gave a very brittle, flakey layer which would not adhere to the oven walls. Considering CaF_2 to be still a good "buffer" material, i. e. a material which reduces contact of the investigated substance with the oven walls, is inert with respect to this substance, and which also has a low vapor pressure at the temperature of the study, we tried an equal volume mixture of AgF and CaF_2. With this mixture the normal one hour run could be performed at 750 – 850 °C and relatively little decomposition occurred. The Ta oven could also be used for two or three such runs before the Ag attack produced holes in the walls.

In the case of CuF the situation was somewhat better since it seems to be more stable than AgF and the CuF_2 starting material remains solid at the working temperature. The existence of the monofluoride in the vapor over CuF_2 has been demonstrated in a molecular beam deflection study [5]. A recent mass spectroscopic study [6] of CuF resulted in a higher calculated dissociation energy for the monofluoride than the difluoride. By simply heating CuF_2 in the Ta oven to 800 – 1100 °C the monofluoride was produced. Judging from the observed line intensities it appears that the conversion to monofluoride is better than 50%. A wide temperature region is indicated above since the higher temperature was often required to get the decomposition reaction started, then it was necessary to quickly reduce the temperature in order to prevent the CuF from vaporizing too quickly. No noticable difference occurred upon mixing CuF_2 with CaF_2. Since the nuclear quadrupole moment of the Cu nucleus produces hyperfine splitting in the rotational spectrum, it was highly desirable to measure the $J=0 \rightarrow 1$ transitions where the splitting is largest. These transitions occur outside the range of the molecular beam spectrometer, so the hot-cell spectrometer [7] was employed. It was found that the $J=0 \rightarrow 1$ lines could be observed only when the CuF_2 was placed directly in the split wave-guide absorption cell which resulted in some variations in the transmission of the cell. The temperature had to be carefully controlled between 650 and 700 °C so that the decomposition reaction would not ocur too swiftly.

The $J=1 \rightarrow 2$ and $2 \rightarrow 3$ rotational transitions of AgF listed in Table 1 were observed with line widths of 450 kHz. Observation of the $v=2$ transitions proved extremely difficult, even when the oven was rapidly heated above the normal observation temperature in order to produce a greater density of absorbing molecules. Success was obtained only after the sensitivity of the detecting system was improved by phase lock-in detection. Although the $v=0$ transition could be measured with a signal to

$J \rightarrow J+1$	v	ν (MHz)	$\Delta\nu$ (MHz)
		$^{107}Ag^{19}F$ (51,35%)	
$1 \rightarrow 2$	0	31 746,846 (30)	0,023
$1 \rightarrow 2$	1	31 517,450 (50)	0,025
$2 \rightarrow 3$	0	47 619,806 (30)	– 0,012
$2 \rightarrow 3$	1	47 275,719 (50)	– 0,016
$2 \rightarrow 3$	2	46 933,000 (100)	– 0,015
		$^{109}Ag^{19}F$ (48,65 %)	
$1 \rightarrow 2$	0	31 659,100 (30)	– 0,032
$1 \rightarrow 2$	1	31 430,625 (50)	0,001
$2 \rightarrow 3$	0	47 488,076 (30)	0,018
$2 \rightarrow 3$	1	47 145,433 (50)	– 0,002
$2 \rightarrow 3$	2	46 804,119 (100)	0,014

Table 1. Observed rotational transitions of AgF. The last column contains the difference between the calculated and measured line frequencies.

[4] R. M. Clements and R. F. Barrow, Chem. Comm. No. 1254, p. 27 [1968].

[5] A. Büchler, J. L. Stauffer, and W. Klemperer, J. Chem. Phys. **40**, 3471 [1964].

[6] D. L. Hildenbrand, J. Chem. Phys. **48**, 2457 [1968].

