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The Rotational Spectrum of Copper Hydride Using Tunable Far-Infrared Radiation

STUART P. BEATON[1] AND K. M. EVENSON

Time and Frequency Division, National Institute of Standards and Technology, Boulder, Colorado 80303

We have detected and measured five low-*J* rotational transitions of ^{63}CuH between 40 and 125 cm^{-1} using coherent tunable far-infrared radiation. A least-squares fit to the data yields two orders of magnitude improvement in the values for the rotational molecular constants. The frequency of the $J = 1 \leftarrow 0$ transition of astronomical interest is predicted to be 468 652.2 (2) MHz.

I. INTRODUCTION

Interest in transition metal hydrides stems from their role in catalysis studies, their usefulness in ab initio molecular theory, and their existence in stars and the interstellar medium. CuH spectra were first observed in 1923 (*1*), and more recently, spectra extending from the vacuum UV to the infrared (*2–4*) have been observed. Ab initio calculations of rotational, vibrational, and electronic transitions are in good agreement with experimentally observed spectra (*5–7*).

The accuracy of the rotational constants reported by Ram *et al.* (*4*) made our search for each line of CuH relatively easy. The predictions from our work provide frequencies for searches for ^{63}CuH in the interstellar medium.

II. EXPERIMENTAL DETAILS

Our tunable far-infrared (TuFIR) spectrometer is described in detail elsewhere (*8*). Two CO_2 lasers and an optional microwave source are focused on a metal–insulator–metal (MIM) diode and FIR radiation is generated. The radiation is passed through an absorption cell and detected by a liquid-helium-cooled photoconductor or bolometer. The frequency of this radiation is accurate to 35 kHz, but the linewidth and signal-to-noise ratio of the spectra limit the experimental accuracy to about 100 kHz. To generate the CuH we used a copper pipe, 1.4 cm i.d. and 60 cm long, as a hollow cathode, with an anode 15 cm from each end. The discharge was through a mixture of argon and hydrogen. Copper was sputtered from the walls to react with atomic hydrogen to form CuH. The optimum Ar and H_2 pressures were 40 Pa (0.3 Torr) and 13 Pa (0.1 Torr), respectively. The signal increased with discharge current up to 150 mA per anode. Above this current little improvement was observed. In order to maximize the signals on the lowest lines, the tube was cooled by a LN_2 bath. The signal-to-noise ratio, with a 300-ms time constant, varied from 20 to 100 depending

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[1] Also at Department of Physics, University of Colorado, Boulder, CO.

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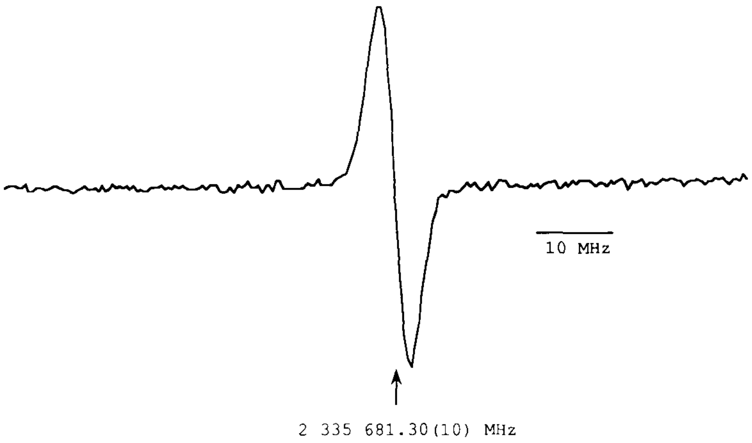

FIG. 1. The $X^1\Sigma^+$ $J = 5 \leftarrow 4$ transition in ^{63}CuH. The scan covers 100 MHz, starting at 2 335 628.577 MHz.

upon the line absorption strength and the efficiency of the particular MIM diode contact used in generating the FIR radiation. Figure 1 shows the $J = 5 \leftarrow 4$ transition on a 100-MHz-wide scan.

