

## Fourier Transform Emission Spectroscopy: The Vibration–Rotation Spectrum of CuH

R. S. RAM AND P. F. BERNATH

*Department of Chemistry, University of Arizona, Tucson, Arizona 85721*

AND

J. W. BRAULT

*National Solar Observatory, National Optical Astronomy Observatories, Tucson, Arizona 85726*

The Fourier transform infrared emission spectrum of CuH was observed. The (1, 0), (2, 1), and (2, 0) vibration–rotation bands of both  $^{63}\text{CuH}$  and  $^{65}\text{CuH}$  were recorded from a copper hollow-cathode discharge in neon and hydrogen. Improved molecular constants for the  $v = 0, 1,$  and 2 levels of CuH are provided. This work is the first observation of a vibration–rotation spectrum of a metal hydride in emission. © 1985 Academic Press, Inc.

### I. INTRODUCTION

The diatomic transition metal hydrides are of considerable experimental and theoretical interest (1–13). Some transition metal hydrides such as TiH and FeH (14) are astrophysically important. Others such as NiH (10) and PdH are often considered as “models” for the chemisorbed hydrogen atom on catalytic metal surfaces. The electronic spectra of CuH are relatively simple and so CuH has been observed in emission (15, 16) and absorption (17–20) from the visible to the vacuum ultraviolet (20).

The most extensive work on CuH has been carried out by Ringström, who observed the  $A^1\Sigma^+$ ,  $b\Delta_2$ ,  $B^3\Pi_0^+$ ,  $C1$ ,  $c1$ , and  $E^1\Sigma^+$  states in the region 25 000–40 000  $\text{cm}^{-1}$  (18, 19). More recently, Brown and Ginter (20) have discovered four new electronic states ( $F1^\pm$ ,  $G0^+$ ,  $H1^\pm$ , and  $I1^\pm$ ) in the region 48 000–53 000  $\text{cm}^{-1}$ . The best ground state ( $X^1\Sigma^+$ ) molecular constants (previous to our work) are provided by Ringström (18).

We have observed the vibration–rotation spectrum of CuH in emission with a Fourier transform spectrometer. The spectrum of CuH was found at the same time as our detection of the infrared emission spectrum of  $\text{NeH}^+$  (21). The CuH was produced in a neon hollow-cathode discharge containing a small amount of hydrogen. The Cu atoms required to create CuH were provided by sputtering of the copper cathode material.

There have been only two previous observations of infrared spectra of metal hydrides. James *et al.* (22) observed the infrared absorption spectrum of LiH present in a hot cell. More recently Haese *et al.* (23) observed the vibration–rotation absorption spectrum of KH with a diode laser. The KH was produced in a long discharge cell and

detected by concentration modulation of the KH by an a.c. discharge (23). Our work thus represents the first detection of the vibration-rotation emission spectrum of a metal hydride.

## II. EXPERIMENTAL DETAILS

The CuH spectrum was excited in a water-cooled copper hollow-cathode lamp at a current of 330 mA. A continuous flow of 2.0 Torr of neon and 30 mTorr of H<sub>2</sub> was maintained through the lamp. A similar experiment was carried out with D<sub>2</sub> instead of H<sub>2</sub> but CuD was not detected.

The spectrum was recorded with the Fourier transform spectrometer associated with the McMath Solar Telescope of the National Solar Observatory located at Kitt Peak. The interval 1800–5000 cm<sup>-1</sup> was recorded at 0.05-cm<sup>-1</sup> resolution using liquid nitrogen-cooled InSb detectors with a wedged Ge filter. The lower wavenumber limit is determined by the red limit of the detector while the upper limit is set by the Ge filter. Sixty four scans were coadded in 2 hr of integration.