[7] J. Hoeft, F. J. Lovas, E. Tiemann, R. Tischer, and T. Törring, Z. Naturforsch. **24 a**, 1217 [1969].

noise ratio of 50 the $v=2$ transition was obtained with only a $2-3$ signal to noise ratio. For a Boltzmann distribution of states at 1000 °K one expects an intensity ratio of 2.2 for transitions from successive vibrational states, thus one would expect a S/N for the $v=2$ transition of about 10. Although a Boltzmann distribution is not expected to rigidly apply due to a non-equilibrium situation in the oven whose apparature is 3 mm × 15 cm, a large departure from the Boltzmann distribution was rather unexpected, because almost no noticable departure had been previously observed with other molecules studied in this spectrometer. Observation of the ^{109}AgF $v=0$ and ^{107}AgF $v=1$ transitions in immediate succession resulted in an intensity ratio of about 8 in comparison to the expected 2.2. Both isotopes are essentially equally abundant and these two lines were selected since they lie relatively close to one another.

The molecular constants derived from the frequency measurements are listed in Table 2 and compare quite well with those from band spectra. A least squares fit was obtained with a computer program that makes use of the dependence of the rotational constants on the molecular reduced mass according to the following equations:

	Present	*Earlier*[4]
ω_e	514,6 (111) cm^{-1}	513,45 cm^{-1}
$\omega_e x_e$	2,95 (9) cm^{-1}	2,59 cm^{-1}
Y_{01}	7965,545 (9) MHz	7967 MHz
Y_{11}	−57,577 (13) MHz	−57 MHz
Y_{21}	0,114 (5) MHz	
Y_{02}	−8,50 (37) kHz	−8,53 kHz
a_1	−3,33 (5)	
a_0	2,481 (10) · 10^5 cm^{-1}	
μ_r^{107}	16,131611 amu	
μ_r^{109}	16,176431 amu	
r_e	1,983171 Å ±0,000023 * ±0,000001 **	1,986 Å

Table 2. Rotational constants for ^{107}Ag^{19}F. The natural constants employed are from COHEN and DUMOND [8] and the isotopic masses were taken from MATTAUCH, THIELE and WAPSTRA [9]. * Error due to natural constants; ** error of measurement.

$$\nu_{v,\,J\to J+1}=2[Y_{01}+Y_{11}(v+\tfrac{1}{2})+Y_{21}(v+\tfrac{1}{2})^2+\dots](J+1)+4[Y_{02}+\dots](J+1)^3+\dots \tag{1}$$

where $Y_{01}\sim 1/\mu_r$, $Y_{11}\sim 1/\mu_r^{3/2}$, and $Y_{21}, Y_{02}\sim 1/\mu_r^2$ (μ_r: reduced mass)

apply. Here Method II described in Ref. [10] was followed.

In our subsequent observation of the $J=1\to 2$ CuF spectrum, the same type of non-Boltzmann distribution of vibrational states was found as occurred for AgF in the molecular beam spectrometer. The ^{63}CuF $J=1\to 2$, $v=0$ strongest transition could be obtained with S/N of better than 50. A Boltzmann distribution would give 2.25 for the intensity ratio of transitions of neighboring vibrational levels at 1100 °K. Thus, one would also expect the corresponding $v=2$ transition with a S/N of 10 or more. However, we were unable to obtain this transition. Intensity measurements on the ^{65}CuF $v=0$ and ^{63}CuF $v=1$ lines, which should be of equal intensity for a Boltzmann distribution, resulted in the $v=1$ line being a factor of 3 weaker. For this reason we also failed to obtain the $v=2$ lines. This discrepancy made observation of the $J=0\to 1$ spectrum in the hot-cell spectrometer, which produces a good thermal equilibrium, even more desirable. These lines were obtained by the technique described above and showed line intensities which corresponded to a Boltzmann distribution. The intensity ratios of rotational transition of neighboring vibrational states for other molecules must be investigated in a similar manner before a definitive physical interpretation can be given to these observations.

