The Pure Rotational Spectra of CuH and CuD in Their Ground States Measured by Tunable Far-Infrared Spectroscopy

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Pure rotational transitions of CuH and CuD within the $X\,^1\Sigma^+$ ($v = 0$) state were measured over the ranges $J'' = 1$ to 10 for CuH and $J'' = 2$ to 18 for CuD, including both the ^{63}Cu and ^{65}Cu isotopes. The rotational parameters B_0, D_0, H_0, and L_0 were separately determined for each of the four isotopomers by least-squares fitting to the observed transitions. For ^{65}CuH, ^{63}CuD, and ^{65}CuD, these parameters are about two orders of magnitude more accurate than those determined by previous workers. Accurate calculated frequencies of all four isotopomers which will be useful in astronomical studies of CuH and CuD are given. © 1994 Academic Press, Inc.

INTRODUCTION

Copper hydride and deuteride were first detected in the 1930s with the observation of their optical spectra (*1*, *2*). The most accurate values for the rotational constants of CuH and CuD within the $X\,^1\Sigma^+$ ground state come from more recent work. Ram *et al.* (*3*) studied the (1, 0), (2, 1), and (2, 0) vibration–rotation bands of CuH in emission with a Fourier transform spectrometer, deriving values for the rotational constants B_v, D_v, and H_v ($v = 0$–2) of both the ^{63}CuH and the ^{65}CuH isotopomers. Fernando *et al.* (*4*) observed the Fourier transform emission spectrum of the $A\,^1\Pi$–$X\,^1\Sigma^+$ system of CuD and determined B_v, D_v, and H_v for $v = 0$ and 1 of ^{63}CuD and ^{65}CuD in both electronic states. The most accurate values of B_0, D_0, and H_0 of the ^{63}CuH isotopomer were obtained by Beaton and Evenson (*5*) in a tunable far-infrared (TuFIR) study performed in our laboratory at NIST.

In the present study we have expanded on the work of Ref. (*5*) by measuring the pure rotational spectra of all four CuH isotopomers with our TuFIR spectrometer. The improvement in the ground state rotational constants for the ^{63}CuH species is minimal, but the accuracy of the constants for the other three isotopomers (^{65}CuH, ^{63}CuD, ^{65}CuD) is improved by about two orders of magnitude. The present study will be of interest to astronomers searching for copper hydride in the interstellar medium. The CuH molecule has been identified in sunspot spectra (*6*) and possibly in the spectrum of the star 19 Piscium (*7*).

EXPERIMENTAL DETAILS

A detailed description of the TuFIR spectrometer has been given by Zink *et al.* (*8*), with recent improvements outlined by Varberg and Evenson (*9*), so only a brief description is presented here. CuH and CuD molecules were produced in a hollow

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cathode discharge cell consisting of a 60-cm long, 1.4-cm inner diameter, grounded copper tube, with a wire anode located 15 cm from each end. Water-cooled brass endcaps held 75-μm thick polypropylene windows at each end. Ar and H_2 (or D_2) were flowed through the cell and a DC electric discharge was ignited and maintained. The strength of the absorption signal did not depend critically on the partial pressures, but was optimized with approximately 30 Pa (230 mTorr) of Ar and 10 Pa (80 mTorr) of H_2 or D_2. The signal strength increased with discharge current, which was kept below 200 mA to keep the discharge tube cool.

By mixing mid-infrared radiation from two CO_2 lasers (with frequencies ν_I and ν_{II}) and microwave radiation (ν_μ) on a metal–insulator–metal (MIM) diode, tunable far-infrared radiation of two frequencies was generated: $\nu_{FIR} = |\nu_I - \nu_{II}| \pm \nu_\mu$. The FIR radiation was passed through the discharge tube and onto a liquid helium-cooled bolometer or photoconductor. The spectra were recorded as first derivatives by frequency modulating one of the two CO_2 lasers at 1 kHz and detecting the absorption signals with a lock-in amplifier. Individual rotational spectra were digitally recorded with a personal computer. The signal-to-noise ratio of the strongest transitions was 100:1 using a 300-msec output time constant. Calculated lineshapes were fitted to the experimental spectra with a computer program employing five adjustable parameters: the transition frequency and intensity, the Gaussian and Lorentzian linewidths, and the spectrometer baseline.

RESULTS AND DISCUSSION

Pure rotational transitions of CuH and CuD within the $X\,^1\Sigma^+$ ($v = 0$) state were measured over the ranges $J'' = 1$ to 10 for CuH and $J'' = 2$ to 18 for CuD. Transitions involving both naturally occurring isotopes of copper (^{63}Cu, 69% relative abundance, and ^{65}Cu, 31%) were observed. The observed transition frequencies of each isotopomer were separately fitted by least squares using the standard energy level expression

$$E(J) = B_0 J(J + 1) - D_0 J^2(J + 1)^2 + H_0 J^3(J + 1)^3 + L_0 J^4(J + 1)^4, \quad (1)$$

where the subscripts on the molecular constants denote the $v = 0$ level.