## III. RESULTS

The (1, 0) band of CuH was noted and easily identified during our NeH<sup>+</sup> work because of its characteristic spectral pattern. A regularly spaced branch with each line doubled and split by about 0.5 cm<sup>-1</sup> was found. The doublets had a 2:1 intensity ratio characteristic of <sup>65</sup>Cu and <sup>63</sup>Cu in natural abundance. Ringström's molecular constants (18) allowed the lines to be unambiguously identified. Once the (1, 0) band had been picked out and fit, the (2, 1) and (2, 0) bands were predicted and found. A section of the spectrum showing the *R*(7) line of both isotopic species is displayed in Fig. 1.

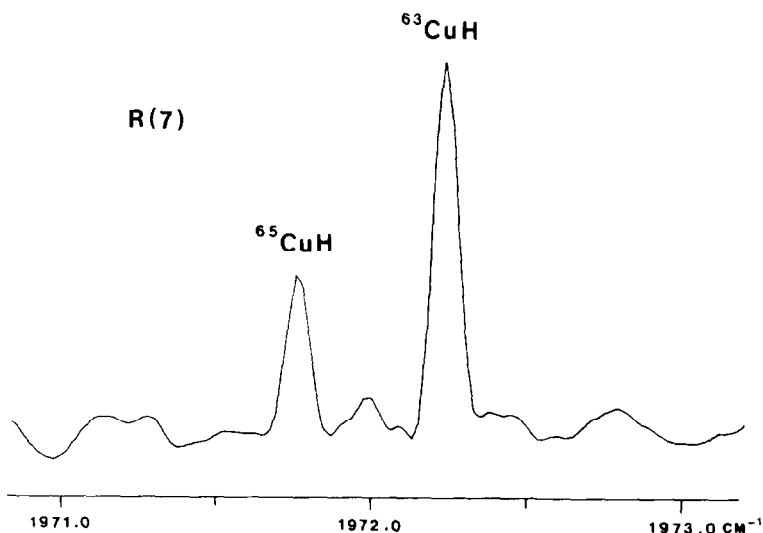


FIG. 1. The *R*(7) transition for both <sup>65</sup>CuH and <sup>63</sup>CuH of the fundamental (1, 0) band.

The line positions of the (1, 0), (2, 1), and (2, 0) bands of  $^{63}\text{CuH}$  and  $^{65}\text{CuH}$  are provided in Tables I and II. Only *R* lines were recorded for the (2, 1) band and just a few *P* lines of the (1, 0) band because of the  $1800\text{-cm}^{-1}$  cutoff of the InSb detector. The CuD (1, 0) band is below  $1800\text{ cm}^{-1}$  and the (2, 0) band was too weak to observe. Since  $^{65}\text{Cu}$  has an abundance of 31%, fewer  $^{65}\text{CuH}$  than  $^{63}\text{CuH}$  lines were found, and the observed  $^{65}\text{CuH}$  lines have a lower signal-to-noise ratio. The best signal-to-noise ratio was about 20 (see Fig. 1).

The spectra of  $\text{H}_2$ , CO, and OH were present in our records. The CO (24) and OH (25) lines were used to provide an absolute calibration accurate to  $\pm 0.001\text{ cm}^{-1}$ . However, the rather modest signal-to-noise ratio for CuH limits the accuracy of our observations to about  $0.005\text{ cm}^{-1}$  for the stronger, unblended lines.

#### IV. ANALYSIS AND DISCUSSION

The line positions of Tables I and II were fit using the customary rotational energy level expression for  $^1\Sigma$  states (26):

$$F_v(J) = T_v + B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3. \quad (1)$$

The  $v = 2, 1,$  and  $0$  energy levels were simultaneously fit for each isotopic species using a nonlinear least squares procedure. The molecular constants from these two fits are provided in Table III. Note that the *H* values of the less abundant  $^{65}\text{CuH}$  were constrained using the expected  $\rho^6$  isotopic dependence and the  $^{63}\text{CuH}$  values (26). An extra digit is provided in Table III: because of correlation (as usual)  $\Delta B$ 's are better determined than *B*'s.