The $J=0\to 1$ spectrum of CuF was measured for the lowest three vibrational states and the $J=1\to 2$ spectrum was obtained for the first two vibrational states. These measurements are shown in Table 3. A low resolution $J=1\to 2$, $v=0$ spectrum is shown in Fig. 1. Since the nuclear quadrupole coupling constant, $e\,q\,Q$, of Cu is small compared to the rotational constant, only first order terms are required to evaluate the hyperfine structure. The hyperfine interaction energy is then expressed as:

$$E=-e\,q\,Q\cdot f(J,I,F)+\tfrac{1}{2}c_{\mathrm{Cu}}[F(F+1)-J(J+1)-I(I+1)] \tag{2}$$

where $F=(I+J), (I+J-1), \dots, |I-J|$. The Casimir function, $f(J,I,F)$, is evaluated in the Tables of TOWNES and SCHAWLOW [11]. The magnetic inter-

[8] E. R. COHEN and J. W. M. DUMOND, Rev. Modern Phys. **37**, 537 [1965].

[9] J. H. E. MATTAUCH, W. THIELE, and A. H. WAPSTRA, Nucl. Phys. **67**, 1 [1965].

[10] J. HOEFT and E. TIEMANN, Z. Naturforsch. **23 a**, 1034 [1968].

$J \to J'$	$F \to F'$	v	ν (MHz)	$\Delta\nu$ (MHz)
			$^{63}Cu^{19}F$	
$0 \to 1$	$3/2 \to 3/2$	0	22 656,083 (20)	– 0,011
	$3/2 \to 5/2$	0	22 650,685 (20)	– 0,011
	$3/2 \to 1/2$	0	22 646,150 (20)	– 0,010
	$3/2 \to 3/2$	1	22 463,905 (20)	– 0,004
	$3/2 \to 5/2$	1	22 458,490 (20)	– 0,001
	$3/2 \to 1/2$	1	22 453,975 (20)	– 0,003
	$3/2 \to 5/2$	2	22 267,792 (40)	– 0,004
$1 \to 2$	$1/2 \to 3/2$, $5/2 \to 5/2$	0	45 308,210 (50)	0,029
	$5/2 \to 7/2$, $3/2 \to 5/2$	0	45 302,569 (30)	0,029
	$3/2 \to 3/2$	0	45 298,563 (50)	0,007
	$3/2 \to 1/2$	0	45 293,020 (50)	0,010
	$5/2 \to 7/2$, $3/2 \to 5/2$	1	44 918,249 (30)	– 0,012
	$3/2 \to 3/2$	1	44 914,190 (50)	0,032
			$^{65}Cu^{19}F$	
$0 \to 1$	$3/2 \to 3/2$	0	22 494,456 (20)	– 0,008
	$3/2 \to 5/2$	0	22 489,474 (20)	– 0,006
	$3/2 \to 1/2$	0	22 485,250 (20)	– 0,006
$1 \to 2$	$5/2 \to 7/2$, $3/2 \to 5/2$	0	44 980,044 (50)	0,009
	$5/2 \to 7/2$, $3/2 \to 5/2$	1	44 599,764 (50)	0,009

Table 3. The $J=0 \to 1$ and $1 \to 2$ measured rotational transition frequencies for CuF. The differences between the calculated and observed line frequencies are shown in the last column.

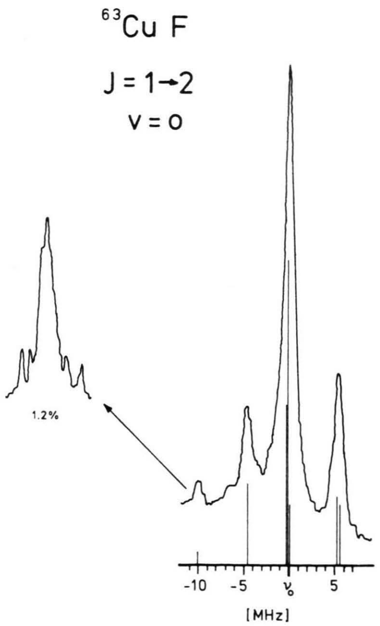

Fig. 1. Low resolution record of the ^{63}CuF $J=1 \to 2$, $v=0$ transition. Hypothetical frequency of transition without hyperfine structure $\nu_0=45\ 303{,}032$ MHz. Nuclear spins of ^{63,65}Cu $I=3/2$.

