Physica Scripta. Vol. T8, 104–106, 1984

Lifetimes of Some Excited Levels in Cu I and Cu II

H. Cederquist, S. Mannervik and M. Kisielinski

Research Institute of Physics, S-104 05 Stockholm 50, Sweden

P. Forsberg and I. Martinson

Department of Physics, University of Lund, S-223 62 Lund, Sweden

and

L. J. Curtis and P. S. Ramanujam

Department of Physics and Astronomy, The University of Toledo, Toledo, OH 43606, U.S.A.

Received October 24, 1983; accepted November 1, 1983

Abstract

Using the beam-foil method we have determined the lifetimes of the $nd\ ^2D$ ($n = 4$–6) and $4s5s\ ^4D$ levels in Cu I and of the $4p\ ^3D$, ^3F, $4f\ ^3H$ and $5s\ ^3D$ levels in Cu II. Special emphasis was placed on the problems of measuring comparatively long lifetimes in heavy atoms with the beam-foil excitation method and corrections of systematic errors were investigated. The final data are in agreement with theoretical values, based on the Coulomb approximation.

1. Introduction

Experimental determinations of lifetimes in Cu I and Cu II may provide information about the effects of electron correlation in these interesting systems. In the neutral Cu atom, there is only one electron outside the $3d^{10}$ core and relatively simple calculations of *f*-values, such as the Coulomb approximation, are therefore expected to give accurate results. However, complications may arise because of perturbing levels of the type $3d^94snl$. The spectrum of Cu II shows greater complexity. The excitation of one electron from the $3d^{10}$ ground configuration leads to singlet and triplet terms similar to those in noble-gas spectra. In addition, there are perturbing levels of the type $3d^8nln'l'$ which can affect the radiative lifetimes.

Some years ago Curtis et al. [1] measured the lifetimes of four terms in Cu I and one in Cu II. At that time there existed very few additional lifetime measurements for these systems. Instead, most of the experimental information originated from emission measurements, the uncertainties of which could be quite substantial, particularly concerning absolute transition probabilities.

In 1975 Bielski [2] presented a complilation of *f*-value and lifetime measurements for Cu I and suggested recommended *f*-values for more than 100 spectral lines. These data complement and extend the earlier critical compilation of Corliss [3]. More recently, some new lifetime measurements have appeared in the literature. Methods based on electron excitation [4–7], laser excitation [8] and level crossing [9] have thereby been used. However, there are strong motivations for additional lifetime investigations, partly because of data needs in astrophysics. Thus, the lifetimes of the $ns\ ^2S$, $nd\ ^2D$ ($n = 5, 6$), $4s4p\ ^4D$ and $4s5s\ ^4D$ levels in Cu I would be of particular interest for accurate determinations of the Cu abundance in the solar photosphere [10].

Some Cu II lifetimes were also given in [5] and additional experimental data are available from beam-gas [11] and electron excitation [12] experiments. There are some astrophysically interesting problems in this ion; e.g., concerning the abundance of Cu in the interstellar medium [13]. Furthermore, transition probabilities in Cu I and Cu II are valuable for the studies of Cu and Cu^+ lasers [14].

2. Experiment

The lifetime measurements were performed at the 400 kV heavy ion accelerator at the Stockholm Research Institute of Physics, also used in the previous Cu study [1]. The light from the foil-excited beam was analyzed with a Heath EUE-700 monochromator, equipped with a cooled EMI 9789 QB photomultiplier. The experimental facilites have been described earlier [15].

The spectra and lifetimes were measured at several energies between 180 and 280 keV. The velocity of the ions after the foil was determined with a 90°, 50 cm radius electrostatic analyzer. The decay curves were analyzed using the computer program DISCRETE [16].

After a few lifetime measurements and preliminary analyses, we found that the multiple scattering of Cu particles in the carbon foil causes some problems. The angular divergence of the foil-excited beam was large and an increasing number of particles did not remain within the view of the monochromator. This fact leads to systematic shortening of lifetimes and we found this effect to become quite serious for lifetimes exceeding 30 ns. To be able to correct for these shortcomings a number of complementary measurements were made. The angular divergence was first determined by keeping the ion beam current constant and varying the distance between the foil and the Faraday cup in the target chamber. The beam current in the cup decreased steadily with increasing distance from the foil. The profile of the Cu^+ beam was further measured at various distances from the foil using a beam scanner. Finally, some air was leaked into the target chamber (to a background pressure of 8×10^{-5} mm Hg) and the excitation of the N_2^+ transition at 3914 Å ($B\ ^2\Sigma$–$X\ ^2\Sigma$) by the fast Cu ions was studied as a function of distance along the beam axis. Without a foil the light yield was uniform, showing that the scattering of the ions by the rest gas was negligible. When the foil was inserted, the angular divergence of the beam could be estimated by deter-