TABLE I

The Observed Line Positions for the Vibration-Rotation Spectra of  $^{63}\text{CuH}$  (in  $\text{cm}^{-1}$ ) [the numbers in parentheses are observed-calculated line positions using the constants of Table III (in  $10^{-3}\text{ cm}^{-1}$ )]

J	(1,0)		(2,1)	(2,0)	
	R(J)	P(J)	R(J)	R(J)	P(J)
0	1881.530 (-2)			3673.090 (-5)	
1	1896.142 (0)	1850.775 (3)		3686.707 (5)	
2	1910.222 (2)	1834.643 (-3)	1834.393 (3)	3699.276 (-2)	a
3	1923.759 (3)	1818.042 (0)	1847.436 (-4)	3710.791 (-22)	3608.601 (-2)
4	1936.739 (1)	1800.968 (-2)	a	a	3590.038 (10)
5	1949.154 (1)		1871.880 (3)	3730.699 (-8)	3570.491 (-9)
6	1960.988 (-2)		1883.242 (-2)	3739.052 (8)	3550.027 (-4)
7	1972.242 (2)		1894.023 (-3)	3746.286 (-10)	3528.636 (2)
8	1982.888 (-2)		1904.212 (-2)		3506.321 (0)
9	1992.931 (-2)		1913.808 (9)		
10	2002.350 (-2)		1922.765 (-4)		
11	2011.144 (0)		1931.114 (-2)		
12	2019.300 (3)		1938.830 (1)		
13	2026.798 (-5)		1945.898 (-3)		
14	2033.657 (7)		1932.323 (2)		
15	2039.826 (-3)				
16	2045.333 (-4)				
17	2050.151 (4)				

a: obscured by an atomic line.

TABLE II

The Observed Line Positions for the Vibration-Rotation Spectra of  $^{65}\text{CuH}$  (in  $\text{cm}^{-1}$ ) [the numbers in parentheses are observed-calculated line positions using the constants of Table III (in  $10^{-3} \text{cm}^{-1}$ )]

J	(1,0)		(2,1)	(2,0)	
	R(J)	P(J)	R(J)	R(J)	P(J)
0	1881.098 (3)			3672.290 (19)	
1	1895.699 (2)	a		3685.859 (-12)	
2	1090.760 (-8)	1834.224 (-9)	1833.984 (4)	3698.443 (4)	
3	1923.299 (2)	1817.631 (-2)	1847.030 (6)	3709.954 (-11)	3607.803 (0)
4	1936.271 (-2)		1859.509 (-8)	3720.440 (3)	c
5	1948.691 (8)		1871.446 (-3)	3729.856 (13)	3569.708 (-2)
6	1960.508 (-9)		1882.808 (-3)		3549.242 (4)
7	1971.761 (-1)		1893.577 (-12)	3745.420 (5)	3527.830 (-3)
8	1982.408 (0)		1903.774 (0)		
9	1992.454 (7)		1913.362 (6)		
10	2001.864 (-1)		b		
11	2010.645 (-8)		a		
12	2018.810 (9)		1938.384 (6)		
13	2026.296 (-3)		b		
14	2033.146 (8)		1951.857 (-3)		
15	2039.300 (-6)				
16	c				
17	2049.593 (2)				

a: obscured by an atomic line.

b: obscured by  $\text{CO}_2$  absorption.

c: badly blended.

