

experimental value of the lifetime of the second doublet  $\lambda 4047-4$  as found above is  $\tau_2 = 3.79 \times 10^{-7}$  sec. This is equal to the product of  $\alpha$  and the reciprocal of the transition probability for this doublet, since  $\tau$  equals the reciprocal of the sum of the probabilities of emission from the upper level. This gives  $\alpha = \tau_2 / 30.3 \tau_1 = 0.46$ , which is considerably larger than our estimate.

It is interesting to compare this with the value  $\alpha = \frac{1}{2}$ , obtained for the sodium doublet  $\lambda 3202-3$ , by Christensen and Rollefson.<sup>9</sup> They illuminated a bulb containing sodium vapor at a pressure of  $10^{-4}$  mm and measured the relative intensities of  $\lambda 5890-6$  and  $\lambda 3202-3$  emitted at right angles to the illumination, from which they

<sup>9</sup> C. J. Christensen and G. K. Rollefson, *Phys. Rev.* **34**, 1157 (1929).

computed  $\alpha$ . On the other hand Weiss<sup>10</sup> found  $\alpha$  to be about 1/25 by comparing the relative intensities of these same doublets emitted by an arc.

The preceding discussion is based on the assumption that all radiation not directly transmitted is absorbed and re-emitted, the mean time for the process being equal to  $\tau$ . Coherent scattering has been assumed negligible and the pressures were too low for dissipative absorption by collision. The effect of coherent scattering superposed on absorption would be to give too small a value for  $\alpha$  as estimated from the lifetime measurements. On the other hand the effect on the results of Christensen's and Rollefson's<sup>9</sup> experiment would be to give too large a value for  $\alpha$ .

<sup>10</sup> C. Weiss, *Ann. d. Physik* **1**, 565 (1929).

## The ${}^1\Sigma^* - {}^1\Sigma$ Band System of Copper Deuteride

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The copper deuteride bands have been photographed with high dispersion and an analysis is given of the  ${}^1\Sigma^* - {}^1\Sigma$  system. The  $\text{Cu}^{63}\text{D}$  and  $\text{Cu}^{65}\text{D}$  isotopic bands are separated and an independent analysis is given for each. From data obtained for the normal  ${}^1\Sigma$  state,  $\rho$  for  $\text{Cu}^{65}\text{D}$  to  $\text{Cu}^{63}\text{D}$  is 0.999503 which agrees with the best mass spectrographic data. A comparison with Heimer and Heimer's  $\text{CuH}$  analysis gives a value of  $\rho$  equal to 0.7131 for  $\text{Cu}^{63}\text{D}$  to  $\text{Cu}^{65}\text{H}$ . The electronic isotope displacement of  $\text{CuD}$  relative to  $\text{CuH}$  is  $19 \text{ cm}^{-1}$ .

### INTRODUCTION

THE spectrum of  $\text{CuH}$  has been photographed by several investigators.<sup>1-4</sup> None of these has given a complete analysis of the copper isotopic bands. The purpose of the present investigation was to obtain data for a comparison of the hydride and deuteride spectra, and also to make a rigorous copper isotope analysis. After the experimental work and much of the analysis was finished it was learned that the copper deuteride spectrum had been photographed in another

laboratory.<sup>5</sup> Since no mention was made of a copper isotope analysis it appeared worth while to complete the present study.

### EXPERIMENTAL

The spectrum was excited in a water-cooled metal arc chamber. Deuterium, produced by the vacuum distillation of heavy water onto powdered zinc, was admitted to the chamber and kept at a pressure of 40 cm of mercury. Following the suggestion of Heimer and Heimer<sup>2</sup> we used an anode of bismuth copper alloy and a cathode of pure copper. The arc chamber was evacuated and refilled with deuterium five or six times during a 24-hour exposure. The arc was run from a 220 volt line and carried a current of approximately 3 amperes.

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<sup>1</sup> Jevons, *Band Spectra of Diatomic Molecules* (1932), p. 300.

<sup>2</sup> A. Heimer and T. Heimer, *Zeits. f. Physik* **84**, 222 (1933).

<sup>3</sup> T. Heimer, *Zeits. f. Physik* **95**, 321 (1935).

