A Review of Oscillator Strengths for Lines of Cu I

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New determinations of oscillator strengths made by Kock and Richter provide for the first time reference standards which permit the adjustment of five previous sets of measurements to an improved scale of absolute oscillator strengths for lines of Cu I. Critical discussions of the several sets of measurements and a consistent list of values for 272 lines in the region 2024 to 8092 Å are presented.

Key words: Atomic spectra; copper; Cu I; oscillator strengths; spectral lines of Cu I.

1. Introduction

Because of its superior electrical and thermal conductivity, relatively high melting point and strength, and its purity and cheapness in commerce, copper is widely used in electrical apparatus. It frequently serves as electrode material in various kinds of arcs and electrical discharges and its spectrum is on that account frequently observed in the laboratory. A good knowledge of the various physical constants associated with its spectrum leads to understanding of the discharges themselves. Although useful in the laboratory, the spectrum of copper is not well developed in stellar atmospheres, and is at present of limited astrophysical interest. About 20 lines of Cu I are observed in the solar spectrum.

The wavelengths and energy levels of the arc spectrum of copper have been thoroughly studied and determined by Shenstone [1948] but knowledge of the oscillator strengths of the lines, which is required if excitation conditions in discharges are to be measured and understood, is rather fragmentary. The reports of measurements are scattered throughout the literature, some of the measurements (my own included) are reduced to oscillator strengths with wrong temperatures, and the quantities reported differ in each report. Nevertheless, much of this data can be evaluated, corrected to proper temperatures, adjusted to an absolute scale, and tabulated in a useful and uniform fashion.

The framework on which this data can be reformed and assembled was provided by Kock and Richter [1966] when they measured 27 Cu I lines over the wavelength range 2618 to 5782 Å and energy level range 30535 to 64472 cm⁻¹. Their data provide lines over a wide enough range of energies to correct for erroneous temperatures used in earlier papers.

2. Published Data

A summary of the data critically reviewed in this paper is given in table 1. All of these measurements were made on relative scales; some were reported on absolute scales.

There are several papers of which the results are not included in this report. The early work at Utrecht by van Lingen [1936] and van den Bold [1945] on the two resonance lines, the six strong green and yellow lines, and the two infrared lines is now mainly of historical interest. Dickerman and Deuel [1964] have measured 12 lines in the blue region with a high-current free-burning arc in argon. Their results show serious and unsystematic disagreement with those of Kock and Richter and others. Riemann [1964] measured the six green and yellow lines and the two strong resonance lines in a wall-stabilized arc.

Ostroumenko and Rossikhin [1965] measured nine resonance lines between 2165 and 3274 Å in absorption with a furnace. Their value for the line at 2225 is an order of magnitude too low when compared with that of Slavenas [1966], who measured the same lines by the hook method. The same lines were also measured by Lvov [1970] using the method of atomic absorption in a flame. His value for the line at 2441 is an order of magnitude too high compared to the measurements of the other authors. With those two exceptions, the three sets of data are in good agreement.

An interesting paper by Vujnovic, Ivezic, and Tonejc-Mejak [1968] included a few calculations according to Bates and Damgaard's coulomb approximation, which were in good agreement with Kock and Richter's experimental results. This prompted us to make further calculations of that kind, which are reported in section 4.
The temperature determinations of other experiments they calculated with Bates and Damgaard's coulomb approximation.

The data reported in this review have been adjusted to the lifetime of this level has been recently determined by the University of Kiel by Maecker [1956]. A great deal of the wall-stabilized arc design originally developed at the University of Kiel by Maecker [1966], Ney [1966] and Link [1967].

Kock and Richter's data are listed in table 3 in the column headed CWA.

2.1. Kock and Richter [1968]

These authors have made the first comprehensive set of measurements of oscillator strengths for lines of Cu I in a light source operating under LTE conditions at accurately specified temperatures and electron densities. The plasma temperatures were determined from the absolute intensity of Ar I lines that have accurately known transition probabilities. The light source was of the wall-stabilized arc design originally developed at the University of Kiel by Maecker [1956]. A great deal of study has been devoted to methods of accurate temperature determination in this arc, both in Germany and the United States. See, e.g., W. L. Wiese [1968].