action of the Cu nucleus is represented by the coupling constant c_{Cu} here. The quadrupole and magnetic hyperfine structure was calculated out of the observed spectra to obtain the unperturbed rotational transitions shown in Table 4. The $J=0 \to 1$

$J \to J+1$	v	ν (MHz) Hypothetical unperturbed rational transition	$\Delta\nu$ (MHz)
		$^{63}Cu^{19}F$	
$0 \to 1$	0	22 651,718	– 0,011
$0 \to 1$	1	22 459,540	– 0,003
$0 \to 1$	2	22 268,836	– 0,004
$1 \to 2$	0	45 303,032	0,019
$1 \to 2$	1	44 918,676	– 0,001
		$^{65}Cu^{19}F$	
$0 \to 1$	0	22 490,424	– 0,007
$1 \to 2$	0	44 980,449	0,009
$1 \to 2$	1	44 600,169	0,009

Table 4. The unperturbed rotational transition frequencies represent the calculated center of the observed hyperfine component spectrum. The differences in the last column result from the difference between the transition frequency calculated from the derived rotational constants and the center frequencies listed above.

spectrum was used to derive these constants since these measurements are more accurate due to narrower line widths of about 200 kHz compared to 0.5 MHz for the $J=1 \to 2$ lines which also consisted of some multiple unresolved transitions. The rotational constants were calculated according to Eq. (1). All the derived molecular constants are listed in Table 5 and where earlier measurements exist, they are included for comparison. The only discrepancy between the present measurements and the earlier band spectra rotational analysis is in $Y_{11} \approx -\alpha_e$. In Calder and Ruedenberg's quantitative correlation of spectroscopic constants [12] the ratio α_e/B_e gave a $+35.6\%$ deviation from their calculated value. The present α_e/B_e ratio is in good agreement with their estimated value. (Note: Calder and Ruedenberg seem to have mistakenly listed α_e instead of α_e/B_e for CuF in their Table VII.)

Since no measurable vibrational dependence was obtained, the average value of the $v=0$ and $v=1$ hyperfine constants was used for the ^{63}CuF, $v=2$ calculation. Likewise, the $v=0$ values were applied to the ^{65}CuF, $v=1$ line.

[11] C. H. Townes and A. L. Schawlow, Microwave Spectroscopy, McGraw-Hill Book Co., Inc., New York 1955, p. 499 ff.

[12] G. V. Calder and K. Ruedenberg, J. Chem. Phys. 49, 5399 [1968].

	Present	*Earlier*[a]
	$^{63}Cu^{19}F$	
Y_{01}	11 374,214 (20) MHz	11 401 MHz
Y_{11}	− 96,826 (25) MHz	− 138 MHz
Y_{21}	+ 0,369 (17) MHz	
ω_e		622,65 cm^{-1}
$Y_{02}(-4 B_e^3/\omega_e^2)$	− 16,89 kHz	− 17 kHz
a_0	2,555 (10) · 10^5 cm^{-1}	
a_1	− 3,33 (5)	
μ_r	14,592836 amu	14,5979 amu
r_e	1,744923 Å ± 0,000020 * ± 0,000001 **	1,743 Å
$e q_0 Q$(Cu)	+ 21,95 (10) MHz	
$e q_1 Q$(Cu)	+ 21,96 (10) MHz	
$c_{Cu}(v=0)$	+ 36 (10) kHz	
$c_{Cu}(v=1)$	+ 31 (10) kHz	
	$^{65}Cu^{19}F$	
Y_{01}	11 293,053 (20) MHz	
Y_{11}	− 95,797 (25) MHz	
Y_{21}	+ 0,363[b] MHz	
Y_{02}	− 16,65[b] kHz	
μ_r	14,697728 amu	
r_e	1,744922 Å ± 0,000020 * ± 0,000001 **	
$e q_0 Q$(Cu)	+ 20,32 (10) MHz	
$c_{Cu}(v=0)$	+ 40 (10) kHz	

[a] G. HERZBERG, Spectra of Diatomic Molecules; D. Van Nostrand Co., Inc., Princeton, N.J. 1950.
[b] Calculated from isotope relations.