From our experience in fitting the pure rotational spectrum of CO measured with the TuFIR spectrometer at NIST (9), we expected to be able to measure transitions of CuH accurately within 10 kHz. However, in fitting Eq. (1) to the transition frequencies, we found the experimental uncertainty of a typical line is significantly larger than 10 kHz. By repeating selected measurements, we found the reproducibility of a measured transition frequency to be about 100 kHz. After completion of the present measurements, we discovered that the accuracy of the synthesized FIR frequency is sensitive to the modulation widths employed in locking the CO_2 lasers: if the frequency modulation is too large, the CO_2 laser does not lock exactly at linecenter. We think that this uncertainty in the FIR radiation is the cause of the relatively large experimental uncertainties. Because of this, we fitted Eq. (1) to the CuH and CuD transition frequencies with all of the data weighted equally, even though the signal-to-noise ratio of the various transitions ranged from 3 to 100. The observed and calculated transition frequencies are listed in Table I and the derived molecular constants for each isotopomer are given in Table II. The standard deviations of the least-squares fits are listed in Table II as well; these range from 47 to 114 kHz, reflecting the uncertainty in the FIR frequency.

The rotational constants determined for the two CuH isotopomers agree with those determined by Ram *et al.* (3) from the vibration–rotation spectrum, but are ~300

TABLE I

Observed and Calculated Rotational Frequencies of CuH and CuD in MHz

$J'-J''$	Observed	Calculated[a]	O – C	Observed	Calculated[a]	O – C
		^{63}CuH			^{65}CuH	
1–0	—	468 652.250 (34)	.....	—	468 427.029 (25)	....
2–1	936 925.149	936 924.949 (58)	0.200	936 474.967	936 474.863 (42)	0.104
3–2	1 404 439.008	1 404 439.070 (66)	–0.062	....	1 403 764.835 (48)	...
4–3	1 870 816.612	1 870 816.629 (60)	–0.017	1 869 919.282	1 869 919.326 (43)	–0.044
5–4	2 335 681.083	2 335 681.201 (55)	–0.118	2 334 562.227	2 334 562.285 (36)	–0.058
6–5	2 798 658.436	2 798 658.427 (62)	0.009	2 797 319.737	2 797 319.729 (37)	0.008
7–6	3 259 376.560	3 259 376.509 (69)	0.051	3 257 820.259	3 257 820.236 (41)	0.023
8–7	3 717 466.730	3 717 466.692 (74)	0.038	3 715 695.436	3 715 695.408 (45)	0.028
9–8	—	4 172 563.734 (94)	—		4 170 580.327 (56)	—
10–9	4 624 306.300	4 624 306.348 (105)	–0.048	4 622 113.936	4 622 113.966 (63)	–0.030
11–10	5 072 337.650	5 072 337.631 (113)	0.019	5 069 939.595	5 069 939.583 (67)	0.012
		^{63}CuD			^{65}CuD	
1–0	—	239 369.095 (08)	—	—	239 142.105 (17)	—
2–1	...	478 639.871 (15)	—	—	478 186.076 (31)	—
3–2	717 714.161	717 714.078 (20)	0.083	717 033.924	717 033.846 (41)	0.078
4–3	....	956 493.605 (24)	—	955 587.604	955 587.488 (47)	0.116
5–4	1 194 880.524	1 194 880.545 (25)	–0.021	1 193 749.198	1 193 749.279 (47)	–0.081
6–5	1 432 777.270	1 432 777.263 (24)	0.007	1 431 421.683	1 431 421.771 (45)	–0.088
7–6	—	1 670 086.467 (22)	—	—	1 668 507.858 (44)	–-
8–7	1 906 711.252	1 906 711.273 (20)	–0.021	—	1 904 910.840 (45)	...
9–8	2 142 555.249	2 142 555.267 (19)	–0.018	2 140 534.513	2 140 534.491 (48)	0.022
10–9	2 377 522.524	2 377 522.577 (21)	–0.053	2 375 283.089	2 375 283.124 (49)	–0.035
11–10	2 611 517.949	2 611 517.930 (23)	0.019	2 609 061.639	2 609 061.648 (48)	–0.009
12–11	2 844 446.770	2 844 446.721 (24)	0.049	2 841 775.699	2 841 775.637 (48)	0.062
13–12	....	3 076 215.067 (25)	·		3 073 331.386 (55)	—-
14–13	3 306 729.868	3 306 729.874 (25)	–0.006	3 303 636.018	3 303 635.967 (64)	0.051
15–14	....	3 535 898.890 (26)	...	3 532 597.177	3 532 597.290 (59)	–0.113
16–15	3 763 630.800	3 763 630.765 (30)	0.035	3 760 124.198	3 760 124.152 (87)	0.046
17–16	3 989 835.053	3 989 835.101 (33)	–0.048			
18–17	—	4 214 422.509 (32)	—			
19–18	4 437 304.669	4 437 304.659 (46)	0.010			