<sup>4</sup> B. Grundstrom, *Zeits. f. Physik* **98**, 128 (1935).

<sup>5</sup> T. Heimer, *Naturwiss.* **23**, 372 (1935).

The plates were taken on a Johns Hopkins University spectrograph, consisting of a 21-foot, 30,000 lines per inch grating in Paschen mounting. The photographs were taken in the first order, which gave a dispersion of about 1.3A/mm. Nearly all the wave numbers given are mean values of measurements of two spectrograms. The wave-lengths should be accurate to within 0.005A.

#### ANALYSIS

The bands analyzed involve the first four vibrational levels in each of the  ${}^1\Sigma$  and  ${}^1\Sigma^*$  states, the former being the normal state of the CuD molecule. They were located when possible by making use of the published data on CuH and theoretical isotope relations. Other bands were found by application of the combination principle. The rotational analysis was done by the usual methods. There is considerable overlapping of bands causing rather numerous blends. Atomic lines of copper, bismuth, and hydrogen obscure many of the CuD lines.

The resolving power is sufficient to permit a complete analysis of the system under consideration for each of the two molecules, Cu<sup>63</sup>D and Cu<sup>65</sup>D, the isotopic lines being completely resolved for the bands involving a change in the vibrational quantum number  $v$  greater than zero. In other bands resolution is not attained at the lower values of the rotational quantum number  $J$ . In Table I are listed the lines identified in twelve different bands with their quantum number assignments. The first entry for a given value of  $J$  is for Cu<sup>63</sup>D, the second for Cu<sup>65</sup>D. Where the lines are unresolved there is a single entry.

#### DERIVATION OF CONSTANTS

The well-known analytic least-squares method given by Birge<sup>6</sup> was used in performing the calculations. In order to use lines belonging to transitions between levels having large  $J$  values the rotational energy function was carried out to the term involving  $(J+\frac{1}{2})^8$ , and expressed as

$$F(v, J) = B_v(J+\frac{1}{2})^2 + D_v(J+\frac{1}{2})^4 + F_v(J+\frac{1}{2})^6 + H_v(J+\frac{1}{2})^8. \quad (1)$$

<sup>6</sup> R. T. Birge, National Research Council Bulletin No. 57, *Molecular Spectra in Gases*, pp. 172-175 (1926).

For each level  $F_v$  was taken equal to  $F_e$  and  $H_v$  to  $H_e$ . This equation forms the basis for the evaluation of the rotational constants. Taking into account the difference between the finite difference and the derivative in the terms in which this difference is appreciable one obtains for the rotational energy intervals

$$\Delta_2 F = 4B_v(J+\frac{1}{2}) + (8D_v+12F_e)(J+\frac{1}{2}) + (8D_v+40F_e)(J+\frac{1}{2})^3 + 12F_e(J+\frac{1}{2})^5 + 16H_e(J+\frac{1}{2})^7. \quad (2)$$

$\Delta_2 F^*$  is now defined as follows:

$$\Delta_2 F^* = \Delta_2 F - (8D_v+12F_e)(J+\frac{1}{2}) - (8D_v+40F_e)(J+\frac{1}{2})^3 - 12F_e(J+\frac{1}{2})^5 - 16H_e(J+\frac{1}{2})^7 = 4B_v(J+\frac{1}{2}). \quad (3)$$

$D_v$ ,  $F_e$ , and  $H_e$  are calculated from the theoretical relations given by Jevons,<sup>1</sup> hence  $\Delta_2 F^*$  may be determined directly from the observed rotational intervals.  $B_v$  then occurs as the slope of a linear least squares equation with  $4(J+\frac{1}{2})$  as the independent and  $\Delta_2 F^*$  as the dependent variable.

The work of Almy and Irwin<sup>7</sup> on the  ${}^1\Sigma - {}^1\Sigma$  system of Li<sub>2</sub> indicates that the accuracy of constants evaluated from lines of large rotational quantum number may be open to question. The close agreement between the values of  $\Delta_2 F^*$  determined directly from the data and those calculated by substituting the least-squares values of  $B_v$  in Eq. (3) indicates that in the normal  ${}^1\Sigma$  state the use of lines having values of  $J$  as great as 45 is justified.