Table I. *Lifetimes in Cu I*

Upper level	Wavelength (Å)	Lifetime (ns)		
		This work	Other experiments[a]	Theory or Compilation[a]
$4d\ ^2D_{3/2}$	5153.2	11.4 ± 1.0	14.5 ± 0.6[b]	12.2;[c] 13.1;[d] 8.0[e]
$^2D_{5/2}$	5218.2	11.6 ± 1.0	14.2 ± 1.3;[b] 11 ± 2[f]	12.3;[c] 13.1;[d] 8.2[e]
$5d\ ^2D_{3/2}$	4022.6	25 ± 3	30.9 ± 1.7[b]	26.8[c]
$^2D_{5/2}$	4062.6	26 ± 2	29.8 ± 2.7[b]	27.1[c]
$6d\ ^2D_{3/2}$	3654.2	50[g]		51.1[c]
$^2D_{5/2}$	3687.7	56 ± 5	55.6 ± 3.5[b]	52.7[c]
$4s5s\ ^4D_{7/2}$	4651.1	7.9 ± 0.5	8.2 ± 0.4[h]	11.0;[d] 10.7[e]

[a] For additional references to previous work, consult [2, 3]. [b] Osherovich et al. [5]. [c] Lindgård et al. [19]. [d] Corliss [3].
[e] Bielski [2]. [f] Curtis et al. [1]. [g] Value uncertain because of blends. [h] Kerkhoff et al. [21].

mining the 3914 Å light yield as a function of the distance from the foil. This optical measurement gave the same result as the two current measurements and fairly reliable correction factors could be deduced. As a final test of these correction methods we measured the decay of the $4s^2\ ^2D_{3/2}$ level in Cu I which has a lifetime exceeding 300 ns and has been quite accurately determined [5, 6, 9]. Our decay measurements yielded apparent "lifetimes" close to 100 ns, because of the scattering in the foil. However, a comparison of our data with the known lifetime gave further support to our correction methods which are expected to be reliable for lifetimes shorter than 80 ns.

Since the Cu I terms with $n > 4$ studied in this work decay to several lower levels, often with transitions in the infrared, a preliminary investigation of the Cu I spectrum between 10 000 and 30 000 Å was carried out at Lund, using a hollow-cathode light source and a Czerny–Turner infrared spectrometer [17]. Several Cu I lines were thereby measured with particular emphasis on relative-intensity determinations. However, no attempts were made to provide accurate transition wavelengths, mostly because the corresponding terms in Cu I are already well established.

3. Results and discussion

The results of our lifetime measurements are given in Tables I and II. Also included are the results of previous experimental and theoretical investigations.

Table II. *Lifetimes in Cu II*

Upper level	Wavelength (Å)	Lifetime (ns)		
		This work	Other experiments	Theory
$3d^94p\ ^3D_2$	2055.0	3.0 ± 0.3		2.3[a]
$^3D_3$	2043.8	3.1 ± 0.3		2.4[a]
$3d^94p\ ^3F_2$	2179.4	2.8 ± 0.3		2.5[a]
$^3F_3$	2149.0		2.5 ± 0.2[a]	2.4[a]
$^3F_4$	2136.0	3.0 ± 0.3	2.5 ± 0.2[a]	2.5[a]
$3d^94f\ ^3H_6$	4909.7	4.9 ± 0.3		4.9[b]
$3d^95s\ ^3D_2$	2506.3	2.1 ± 0.2	5.6 ± 0.5[c]	2.2[a]
$^3D_3$	2544.8	2.2 ± 0.15	4.2 ± 0.5[c]	2.3[a]

[a] Kono and Hattori [12]. [b] This work. [c] Osherovich et al. [5].

3.1. *Cu I*

In this spectrum we measured the lifetimes of the 4*d*, 5*d* and $6d\ ^2D_{3/2,5/2}$ levels by studying the transitions to the $4p\ ^2P_{1/2,3/2}$ term. The lifetime of the $4s5s\ ^4D_{7/2}$ level was determined from the decay of the transition to the $4s4p\ ^4F_{9/2}$ level (4651.1 Å). As a test of the present method we also remeasured the lifetimes of the $4p\ ^2P_{1/2}$ and $^2P_{3/2}$ levels, obtaining results very close to previous data [1–3].

