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Fourier Transform Emission Spectroscopy of the $A^1\Sigma^+ - X^1\Sigma^+$ Transition of CuD

The $A^1\Sigma^+ - X^1\Sigma^+$ transition of CuD near 4300 Å was previously recorded by Heimer (*1*), Jeppesen (*2*), and Ringström (*3*). Many of the excited vibrational levels of the $A^1\Sigma^+$ state are perturbed (*3*) and, for CuH, display some evidence of predissociation by a $^3\Sigma^+$ state (*4*, *5*).

The CuH molecule is of astrophysical interest. Hauge (*6*) observed the $A^1\Sigma^+ - X^1\Sigma^+$ transition in the spectrum of a sunspot. CuH was also tentatively identified in the spectrum of the star 19 Piscium (*7*).

In the course of our work on BD, we identified the 0–0, 0–1, and 1–1 bands of the $A^1\Sigma^+ - X^1\Sigma^+$ transition of CuD. These Fourier transform data provide much improved spectroscopic constants for ^{63}CuD and ^{65}CuD including rotational constants and a value for $\Delta G_{1/2}$ in the ground state. The new CuD ground state constants complement our recent observations of the vibration–rotation spectrum of CuH (*8*).

The CuD molecule was made in a hollow cathode discharge. In this experiment, a 1:3 mixture of B_4C powder and copper powder was pressed and drilled to form a hollow cathode. The composite-wall hollow cathode was operated at 400 mA with a flow of 1.6 Torr of Ar gas and 35 mTorr of D_2 gas.

The emission from the hollow cathode was observed with the McMath Fourier transform spectrometer of the National Solar Observatory at Kitt Peak. 33 scans were coadded in 1.5 hr of integration with an unapodized resolution of 0.05 cm^{-1}.

A prism monochromator, acting as a filter, limited the wavelength response of the cooled GaAs photomultiplier detectors to approximately 21 700–24 000 cm^{-1}. The spectra were calibrated to an absolute accuracy of about 0.002 cm^{-1} with the Ar^+ atomic line positions of Norlen (*9*).

The line positions were determined from the spectrum by a data-reduction program, PC-DECOMP, developed at Kitt Peak. This program fits the spectral features with Voigt lineshape functions to determine

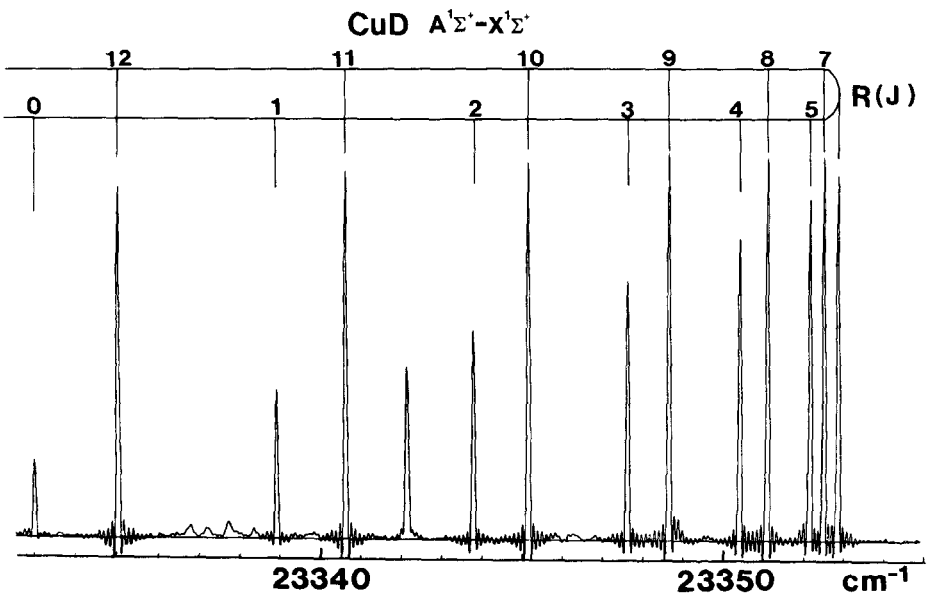

FIG. 1. The *R*-branch for the 0–0 band of the $A^1\Sigma^+ - X^1\Sigma^+$ transition of CuD.