In the  ${}^1\Sigma^*$  state it was found that lines of large rotational quantum number could not be used. Beginning at approximately  $J=20$  the calculated  $B_v$ 's for a given level show a gradual decrease. Apparently  $D_v$  in the rotational energy function should have a larger absolute value than that given by the theoretical relations, and should increase rather than decrease (in absolute value) with  $v$ . Instead of using empirical values of  $D_v$  it was thought best to use the theoretical ones having their usual significance and limit the calculations to low values of  $J$ . For small values of  $J$  the derived constants would have the same value in either case. Anomalous behavior of the rotational energy function for the  ${}^1\Sigma^*$  state was also observed in the copper hydride spectrum,<sup>2</sup> where it was found necessary to use a *positive D*

<sup>7</sup> G. M. Almy and G. R. Irwin, Phys. Rev. **49**, 72 (1936).



TABLE II. Values of  $B_v$  for the normal  ${}^1\Sigma$  state.

	Cu <sup>63</sup> D		Cu <sup>65</sup> D	
	Obs.	Obs.-Calc.	Obs.	Obs.-Calc.
$B_0$	3.99197	+0.00013	3.98804	+0.00002
$B_1$	3.90034	-0.00011	3.89698	0.00000
$B_2$	3.80900	-0.00004	3.80589	-0.00006
$B_3$	3.71795	+0.00031	3.71498	+0.00006

TABLE III. Values of  $B_v$  for the  ${}^1\Sigma^*$  state.

	Cu <sup>63</sup> D		Cu <sup>65</sup> D	
	Obs.	Obs.-Calc.	Obs.	Obs.-Calc.
$B_0$	3.4740	-0.0005	3.4711	-0.0010
$B_1$	3.3809	+0.0001	3.3777	+0.0003
$B_2$	3.2829	-0.0002	3.2788	-0.0003
$B_3$	3.1819	+0.0004	3.1785	+0.0010

TABLE IV. Summary of constants.

	Cu <sup>63</sup> D		Cu <sup>65</sup> D	
	${}^1\Sigma$	${}^1\Sigma^*$	${}^1\Sigma$	${}^1\Sigma^*$
$\omega_e$	1384.38	1213.16	1383.65	1212.60
$x_e\omega_e$	19.14	20.65	19.12	20.45
$y_e\omega_e$	0.037	-0.41	0.027	-0.45
$T_e$	0	23412	0	23412
$B_e$	4.03754	3.5199	4.03353	3.5182
$\alpha_e$	0.09140	0.0898	0.09103	0.0919
$\gamma$		-0.0020		-0.0017
$D_e$	$-1.3737 \times 10^{-4}$	$-1.185 \times 10^{-4}$	$-1.3710 \times 10^{-4}$	$-1.183 \times 10^{-4}$
$\beta_e$	$1.442 \times 10^{-5}$	$5.51 \times 10^{-7}$	$1.241 \times 10^{-5}$	$4.28 \times 10^{-7}$
$F_e$	$3.285 \times 10^{-9}$	$1.901 \times 10^{-9}$	$3.317 \times 10^{-9}$	$2.058 \times 10^{-9}$
$H_e$	$-1.20 \times 10^{-13}$	$-8.34 \times 10^{-14}$	$-1.28 \times 10^{-13}$	$-9.33 \times 10^{-14}$

for the  $v=3$  level. The perturbation giving rise to this abnormal value is evidently removed in the copper deuteride molecule. Here  $D_3$  is negative as theory demands.

The values of  $B_v$  for the normal  ${}^1\Sigma$  state are given by the following least-squares equations:

$$\text{For Cu}^{63}\text{D: } B_v = 4.03754 - 0.09140(v + \frac{1}{2}). \quad (4)$$

$$\text{For Cu}^{65}\text{D: } B_v = 4.03353 - 0.09103(v + \frac{1}{2}). \quad (5)$$

In the determination of the constants of these equations each value of  $B_v$  was given a weight proportional to the number of values of  $\Delta_2 F^*$  used in its calculation.