III. RESULTS AND ANALYSIS

We fitted the data to the standard rotational energy expression (*9*) of the form

$$E_R = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3. \qquad (1)$$

This yielded the results given in Table I. Our values for B and D are about two orders of magnitude more accurate than, and are in agreement with, those from Ref. (*4*). Although the value for H agrees only approximately, ours is much better determined from the fit, and we believe that a fourth-order term may also be needed to fit properly the high J lines (up to $J'' = 17$) which Ram *et al.* measured. For the low-J lines which we measured, however, including a fourth term does not improve the quality of the fit as measured by the variance.

Revised values of the equilibrium constants are not reported here, because their precision is limited by the precision of the vibrational constants reported by Ref. (*4*).

TABLE I

Rotational Parameters for ^{63}CuH $X^1\Sigma^+$

	MHz	cm^{-1}	Ref. 4 (cm^{-1})
B	234 357.748 (31)	7.817 333 (1)	7.817 45 (22)
D	15.819 56 (78)	5.276 84 (26) $\times 10^{-4}$	5.341 (40) $\times 10^{-4}$
H	7.13 (6) $\times 10^{-4}$	2.38 (2) $\times 10^{-8}$	8.8 (37) $\times 10^{-8}$

Note. Uncertainties of 1-σ in last digits are in parentheses.

TABLE II

Observed and Calculated Transition Frequencies (in MHz) for ^{63}CuH $X\,^1\Sigma^+$

J"	Observed	Calculated	O-C	1-σ uncertainty
0		468 652.22		0.19
1		936 924.92		0.22
2	1 404 439.054	1 404 439.05	-0.001	
3		1 870 816.65		0.22
4	2 335 681.316	2 335 681.25	0.067	
5	2 798 658.314	2 798 658.45	-0.14	
6	3 259 376.530	3 259 376.43	0.10	
7	3 717 466.404	3 717 466.43	-0.025	
8		4 172 563.29		0.61

Note. The 1-σ measurement uncertainty is about 0.1 MHz.

Using the data in Table I, we have calculated the frequencies for the lowest nine lines of ^{63}CuH. These are given in Tables II and III in MHz and cm^{-1}, respectively. The 1-σ uncertainty in the predicted frequency as determined from the variance of the fit is presented.

We attempted to observe hyperfine structure due to the ^{63}Cu nucleus by using a small (1 MHz) modulation on the $J = 3 \leftarrow 2$ line. Unfortunately, this was one of the weakest lines we observed. The observed linewidth is approximately 3 MHz, with

TABLE III

Observed and Calculated Transition Frequencies (in cm^{-1})^a for ^{63}CuH $X\,^1\Sigma^+$

J"	Observed (cm^{-1})	Calculated (cm^{-1})	O-C (cm^{-1} x 10^{-6})	1-σ uncertainty (cm^{-1} x10^{-6})
0		15.632 556		6.3
1		31.252 451		7.2
2	46.847 044	46.847 044	-0.038	
3		62.403 726		7.3
4	77.909 942	77.909 940	2.2	
5	93.353 193	93.353 197	-4.6	
6	108.721 098	108.721 095	3.4	
7	124.001 332	124.001 333	-0.83	
8		139.181 730		20

Note. The 1-σ measurement uncertainty is about 3×10^{-6} cm^{-1}.
[a] Conversion from MHz to wavenumbers based on c = 299 792 458 m/s.

no evidence of quadrupole splitting. The smallness of the hyperfine structure indicates that the charge distribution is nearly spherically symmetric about the copper atom. This agrees with the calculations by Hliwa *et al.* (*7*), which predict the ground state bond to be formed primarily from the configurations $\mathrm{Cu}(d^{10}s^1) + \mathrm{H}(s^1)$ and the ionic $\mathrm{Cu}^+(d^{10}) + \mathrm{H}^-(s^2)$.

Our predicted frequency for the $1 \leftarrow 0$ transition may make possible heterodyne detection of CuH in the interstellar medium. In addition, TuFIR measurements of other astronomically important transition metal hydrides, such as FeH, CoH, and NiH, may also be feasible. Since these metals are less volatile than copper, a sputtering source may not yield a sufficient density of metal hydride, but volatile carbonyl compounds of these metals are available and can produce the hydrides. Although these hydrides have been accurately measured by FIR laser magnetic resonance spectroscopy (*10*), their observation with the TuFIR spectrometer will increase the precision of the transition frequencies by at least an order of magnitude, which will allow more accurate astronomical searches to be made.

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