Table 5. Rotational and hyperfine constants for CuF. The natural constants employed are from COHEN and DUMOND [8] and the isotopic masses were taken from MATTAUCH, THIELE and WAPSTRA [9]. * Error due to natural constants; ** error of measurement.

The ratio of the nuclear quadrupole moments of the Cu isotopes, obtained from the ratio of the quadrupole coupling constants, appears in Table 6. The agreement is excellent with those determined by nuclear quadrupole resonance on CuO_2 and $CuK(CN)_2$.

Measurement of the AgF electric dipole moment was accomplished with the molecular beam spectrometer and that of CuF in the hot-cell spectrometer. A cross section of the cells used for the Stark measurements is shown and described in Ref. [7]. The method used in these measurements simply consisted of applying a 110 kHz square wave voltage, V, to one electrode and grounding the other. In this way both the zero field line and the $\Delta M_J = \pm 1$ Stark components can be observed simultaneously. The square wave amplitude is measured on a calibrated oscilloscope to an accuracy of 1 − 2%. The dipole moment μ may be calculated from the 2nd order equation for a $(J, M) \to (J+1, M+1)$ transition:

$$\Delta\nu_{\text{Stark}} = [f(J+1, M+1) - f(J, M)] \frac{\mu^2 V^2}{d^2 B_v} \qquad (3)$$

where $f(J, M) = \dfrac{J(J+1) - 3 M^2}{2 J(J+1)(2 J+3)(2 J-1)}$

and d = 13 mm in the molecular beam apparatus. Since the hot-cell electrode spacing, d, does not necessarily remain constant from one run to the next, a standardizing substance is always measured at or close to the temperature required for the material under investigation. In the CuF measurements TlF served as the standard. The $J = 0 \to 1$, $F = |M_F| = 3/2 \to 5/2$ was observed since it is the most intense and behaves according to Eq. (3) above like a transition $J, |M| = 0, 0 \to 1, 1$. The single measurements and the average moment derived therefrom are presented in Table 7.

[13] R. v. BOECKH, G. GRÄFF, and R. LEY, Z. Phys. **179**, 285 [1964].

Molecule	$e q Q_{Cu}$	$(e q Q)_{63}/(e q Q)_{65}$
^{63}CuF	21,95 MHz	1,080
^{65}CuF	20,32 MHz	
$^{63}CuO_2$[a]	52,04 MHz	1,080$_6$
$^{65}CuO_2$[a]	48,16 MHz	
$^{63}CuK(CN)_2$[a]	66,96 MHz	1,080$_7$
$^{65}CuK(CN)_2$[a]	61,96 MHz	

[a] H. KRÜGER and U. MEYER-BERKHOUT, Z. Phys. **132**, 171 [1952].

Table 6. Nuclear quadrupole moment ratios Q_{63}/Q_{65}.

μ_0(CuF)	μ_0(AgF)
5,70	6,29
5,86	6,17
5,71	6,36
5,72	6,10
5,74	6,20
5,86	6,19
$\bar{\mu}_0$ = 5,77 (20) Debye	$\bar{\mu}_0$ = 6,22 (20) Debye

Table 7. The electric dipole moments of CuF and AgF. An error weighted average of the CuF measurements was obtained. For CuF the $J = 0 \to 1$, $F = |M_F| = 3/2 \to 5/2$ Stark transition was measured and the $J = |M_J| = 1 \to 2$ transition of AgF was observed. TlF was used for calibration in the CuF measurements. BOECKH, GRÄFF and LEY [13] give μ_0 (^{205}TlF) = 4,2282 (8) D.

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