Kock and Richter included among the 27 lines they measured the three lines which depopulate the 4p 4D 3/2 upper level of the strong resonance line at 3247 Å. The lifetime of this level has been recently determined by three independent experiments; Levin and Budick [1966], Ney [1966] and Cunningham and Link [1967]. The value 7.1 ns is within the uncertainty of all three measurements and has been adopted by Kock and Richter to put their relative values on an absolute scale. The data reported in this review have been adjusted to their scale.

Kock and Richter's data are listed in table 3 in the column headed KR. A typographical error in their value for the line at 4480.35 Å has been corrected. The values they gave for the two strong lines near 8000 Å they calculated with Bates and Damgaard's coulomb approximation.

2.2. Allen [1932]

The first quantitative intensity measurements in Cu I were made in 1932 by C. W. Allen at Canberra in the course of a study of the behavior of the relative intensity of the sharp and diffuse lines arising from the 5s 4D term which lies above the first ionization potential of Cu I. The 4D 5/2 and 4D 3/2 levels are broad and decay mainly by autoionization. Allen measured the relative intensities of all 27 lines of the 4p 4P o − 5s 4D, 4p 4F o − 5s 4D, and 4p 4D − 5s 4D multiplets at various currents from 1 to 19 A in a free-burning copper arc in air at atmospheric pressure. He found that the broad lines increased in intensity relative to the sharp ones as the current was increased but that the ratio reached a constant value for currents above 12 A. These limiting relative intensities were in fair agreement with Russell's multiplet sum rules. At small currents (or at low electron densities) the broad lines disappear.

Of the 27 lines in these three multiplets, 8 have been measured by Kock and Richter. A least squares fit of a straight line to the plot log Iχ 3 /g f (KR) versus E (upper) for these eight transitions provided the relationship by which oscillator strengths were calculated from Allen's intensities. The standard deviation of the points from the fitted line was 1.08 dex (± 50 percent). These results are listed in table 3 in the column headed CWA.

2.3. Meggers, Corliss, and Scribner [1961]

In order to provide quantitative intensity data on a uniform scale for thousands of spectral lines of the metallic elements, Meggers, Corliss, and Scribner at NBS diluted each of 70 elements to the extent of one atom of each element in 1000 atoms of copper and observed the spectra radiated from a 10-A free-burning arc in air between electrodes of the copper. To observe the corresponding data for copper, silver was used as the electrode material. The intensities of the copper lines in the silver arc were brought onto the same scale as the lines of the other elements by including atoms of Au and Zn in the silver electrodes. At the time that the work was done, no method of calibrating the intensity scale below 2500 Å was available. Subsequently, Corliss [1967] applied a calibration to the lines below 2500 Å.

Of the 27 Cu I lines reported by Kock and Richter, 20 are found in these NBS Intensity Tables. To correlate the two sets of data we have plotted as open circles in figure 1, log (Iχ 3 )MCS /g f (KR) versus upper energy level for 18 of the lines. The two strong resonance lines at 3247 and 3274 Å have been omitted because of the possibility of systematic error in their intensity. They do not, however, deviate markedly from the least squares fitted line in the figure. The standard deviation of all the points in figure 1 from the line is 0.22 dex (± 66%). Values of log g f were calculated from the intensities of the 46 Cu I lines in the NBS Intensity Tables by using the line in figure 1. They are reported in the column headed MCS in table 3.

\[ 0.18 \text{ dex} = 10^{-0.18}. \]

<table>
<thead>
<tr>
<th>Reference</th>
<th>Date</th>
<th>No. of lines</th>
<th>Wavelength range</th>
<th>Energy level range</th>
<th>Type of experiment</th>
<th>Quantity reported</th>
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<td>Å</td>
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<td>Arc in air</td>
<td>Iχ^3.</td>
</tr>
<tr>
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<td>1957</td>
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<td>Å</td>
<td>cm⁻¹</td>
<td>Arc in air</td>
<td>log g f</td>
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<td>Meggers, Corliss, and Scribner</td>
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<td>46</td>
<td>Å</td>
<td>cm⁻¹</td>
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<td>I</td>
</tr>
<tr>
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<td>Å</td>
<td>cm⁻¹</td>
<td>Arc in air</td>
<td>I</td>
</tr>
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<td>Slavenas</td>
<td>1966</td>
<td>9</td>
<td>Å</td>
<td>cm⁻¹</td>
<td>Furnace</td>
<td>f</td>
</tr>
<tr>
<td>Corliss</td>
<td>1967</td>
<td>13</td>
<td>Å</td>
<td>cm⁻¹</td>
<td>Arc in air</td>
<td>I</td>
</tr>
<tr>
<td>Kock and Richter</td>
<td>1968</td>
<td>27</td>
<td>Å</td>
<td>cm⁻¹</td>
<td>Stabilized in Ar</td>
<td>A, log g f</td>
</tr>
</tbody>
</table>