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TABLE I

The Observed Line Positions for the $A\,^1\Sigma^+ - X\,^1\Sigma^+$ Transition of CuD (in cm^{-1})

	^{63}CuD				^{65}CuD			
J	P(J)	O-C[a]	R(J)	O-C	P(J)	O-C	R(J)	O-C
				0 - 1 Band				
0			21986.7598	-4			21987.3806	21
1	21971.9987	-115	21992.8541	-22	21972.6524	-95	21993.4744	57
2	21963.3597	-26	21998.0969	6	21964.0054	17	21998.7099	61
3	21953.8628	-78	22002.4786	6	21954.5137	-78	22003.0837	23
4	21943.5342	-49	22006.0019	24	21944.1931	-71	22006.6129	131
5	21932.3709	-8	22008.6619	24	21933.0266	-175	22009.2583	7
6	21920.3627	-107	22010.4584	17	21921.0473	-102	22011.0521	-14
7	21907.5451	-39	22011.3908	3	21908.2395	-63	22011.9864	-4
8	21893.9002	-34	22011.4557	-47	21894.6030	-108	22012.0533	-37
9			22010.6709	48			22011.2637	-3
10			22009.0121	40			22009.6120	41
11			22006.4886	17			22007.0922	29
12			22003.1008	-24			22003.7115	24
13			21998.8616	32			21999.4693	10
14			21993.7529	-10			21994.3687	1
15			21987.7936	22			21988.4096	-18
16			21980.9750	19			21981.5978	-12
17			21973.3009	-5			21973.9272	-64
18			21964.7743	-45			21965.4248	71
19			21955.4091	10			21956.0539	-2
20			21945.1732	-188			21945.8463	4
				1 - 1 Band				
0			23157.1765	10			23157.2671	64
1	23142.6158	36	23162.8990	9	23142.7131	14	23162.9748	-30
2	23133.7746	-30	23167.5823	42	23133.8873	15	23167.6613	81
3	23123.9118	-8	23171.2159	31	23124.0345	40	23171.2746	98
4	23113.0184	-24	23173.7967	-37	23113.1499	3	23173.8703	6
5	23101.0996	-69	23175.3397	5	23101.2488	18	23175.4086	12
6	23088.1718	-23	23175.8276	-4	23088.3264	-11	23175.8906	-56
7	23074.2268	-17	23175.2693	37	23074.3964	8	23175.3296	-54
8	23059.2753	6	23173.6544	30	23059.4532	-33	23173.7297	65
9	23043.3137	-45	23170.9842	-8	23043.5111	-46	23171.0558	-45
10	23026.3636	-7	23167.2663	2	23026.5831	-47	23167.3473	13
11	23008.4188	-3	23162.4941	-7	23008.6536	27	23162.5800	-8
12	22989.4879	-8	23156.6719	2	22989.7376	-14	23156.7662	15
13	22969.5795	0	23149.8002	31	22969.8462	-30	23149.9056	72
14	22948.6928	-50	23141.8725	6	22948.9916	37	23141.9841	15
15	22926.8509	4	23132.8981	9	22927.1599	-19	23133.0202	18
16	22904.0452	6	23122.8731	-11	22904.3760	-18	23123.0043	-25
17	22880.2884	14	23111.8053	10	22880.6401	-28	23111.9513	20
18	22855.5852	2	23099.6869	-21	22855.9623	-20	23099.8488	20
19	22829.9496	37	23086.5273	-26	22830.3452	-38	23086.7009	-13
20	22803.3800	29	23072.3260	-30	22803.8056	12	23072.5161	4
21	22775.8839	-20	23057.0894	14	22776.3374	-5	23057.2884	-11
22	22747.4791	-9	23040.8105	16	22747.9564	-3	23041.0303	49

[a] Observed minus calculated line positions using the constants of Table II (in units of 10^{-4} cm^{-1}).

the peak positions. Because the spectrum was slightly under-resolved, most of the strong lines produced ringing. A special option in PC-DECOMP called "filtered fitting" was used to improve the resolution by removing the effect of the instrumental sinc function lineshape.

Lines for ^{63}CuD and for ^{65}CuD were measured for 0–0, 1–1, and 0–1 bands of the $A\,^1\Sigma^+ - X\,^1\Sigma^+$ transition and are listed in Table I. Part of the R head of the 0–0 band is shown in Fig. 1. The observed linewidth of the CuD lines was approximately .095 cm^{-1} and the transitions were easily assigned with the help of Jeppesen's work (*2*).

Copper has two stable isotopes, ^{63}Cu and ^{65}Cu (69.2 and 30.8%). At higher J values a doublet pattern due to the two isotopomers was observed in the 0–0 and 1–1 bands. In the 0–1 band, the lines from the two isotopomers were well separated.

All of the lines for the 0–0, 1–1, and 0–1 vibrational bands were fitted together for each isotopomer using the customary energy level expression