The present results for the $4d\ ^2D_{3/2,5/2}$ levels are in agreement with the previous beam-foil results [1] as well as with the data of Kock and Richter [18] who performed emission measurements using a wall-stabilized arc. Their *f*-value scale was normalized using the accurately known $4p\ ^2P_{1/2,3/2}$ lifetimes. Agreement is good also with the electron-excitation experiment of Osherovich et al. [5]. The latter authors discuss a previous study of Malakhov [4] which seems to suffer from large systematic errors. The beam-foil data are also in excellent accord with the theoretical results of Lindgård et al. [19] who used a numerical Coulomb-approximation procedure. A comparison is also made with the critically evaluated data of Corliss [3] and Bielski [2]. The former recommends the Kock and Richter value [18] whereas Bielski has given too much weight to an early emission measurement [20] resulting in a too short "recommended" lifetime.

Our results for the $5d\ ^2D$ and $6d\ ^2D$ terms have relatively large uncertainties mostly caused by the correction procedures discussed above. Because of line blends an additional uncertainty persists for the $6d\ ^2D_{3/2}$ lifetime. However, the beam-foil data agree both with the electron-excitation measurements [5] and with the Coulomb approximation-calculations [9]. Most previous *f*-value measurements and calculations only concern the 4*p*–5*d* and 4*p*–6*d* transitions; and, because of the decays to higher *np* levels, no direct comparison with our 5*d* and 6*d* lifetimes is possible. Using the infrared instrument we investigated the relative intensities of the 4*p*–5*d* and 5*p*–5*d* transitions, obtaining a result in close agreement with the theoretically expected branching ratio [19]. The $5d\ ^2D$ and $6d\ ^2D$ levels can also decay to the $4s4p\ ^2P$, ^2D and ^2F terms with two-electron transitions in the near infrared region. However, a spectral investigation did not reveal the corresponding lines and these decay modes should thus not influence the $5d\ ^2D$ and $6d\ ^2D$ lifetimes to a measurable extent.

In 1976 we quoted a lifetime of 12 ± 2 ns for the $5p\ ^2P$ level in Cu I; in agreement with previous work [3]. Subsequently Osherovich et al. [5] obtained 27–28 ns from measurement of the $4s^2\ ^2D$–$5p\ ^2P$ transitions (2766 and 2618 Å). We have now investigated this discrepancy and find that the 2024 Å ($4s\ ^2S$–$5p\ ^2P$) resonance lines, measured in [1] may be blended by the $4s\ ^3D$–$4p\ ^1D$ transition in Cu II (2025.5 Å) in beam-foil spectra and the beam-foil result could thus be uncertain. However, if we combine the theoretical f-values for the $4s$–$5p$ and $5s$–$5p$ multiplets [19] with the $4s^2\ ^2D$–$5p\ ^2P$ transition rates of Kock and Richter [18] we obtain a $5p\ ^2P$ lifetime of 18 ns. The problem should thus be further investigated.

The $4s5s\ ^4D$ term lies at 62 403–64 472 cm^{-1} above the $4s\ ^2S$ ground state and also 86–2155 cm^{-1} above the $3d^{10}\ ^2S_0$ ground state of Cu II. Using stepwise collisional and laser excitation Kerkhoff et al. [21] have made an interesting study of the $4s5s\ ^4D_{1/2,3/2,5/2,7/2}$ levels. Their results show that the $^4D_{3/2,5/2}$ levels have very short lifetimes due to autoionization to the $3d^{10}\epsilon d$ continuum whereas the $^4D_{1/2,7/2}$ levels decay by radiative transitions to lower levels in Cu I. Our lifetime for the $^4D_{7/2}$ level is in very good agreement with the result of Kerkhoff et al. [21]. This is particularly satisfying because of the high accuracy of the laser experiment. The compilations of Corliss [3] and Bielski [2], which include decay modes to $4s4p$ quartet and doublet terms, result in a somewhat longer $4s5s\ ^4D_{7/2}$ lifetime.

3.2. *Cu II*

In this spectrum we measured the lifetimes of seven levels, belonging to four different terms, $3d^9 4p\ ^3D$, ^3F, $3d^9 4f\ ^3H$ and $3d^9 5s\ ^3D$. All these levels are involved in producing laser lines in hollow cathode discharges where they are populated by collisions with He or Ne atoms in metastable states [14].

Our lifetimes are given in Table II. Also included are the previous measurements of Osherovich et al. [5] and Kono and Hattori [12]. The latter authors also performed Coulomb-approximation calculations. We have also made such calculations using a program written by Theodosiou [22]. The results are in excellent agreement with previous calculations [12]. The experimental lifetimes of the $3d^9 4p\ ^3D_2$ and $^3D_3$ levels are somewhat longer than the theoretical values which may indicate that the Coulomb approximation has its limitations for low-lying levels in this spectrum where electron correlation effects are quite substantial. From the experimental point of view, it would have been desirable to perform ANDC analysis but this is extremely time-consuming in this relatively complex system where the levels under study are fed from many high-lying terms.