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To reduce the observations of Meggers, Corliss, and Scribner to a true scale of relative intensities, numerous lines of Cu I were selected to serve as reference standards of intensity. The relative power radiated by these lines was measured by comparison with a ribbon filament lamp and with a calibrated hydrogen continuum. The measurements were made by the methods of heterochromatic photographic photometry and are described in the NBS Tables. From 2 to 24 determinations were made on each of 207 lines of Cu I. The average number of determinations per line was 9 and the standard deviation of an individual determination is about 3 percent. The results for 180 lines were reported by Corliss [1962], who also calculated gf-values from the intensities using an arc temperature of 5100 K and a normalization function from Corliss and Bozman [1962]. Huber and Tobey [1968] and subsequently others have shown that this normalization function should in fact be a constant. Since this function changed more than two orders of magnitude between 50 000 and 75 000 cm⁻¹ and since Cu I is peculiar among the metallic atoms in that most of its lines originate at those high energies, Corliss' derived gf-values for Cu I are seriously in error.

The work of Kock and Richter provides an opportunity for an accurate reduction of Corliss' intensities to oscillator strengths. The intensity scale of the NBS Tables should be identical with that of Corliss [1962b] except for a factor 1000 arising from the dilution. The intensities from MCS were therefore multiplied by 1000 before plotting in figure 1. Four lines from Corliss' [1962b] list that are also in Kock and Richter are plotted as crosses in figure 1. It is remarkable that these four points fall accurately on the least squares line. We have, therefore, calculated gf-values from Corliss' [1962b] intensities with the same relationship used for MCS. Several lines reported by Corliss which arise from broad levels as noted by Shenstone are now omitted. The remaining 163 lines are found in table 3 in the column headed C.

### 2.5. Allen and Asaad [1957]

Allen and Asaad at the University of London Observatory measured oscillator strengths for numerous spectra by the method of dilution in copper electrodes, and in the course of their work they also measured oscillator strengths for about 130 Cu I lines. A few of the stronger lines were affected by self-absorption, but the remaining measurements seem to be of good quality. Unfortunately, the measurements were reduced with an arc temperature of 4300 K which was based primarily on oscillator strengths measured by R. B. King in an absorption furnace. It now seems, v. Garz and Kock [1969], that these early values are subject to systematic errors dependent on excitation potential. This same source of error affected the subsequent work of Corliss [1962a], who determined the temperature of his copper arc with numerous sets of furnace f-values. He derived a temperature of 5100 K, but the present comparison with the data of Kock and Richter in figure 1 shows that the correct value is more nearly 7000 K.

With this in mind, a readjustment of Allen and Asaad's results to the temperature scale of Kock and Richter has been made. There are 10 lines in common to the two lists, but eight of these arise from the 5s⁴D term. To make a readjustment to the new temperature scale, a wider range of energy levels is required. It is preferable, therefore, to adjust Allen and Asaad's values with 63 lines in common with Corliss' list. These span a range of 35000 cm⁻¹ and provide a useful relationship for removing Allen and Asaad's systematic error. A linear least squares fit was made to a plot of log (AA/C) versus upper energy level. The standard deviation of the residuals is 0.11 dex (±30%). The corrected values are listed in table 3 in the column headed AA.

### 2.6. Slavenas [1966]

Slavenas measured relative oscillator strengths for nine resonance lines of Cu I by the hook method, using a vacuum furnace for his absorption cell. His values have been adjusted to the absolute scale adopted by Kock and Richter for the lines at 3247 and 3274 Å and are reported in the column headed S in table 3.

### 3. Absolute Scale

A thorough summary of recent determinations of absolute values for Cu I 3247 Å is given by Bell and Tubbs [1970]. Inspection of the 11 values determined since 1957 in their table 1 leaves little doubt that at present the best f-value for 3247 Å is 0.43 corresponding to log gf = -0.07. This is in excellent agreement with the value -0.05 adopted by Kock and Richter.