[a]Values in parentheses are the calculated 1σ uncertainties in units of the last digits. The 95% confidence limits correspond to 2.6σ for CuH and 2.4σ for CuD.

times more accurate. Our constants for the ^{63}CuH isotopomer also agree with those determined in the earlier TuFIR study of Beaton and Evenson (5); they determined the values $B_0 = 234\ 357.748\ (31)$, $D_0 = 15.819\ 56\ (78)$, and $H_0 = 7.13\ (6) \times 10^{-4}$ MHz. Our values are slightly more precise because we observed a larger number of

TABLE II

Molecular Parameters of CuH and CuD in Their $X\ ^1\Sigma^+$ State[a]

	^{63}CuH	^{65}CuH	^{63}CuD	^{65}CuD
B_0	234 357.763 (18)	234 245.123 (13)	119 692.741 6 (40)	119 579.231 7 (85)
D_0	15.820 43 (51)	15.805 66 (35)	4.097 367 (37)	4.089 71 (11)
H_0	7.280 (56) $\times$ 10^{-4}	7.339 (37) $\times$ 10^{-4}	9.549 (13) $\times$ 10^{-5}	9.580 (59) $\times$ 10^{-5}
L_0	–6.7 (20) $\times$ 10^{-8}	–9.5 (13) $\times$ 10^{-8}	–3.36 (16) $\times$ 10^{-9}	–4.2 (10) $\times$ 10^{-9}
σ^b	0.114	0.068	0.047	0.090

[a]All values are in MHz, with 1σ uncertainties of the last digits listed in parentheses.
[b]Standard deviation of the least-squares fit.

transitions. We have also determined a value for the centrifugal distortion constant L_0, which was not determinable in the previous work.

In contrast, the values of the rotational constants determined in this work for the two CuD isotopomers differ from those determined by Fernando *et al.* (*4*) in their Fourier transform emission study of the $A\,^1\Sigma^+ - X\,^1\Sigma^+$ system. These authors found $B_0 = 119\,689.0\ (6)$, $D_0 = 4.086\,1\ (8)$, and $H_0 = 8.45\ (3) \times 10^{-5}$ MHz for ^{63}CuD, and $B_0 = 119\,571.7\ (8)$, $D_0 = 4.074\,3\ (13)$, and $H_0 = 8.35\ (6) \times 10^{-5}$ MHz for ^{65}CuD (1σ uncertainties in parentheses), all of which are 10–20 standard deviations smaller than our more precisely determined values (Table II). The parameter uncertainties given in Ref. (*4*) reflect only the random errors in the Fourier transform spectrum and are not sensitive to small, systematic errors arising from the calibration of the spectrum. Thus while the precision of the derived constants is very high, the absolute accuracies are overestimated by the reported uncertainties (*10*).

The internal consistency of the molecular constants determined in the present work is demonstrated by considering their isotopic scaling. The relationships $D_0 = \rho^4 D_0^i$, $H_0 = \rho^6 H_0^i$, and $L_0 = \rho^8 L_0^i$ (*11*), where $\rho^2 = \mu/\mu_i$ is the ratio of the reduced masses of the ^{63}CuH(D) and ^{65}CuH(D) isotopomers, are obeyed at the 1σ level for both CuH and CuD. These isotopic scaling relationships will strictly hold under the Born–Oppenheimer approximation only for parameters evaluated at the equilibrium bond length, rather than in the $v = 0$ level, but the difference is expected to be negligible for all of the rotational constants except B_0.

Finally, to aid in astronomical searches for CuH and CuD we have also listed in Table I the calculated rotational frequencies and the statistical estimates of their 1σ uncertainties (*12*). In particular, the $J = 1$–0 transition of ^{63}CuH is calculated to lie at $468\,652.25 \pm 0.07$ MHz, where the 2σ uncertainty given corresponds to the 90% confidence limits.

To summarize, we have observed pure rotational transitions within the ground state of CuH and CuD. Least-squares fits to the transition frequencies provide accurate rotational constants for all four isotopomers. The accuracy of these constants for the ^{65}CuH, ^{63}CuD, and ^{65}CuD isotopomers has been improved by two orders of magnitude.

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