Equilibrium molecular parameters were derived for each isotopic species using the equations

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) + \gamma_e(v + \frac{1}{2})^2 \quad (2)$$

and

$$D_v = D_e + \beta_e(v + \frac{1}{2}). \quad (3)$$

In addition, the vibrational constants were determined from (26)

$$T_{1,0} = \omega_e - 2\omega_e x_e \quad (4)$$

TABLE III

Molecular Constants (in  $\text{cm}^{-1}$ ) for the  $X^1\Sigma^+$  States of the  $^{63}\text{CuH}$  and  $^{65}\text{CuH}$  Molecules

Molecular Constants <sup>a</sup>	v = 0		v = 1		v = 2	
	$^{63}\text{CuH}$	$^{65}\text{CuH}$	$^{63}\text{CuH}$	$^{65}\text{CuH}$	$^{63}\text{CuH}$	$^{65}\text{CuH}$
$T_v$	0.0	0.0	1866.4048(19)	1865.9757(23)	3658.4682(25)	3657.6531(34)
$B_v$	7.81745(22)	7.81356(25)	7.56472(24)	7.56075(25)	7.31425(25)	7.31021(23)
$10^4 D_v$	5.341(40)	5.166(30)	5.276(45)	5.133(25)	5.217(42)	5.097(19)
$10^8 H_v$	8.8(37)	8.8 <sup>b</sup>	7.4(31)	7.4 <sup>b</sup>	6.5(23)	6.5 <sup>b</sup>

a: The numbers in the parentheses are one standard deviation in the last digit.

b: Fixed values (see text).

and

$$T_{2,0} = 2\omega_e - 6\omega_e x_e. \quad (5)$$

The equilibrium constants are reported in Table IV. Note that all of our determinations are essentially exact fits so that the uncertainties of Table IV were computed by using the uncertainties of Table III and the customary rules for error propagation. The actual uncertainties for  $\omega_e$  and  $\omega_e x_e$  are expected to be much higher than the numbers quoted in Table IV because of the neglect of the  $\omega_e y_e$  term. With only a  $\Delta G_{1/2}$  and a  $\Delta G_{3/2}$ ,  $\omega_e y_e$  cannot be determined from our data but is certainly not negligible. The usual isotopic relationships between the  $^{63}\text{CuH}$  and  $^{65}\text{CuH}$  equilibrium constants are obeyed within the quoted errors.

The molecular constants of Tables III and IV are in reasonable agreement with, but more accurate than, the previous determinations. Ringström's (19) parameter values,  $B_0 = 7.8163(3)$ ,  $B_1 = 7.5631(3)$ ,  $B_2 = 7.3130(3)$ ,  $T_{1,0} = 1866.46(2)$ , and  $T_{2,0} = 3658.50(2)$  are slightly, but systematically, different from those reported in Table III. The customary Pekeris and Kratzer relationships were used to test the self-consistency of the molecular constants of Table IV. The Pekeris relation (26) predicts an  $\alpha_e = 0.22695$  compared to the observed  $0.25499(55) \text{ cm}^{-1}$  for  $^{63}\text{CuH}$ . This disagreement is likely a reflection of the inadequacy of the Morse potential curve (from which the Pekeris relationship is derived) and of our neglect of  $\omega_e y_e$ . The Kratzer relation predicts a  $D_e = 5.325 \times 10^{-4} \text{ cm}^{-1}$  for  $^{63}\text{CuH}$ , in good agreement with the observed  $5.372 \times 10^{-4} \text{ cm}^{-1}$ .

The first emission observation of a metal hydride vibration-rotation spectrum opens up a number of interesting possibilities. Not only might the alkali and alkaline earth hydrides be observed in their  $\Delta v = 2$  sequence, but additional transition metal hydrides may be detected. The transition metal hydrides have complicated visible transitions, largely because of extensive perturbations among the numerous excited states. The infrared vibration-rotation spectra and infrared electronic transitions may be relatively unperturbed and amenable to analysis.

TABLE IV  
Equilibrium Molecular Constants (in  $\text{cm}^{-1}$ ) for the  $X^1\Sigma^+$  State of CuH

Constants	$^{63}\text{CuH}$	$^{65}\text{CuH}$
$\omega_e$	1940.7462 (41) <sup>a</sup>	1940.2740 (47)
$\omega_e x_e$	37.1707 (23)	37.1492 (41)
$B_e$	7.94467 (37)	7.94082 (1)
$\alpha_e$	0.25499 (56)	0.25507 (60)
$\gamma_e$	0.00113 (24)	0.00113 (24)
$10^4 D_e$	5.372 (72)	5.184 (49)
$10^5 B_e$	-0.62 (60)	-0.35 (39)
$r_e (\text{\AA})$	1.46257	1.46257

a: See text for a discussion of how the uncertainties were determined.