$$F(J) = v_0 + BJ(J+1) - D[J(J+1)]^2 + H[J(J+1)]^3.$$

TABLE I—*Continued*

J	^{63}CuD P(J)	O-C	^{63}CuD R(J)	O-C	^{65}CuD P(J)	O-C	^{65}CuD R(J)	O-C
				0 - 0 Band				
0			23332.9764	-10			23332.9764	20
1	23318.0446	12	23338.8887	-9	23318.0539	-12	23338.8807	-2
2	23309.0252	-27	23343.7601	-17	23309.0474	-10	23343.7474	-10
3	23298.9912	65	23347.5898	-22	23299.0092	-59	23347.5748	-1
4	23287.9195	16	23350.3760	-24	23287.9555	-36	23350.3590	3
5	23275.8356	38	23352.1155	-42	23275.8843	-6	23352.0961	-24
6	23262.7362	48	23352.8118	-30	23262.8015	42	23352.7923	-9
7	23248.6259	42	23352.4614	-19	23248.7055	41	23352.4405	-19
8	23233.5056	-27	23351.0631	-19	23233.6065	38	23351.0449	-9
9	23217.3942	-27	23348.6193	-7	23217.5130	59	23348.6016	-20
10	23200.2916	-23	23345.1289	2	23200.4256	49	23345.1155	-8
11	23182.2071	14	23340.5941	18	23182.3513	12	23340.5838	-10
12	23163.1408	15	23335.0162	44	23163.3007	-14	23335.0093	-11
13	23143.1038	20	23328.3930	42	23143.2794	-46	23328.3914	-32
14	23122.1028	20	23320.7278	25	23122.3056	25	23320.7403	9
15	23100.1445	6	23312.0215	-20	23100.3759	86	23312.0465	-5
16	23077.2406	14	23302.2839	-20	23077.4894	48	23302.3185	-13
17	23053.3981	30	23291.5114	-39	23053.6635	3	23291.5597	-11
18	23028.6229	27	23279.7155	6	23028.9123	5	23279.7750	19
19	23002.9250	19	23266.8883	2	23003.2420	29	23266.9615	15
20	22976.3175	46	23253.0412	28	22976.6573	32	23253.1223	-29
21	22948.7964	-23	23238.1680	-18	22949.1647	-12	23238.2778	53
22	22920.3941	40	23222.2832	-31	22920.7835	-5	23222.4092	32
23	22891.0971	7	23205.3879	-44	22891.5202	25	23205.5341	41
24	22860.9256	-17	23187.4911	-11	22861.3743	-26	23187.6476	-14
25	22829.8880	-46	23168.5888	-18	22830.3641	-70	23168.7628	-49
26	22798.0017	-5	23148.6911	-13	22798.5068	-35	23148.8902	-5
27	22765.2646	-13	23127.8016	-9	22765.8059	15	23128.0226	-5
28	22731.6920	-16	23105.9195	-63	22732.2648	15	23106.1686	-11
29	22697.2922	-33	23083.0701	27	22697.8957	-13	23083.3363	6
30	22662.0808	-6	23059.2343	17	22662.7132	-21	23059.5246	-17
31	22626.0603	-9	23034.4286	23	22626.7302	18	23034.7439	-26
32	22589.2416	-32	23008.6536	-3	22589.9517	58	23009.0020	4
33	22551.6434	14	22981.9304	98	22552.3783	7	22982.2994	28
34	22513.2645	22	22954.2316	6	22514.0318	-14	22954.6396	29
35	22474.1155	2	22925.5940	34	22474.9233	12	22926.0244	-23
36	22434.2128	26	22896.0065	24	22435.0472	-65		
37	22393.5553	-8	22865.4752	-11	22394.4384	15		
38	22352.1641	24	22834.0077	-40	22353.0857	50		
39	22310.0375	19			22310.9974	40		
40	22267.1826	-35			22268.1775	-59		

TABLE II

Molecular Constants for the $A^1\Sigma^+$–$X^1\Sigma^+$ Transition of CuD (in cm^{-1}).

Constant	$X^1\Sigma^+$ v = 0	$X^1\Sigma^+$ v = 1	$A^1\Sigma^+$ v = 0	$A^1\Sigma^+$ v = 1
		^{63}CuD		
T_v	0.0	1346.2171(12)	23326.02770(64)	24496.6296(14)
B_v	3.992396(20)	3.900452(31)	3.475075(20)	3.381743(34)
D_v 10^4	1.36296(27)	1.3485(12)	1.20200(28)	1.2149(13)
H_v 10^9	2.819(11)	2.69(16)	1.565(11)	8.5(16)
		^{65}CuD		
T_v	0.0	1345.5958(15)	23326.03150(83)	24496.1001(19)
B_v	3.988482(27)	3.896603(44)	3.471678(28)	3.378417(47)
D_v 10^4	1.35903(43)	1.3429(16)	1.19831(47)	1.2085(18)
H_v 10^9	2.785(19)	2.62(22)	1.535(22)	5.8(23)

Note. One standard deviation uncertainty is enclosed in parentheses.

The molecular constants from our two fits are provided in Table II. These constants are in reasonable agreement with less accurate previous values.

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W. T. M. L. FERNANDO
L. C. O'BRIEN[1]
P. F. BERNATH[2]

Department of Chemistry
The University of Arizona
Tucson, Arizona 85721
Received October 10, 1989

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[1] Current address: Food and Drug Administration, Division of Drug Analysis, 1114 Market St., St. Louis, Missouri 63101.

[2] Alfred P. Sloan fellow; Camille and Henry Dreyfus teacher–scholar.