In the  ${}^1\Sigma^*$  state the  $B_v$ 's are given by the following quadratic equations:

$$\text{For Cu}^{63}\text{D: } B_v = 3.5199 - 0.0898(v + \frac{1}{2}) - 0.00197(v + \frac{1}{2})^2. \quad (6)$$

$$\text{For Cu}^{65}\text{D: } B_v = 3.5182 - 0.0913(v + \frac{1}{2}) - 0.00173(v + \frac{1}{2})^2. \quad (7)$$

Table II gives the experimental values of  $B_v$  for

the normal  ${}^1\Sigma$  state as determined from Eq. (3), and the differences between these values and those calculated from Eqs. (4) and (5). Table III gives similar information for the  ${}^1\Sigma^*$  state.

The vibrational intervals  $\Delta G_{v+\frac{1}{2}}$  are obtained from the observed band lines by the use of relations such as these:

$$\Delta G_{1\frac{1}{2}} = R_{(0-1)}(J) - R_{(0-2)}(J) + \alpha J(J+1) - \beta J^2(J+1)^2 = P_{(0-1)}(J) - P_{(0-2)}(J) + \alpha J(J+1) - \beta J^2(J+1)^2. \quad (8)$$

In each case  $\alpha$  and  $\beta$  are obtained from the rotational data already given.

The values of the vibrational constants  $\omega_e$ ,  $x_e\omega_e$ , and  $y_e\omega_e$  were obtained from the equation

$$\Delta G_{v+\frac{1}{2}} = \omega_e - 2x_e\omega_e(v + \frac{1}{2}) + 3y_e\omega_e(v + \frac{1}{2})^2, \quad (9)$$

into which the observed  $\Delta G_{v+\frac{1}{2}}$  were substituted. A summary of the usual band spectra constants is given in Table IV.

#### ISOTOPE RELATIONS

Corrections that may be applied to the band spectra values of  $\rho$  have been conveniently listed by Watson.<sup>8</sup> In view of the irregularities observed in the  ${}^1\Sigma^*$  state in CuH and to a lesser degree in CuD there is probably quantum-mechanical interaction with the neighboring  ${}^1\Pi$  states<sup>3</sup> which would make the  $B_v$  determined from the data an *effective B* not having the simple relation to the true moment of inertia. Analysis of the CuH spectrum is not sufficiently complete to permit a calculation of this correction in the present paper. Accordingly, the values of  $\rho$  which are considered to be most accurate are determined from the normal state.

TABLE V. Isotope ratios. (Heimer and Heimer's values of the constants for Cu<sup>63</sup>H are used for the Cu<sup>63</sup>D to Cu<sup>65</sup>H ratios.)

	Cu <sup>65</sup> D : Cu <sup>63</sup> D		Cu <sup>63</sup> D : Cu <sup>63</sup> H	
	${}^1\Sigma$	${}^1\Sigma^*$	${}^1\Sigma$	${}^1\Sigma^*$
$(B_e^i/B_e)^{\frac{1}{2}}$	0.999503	0.99976	0.7131	0.7153
$\omega_e^i/\omega_e$	0.99947	0.99954	0.7135	0.7129
$(\mu/\mu_i)^{\frac{1}{2}}$	0.99952		0.7129	

<sup>8</sup> W. W. Watson, Phys. Rev. **49**, 70 (1936).

A consideration of the other corrections indicates that the only ones which might be appreciable in the normal state are those given by Dunham<sup>9</sup> for the anharmonicity terms. They involve a power series in  $B_e^2/\omega_e^2$ , which is of the order of  $10^{-6}$  for the CuD molecule, making even these corrections negligible.

The values of  $\rho$  calculated from the vibrational and rotational constants are given in Table V and compared with the value of  $(u/u_i)^{\frac{1}{2}}$  from mass-spectrograph data. The agreement is excellent with the exception of  $(B_e^i/B_e)^{\frac{1}{2}}$  in the  $^1\Sigma^*$  state. Here the value is 0.99976 for Cu<sup>65</sup>D to Cu<sup>63</sup>D, which differs by 0.00024 from the calculated value. This difference may be due in part to difficulty in reduction of the data as is indicated above since only the low values of  $J$  can be used in this state. The fact that  $(B_e^i/B_e)^{\frac{1}{2}}$  for CuD to CuH in the  $^1\Sigma^*$  state is also much larger than the calculated value indicates that the discrepancy is real, however, and that  $B_e$  should in this case be corrected as mentioned above.