### 4. Coulomb Approximation

The success of Kock and Richter and of Vujnovic, Ivezić, and Toneič-Mejaski in calculating good values for several Cu I lines by the method of Bates and Damgaard [1949] prompted me to apply that method to
19 of the lines measured by Kock and Richter. The results are given in table 2 and compared with the measured values. It is seen that, with the exception of the three lines involving the metastable $3d^44s^22D$ term, the two sets of values show some agreement.

**Table 2. Values of log gf from the coulomb approximation (CA) compared with measured values (KR).**

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>Configurations and Terms</th>
<th>CA</th>
<th>KR</th>
</tr>
</thead>
<tbody>
<tr>
<td>3247.54</td>
<td>$3d^{10}(S)4s^3S_{1/2} - 3d^{10}(S)4p^2D_{3/2}$</td>
<td>-0.01</td>
<td>-0.05</td>
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<td>3273.96</td>
<td>$3d^{10}(S)4s^3S_{1/2} - 3d^{10}(S)4p^2P_{3/2}$</td>
<td>-0.32</td>
<td>-0.35</td>
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<tr>
<td>2961.16</td>
<td>$3d^44s^24D_{5/2} - 3d^44s^24p^2F_{7/2}$</td>
<td>0.09</td>
<td>-1.40</td>
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<td>3063.41</td>
<td>$3d^44s^24D_{5/2} - 3d^44s^24p^2P_{3/2}$</td>
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<td>-2.06</td>
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<tr>
<td>2824.37</td>
<td>$3d^44s^24D_{5/2} - 3d^44s^24p^2P_{3/2}$</td>
<td>0.14</td>
<td>-1.25</td>
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<tr>
<td>5218.20</td>
<td>$3d^{10}(S)4p^2P_{3/2} - 3d^{10}(S)4d^2D_{5/2}$</td>
<td>0.30</td>
<td>0.27</td>
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<tr>
<td>5220.07</td>
<td>$3d^{10}(S)4p^2P_{3/2} - 3d^{10}(S)4d^2D_{5/2}$</td>
<td>-0.65</td>
<td>-0.61</td>
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<td>5153.23</td>
<td>$3d^{10}(S)4p^2P_{1/2} - 3d^{10}(S)4d^2D_{5/2}$</td>
<td>0.04</td>
<td>-0.01</td>
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<td>4530.78</td>
<td>$3d^{10}(S)4p^2P_{3/2} - 3d^{10}(S)6s^3S_{1/2}$</td>
<td>-1.38</td>
<td>-1.28</td>
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<td>4480.35</td>
<td>$3d^{10}(S)4p^2P_{3/2} - 3d^{10}(S)6s^3S_{1/2}$</td>
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<td>4062.64</td>
<td>$3d^{10}(S)4p^2P_{3/2} - 3d^{10}(S)5d^2D_{5/2}$</td>
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<td>-0.50</td>
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<td>4022.63</td>
<td>$3d^{10}(S)4p^2P_{3/2} - 3d^{10}(S)5d^2D_{5/2}$</td>
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<td>4275.11</td>
<td>$3d^44s^24p^2P_{3/2} - 3d^44s^24d^2D_{5/2}$</td>
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<td>4561.12</td>
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<td>4509.37</td>
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<td>-0.77</td>
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</table>

5. Results

The results of this review are tabulated in table 3. The wavelengths, estimated intensities and energy levels of the lines are taken from Shenstone [1948]. In the intensity column, R indicates lines easily reversed or self-absorbed in the arc and H, HH, or HHH indicates the degree of broadening depending on the nature of the upper levels. The next five columns contain the various sets of data reduced to the scale of Kock and Richter as discussed in section 2. The last column gives a value which, in my judgment, is the best. In many cases it is the only value, in some cases it is Kock and Richter's value, in some cases the mean value, and in a few cases a weighted mean.

The uncertainty assigned by Kock and Richter to their results lies between 12 and 20 percent. The comparisons made in section 2 of this paper suggest that the uncertainty of the remaining values cannot be less than 30 to 66 percent.
<table>
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<tr>
<th>Wavelength Estimate</th>
<th>Energy Levels</th>
<th>KR</th>
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<th>MCS</th>
<th>C</th>
<th>AA</th>
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