Our lifetimes of the $3d^9 4p\ ^3F_2$ and $^3F_3$ levels essentially agree with the previous experimental results as well as with the theoretical estimates, although the latter tend to be slightly shorter even in this case.

No previous measurements are available for the $3d^9 4f\ ^3H_6$ lifetime. The experimental result obtained here is in perfect agreement with the theoretically calculated value. The beam-foil lifetimes for the $3d^9 5s\ ^3D_2$ and $^3D_3$ levels are about a factor of two shorter than the previous experimental values [5]. However, in the latter experiment the width of the exciting electron pulse was 10–40 ns which appears as too large for measuring lifetimes in the 2–3 ns range. Our lifetimes for the $^3D_2$ and $^3D_3$ levels are further in very good accord with the theoretical values (Table II).

The present experimental data for the levels in Cu II also show that the semiempirical Coulomb approximation method provides comparatively reliable f-values in this ion. Froese Fischer and Glass [23] have employed more elaborate ab initio methods to study correlation effects in Cu II. Their calculated lifetime for the $3d^9 4p\ ^1P$ level agrees with experimental results [1, 12]. However, it would be interesting to apply the MCHF method to other transitions in Cu II.

Acknowledgements

We are grateful to G. Astner, E. Biėmont, D. G. Ellis, N. Grevesse, U. Litzén and C. E. Theodosiou for valuable discussions and advice. This work was supported by the Swedish National Science Research Council (NFR) and the Swedish Energy Research Commission (EFN).

References

1. Curtis, L. J., Engman, B. and Martinson, I., Physica Scripta **13**, 109 (1976).
2. Bielski, A., J. Quant. Spectrosc. Radiat. Transfer **15**, 463 (1975).
3. Corliss, C. H., J. Res. Nat. Bur. Stand. **74A**, 781 (1970).
4. Malakhov, Yu. I., Opt. Spectrosc. (USSR) **44**, 125 (1978).
5. Osherovich, A. L., Phekhotina, G. L. and Obidin, V. R., Opt. Spectrosc. (USSR) **50**, 576 (1981).
6. Kono, A. and Hattori, S., J. Quant. Spectrosc. Radiat. Transfer **28**, 383 (1982).
7. Bezuglov, N. N., Gorshkov, V. N., Osherovich, A. L. and Phekothina, G. L., Spectrosc. (USSR) **53**, 239 (1983).
8. Kerkhoff, H., Micali, G., Werner, K., Wolf, A. and Zimmermann, P., Z. Phys. **A300**, 115 (1981).
9. Krellmann, H., Siefart, E. and Weihreter, E., J. Phys. **B8**, 2608 (1975).
10. Biėmont, E. and Grevesse, N., Physica Scripta **16**, 39 (1977) and private communication.
11. Maleki, L., King, D. G., Head, C. E. and Lawrence, T. N., in Beam-Foil Spectroscopy (Edited by I. A. Sellin and D. J. Pegg), p. 217. Plenum, New York (1976).
12. Kono, A. and Hattari, S., J. Opt. Soc. Am. **72**, 601 (1982).
13. Morton, D. C. and Smith, W. H., Astrophys. J. Suppl. Ser. **26**, 333 (1973).
14. Bridges, W. B., in Methods of Experimental Physics, Vol. 15A, p. 120 Academic, New York (1979) (and references quoted therein).
15. Martinson, I., Curtis, L. J., Huldt, S., Litzén, U., Liljeby, L., Mannervik, S. and Jelenkovic, B., Physica Scripta **19**, 17 (1979).
16. Provencher, S. W., J. Chem. Phys. **64**, 2772 (1976).
17. Litzén, U., Physica Scripta **2**, 84 (1970).
18. Kock, M. and Richter, J. Z., Astrophys. **69**, 180 (1968).
19. Lindgård, A., Curtis, L. J., Martinson, I. and Nielsen, S. E., Physica Scripta **21**, 47 (1980).
20. Huldt, L., Arkiv. Mat. Astr. Fys. **36A**, 3 (1948).
21. Kerkhoff, H., Micali, G., Werner, K., Wolf, A. and Zimmermann, P., Z. Physik **A300**, 115 (1981).
22. Theodosiou, C. E. (to be published).
23. Froese Fischer, C. and Glass, R., Physica Scripta **21**, 525 (1980).