Rather limited data are available for the determination of the  $\Delta G_{v+\frac{1}{2}}^{\circ}$  values for Cu<sup>65</sup>D, especially in the normal state. This makes the uncertainty in the value of  $\omega_e^i/\omega_e$  much greater than

<sup>9</sup> J. L. Dunham, Phys. Rev. **41**, 721 (1932).

the uncertainty in  $(B_e^i/B_e)^{\frac{1}{2}}$  for this state. An estimate of the probable error in  $\omega_e^i/\omega_e$  based on the individual probable errors in the values of  $\Delta G_{v+\frac{1}{2}}^{\circ}$  is 0.00015. In the  $^1\Sigma$  state  $\omega_e^i/\omega_e$  for Cu<sup>65</sup>D to Cu<sup>63</sup>D has the value 0.99947, and in the  $^1\Sigma^*$  state 0.99954. The corresponding values for Cu<sup>63</sup>D to Cu<sup>63</sup>H are 0.7135 and 0.7129, respectively.

The large number of individual values used in the determination of the  $B_v$  constants makes  $(B_e^i/B_e)^{\frac{1}{2}}$  for the normal state the most reliable value of  $\rho$  determined from the present work. This value for the molecules Cu<sup>65</sup>D and Cu<sup>63</sup>D is 0.999503. The calculated values of the probable errors of the values of  $B_e$  as given by Eqs. (4) and (5) are 0.000071 and 0.000018, respectively. A consideration of the probable error of the individual values of  $B_v$  would indicate that these values are too small. It is believed, however, that  $(B_e^i/B_e)^{\frac{1}{2}}$  for Cu<sup>65</sup>D to Cu<sup>63</sup>D can have a probable error no greater than 0.00006. The value of this ratio for Cu<sup>63</sup>D to Cu<sup>63</sup>H for the  $^1\Sigma$  state is 0.7131.

In conclusion the author wishes to express his sincere thanks to the Physics Department of The Johns Hopkins University for the use of the spectrograph on which the plates were taken.

## The Temperature Variation of the Elastic Moduli of NaCl, KCl and MgO

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The principal adiabatic and isothermal elastic moduli and elastic constants of NaCl, KCl and MgO have been measured over the temperature ranges 80°K to 270°K (Balamuth and Rose) and 270°K to 480°K for NaCl; 80°K to 280°K for KCl; and 80°K to 560°K for MgO. The Debye characteristic temperatures of these substances at 80°K, calculated from the adiabatic elastic constants, are 320°K, 246°K and 946°K, respectively. The variation of the isothermal  $c_{11}$  and  $c_{44}$  with temperature is described very accurately by the formula:  $(c_{ii})_u = (c_{ii})_0 \exp(-A_{ii}F_{ii}(u))$ ,

where  $u = (T/\theta)$ ,  $T$  is the absolute temperature and  $\theta$  the characteristic temperature,  $(c_{ii})_0$  denotes the value at absolute zero,  $A_{ii}$  is a constant of the material, and  $F_{ii}(u)$  is a function of  $u$  which assumes the value unity when  $u=1$ , and which is the same for all three substances. Experimental values of  $F_{11}(u)$  and  $F_{44}(u)$  are given for values of  $u$  between 0.1 and 1.5. The isothermal  $c_{12}$  does not vary with temperature, over the specified ranges, by more than the error of measurement.

THE temperature variations of the three principal elastic constants of sodium chloride between 80°K and 270°K have been reported in this journal by Balamuth<sup>1</sup> and Rose.<sup>2</sup> These

investigators perfected their experimental method for use only at temperatures below that of melting ice. The object of the present research is, in the first instance, to extend the scope of the method and the observations on sodium chloride to higher temperatures. In addition, observations

<sup>1</sup> Balamuth, Phys. Rev. **45**, 715 (1934).

<sup>2</sup> Rose, Phys. Rev. **49**, 50 (1936).