## ACKNOWLEDGMENTS

We thank Rob Hubbard for expert technical support during our data run. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the ACS, for partial support of this research. This research was also supported by Grants NSF CHE-8306504 and ONR N00014-84-K-0122.

RECEIVED: March 14, 1985

## REFERENCES

1. R. E. SMITH, *Proc. R. Soc. Lond. A*, **332**, 113–127 (1973).
2. R. B. WRIGHT, J. K. BATES, AND D. M. GRUEN, *Inorg. Chem.* **17**, 2275–2278 (1978).
3. R. SCULLMAN, S. LÖFGREN, AND S. ADAKKAI KADAVATHU, *Phys. Scr.* **25**, 295–301 (1982).
4. W. J. BALFOUR, B. LINDGREN, AND S. O'CONNOR, *Chem. Phys. Lett.* **96**, 251–252 (1983).
5. R. J. VAN ZEE, T. C. DEVORE, J. L. WILKERSON, AND W. WELTNER, JR., *J. Chem. Phys.* **69**, 1869–1875 (1978).
6. B. KLEMAN AND U. UHLER, *Canad. J. Phys.* **37**, 537–549 (1959).
7. L. KLYNNING AND M. KRONEKVIST, *Phys. Scr.* **24**, 21–22 (1981).
8. A. E. STEVENS, C. S. FEIGERLE, AND W. C. LINEBERGER, *J. Chem. Phys.* **78**, 5420–5431 (1983).
9. P. S. BAGUS AND C. BJORKMAN, *Phys. Rev. A* **23**, 461–472 (1981).
10. M. R. A. BLOMBERG AND P. E. M. SEIGBAHN, *Mol. Phys.* **47**, 127–143 (1982).
11. S. P. WALCH AND C. W. BAUSCHLICHER, JR., *J. Chem. Phys.* **78**, 4597–4605 (1983).
12. G. DAS, *J. Chem. Phys.* **74**, 5766–5774 (1981).
13. G. H. JEUNG AND J. C. BARTHELAT, *J. Chem. Phys.* **78**, 2097–2099 (1983).
14. R. F. WING, J. COHEN, AND J. W. BRAULT, *Astrophys. J.* **216**, 659–664 (1977).
15. A. HEIMER AND T. HEIMER, *Z. Phys.* **84**, 222–235 (1933).
16. B. KLEMAN, *Ark. Fys.* **6**, 17–24 (1952).
17. B. GRUNDSTRÖM, *Z. Phys.* **98**, 128–132 (1935).
18. U. RINGSTRÖM, *Ark. Fys.* **32**, 211–239 (1966).
19. U. RINGSTRÖM, *Canad. J. Phys.* **46**, 2291–2300 (1968).
20. C. M. BROWN AND M. L. GINTER, *J. Mol. Spectrosc.* **80**, 145–157 (1980).
21. R. S. RAM, P. F. BERNATH, AND J. BRAULT, *J. Mol. Spectrosc.*, in press.
22. T. C. JAMES, W. G. NORRIS, AND W. KLEMPERER, *J. Chem. Phys.* **32**, 728–734 (1960).
23. N. N. HAESE, D. LIU, AND R. S. ALTMAN, *J. Chem. Phys.* **81**, 3766–3773 (1984).
24. G. GUELACHVILLI, *J. Mol. Spectrosc.* **75**, 251–269 (1979).
25. T. AMANO, *J. Mol. Spectrosc.* **103**, 436–454 (1984).
26. G. HERZBERG, "Spectra of Diatomic Molecules," 2nd ed., Van Nostrand-Reinhold, New York, 1950.