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Spectroscopy of the $3s^23p^n$ shell from Cu to Mo

ABSTRACT

The $3s^2 3p^n$ isoelectronic sequences from Cu to Mo have been actively investigated in the past 15 years largely because of the importance of these spectra for tokamak plasma diagnostics. Many magnetic dipole transitions within these configurations were identified in tokamak plasmas even before anything was known of many of these ions. We give a brief review of the major spectroscopic studies that have been carried out with these ions. Revised tables of M1 lines for the isoelectronic sequences $3s^2 3p^2$ and $3s^2 3p^4$ from Cu to Mo are given.

This review will show how user needs (in this case tokamak research) stimulated spectroscopic research and led to a large body of new data for highly ionized atoms for the elements Cu to Mo and beyond where practically nothing was previously known. These data have found other uses as well, such as advancing the art of atomic structure calculations, providing internal wavelength standards for spectra of hot plasmas, and for extending spectral interpretation to even heavier ions.

Tokamak plasmas are "blessed" with many impurities: Cr, Fe, and Ni coming from the stainless steel interior walls and at various times W, Mo, C, and Ti from the aperture limiters. All these elements have been observed at the hot center of the plasma in highly stripped condition. To measure and interpret the consequent radiation from these as well as other elements intentionally injected into the plasma for diagnostic purposes has provided work for the last decade and one-half. The last generation of tokamaks such as the PLT at Princeton and the TEXT at the University of Texas are 1-2 keV machines and can ionize iron period elements down to the L-shell and heavier elements through Mo to the M-shell. The new generation of tokamaks such as TFTR, JET, and JT60 generate plasmas at 5-10 keV and can strip the heavier elements down to the L-shell.

Some of these impurity elements were eliminated early, such as W and Mo, because they held down the achievable temperature. Hinnov and Mattioli (1978) show two types of temperature profiles obtained in the PLT with a W limiter. The usual profile is peaked at the center but often the profile develops a central depression. After the Ag and Pd isoelectronic sequences were well understood it became clear that these features were mainly from these sequences. Limiters are now made of lighter elements, such as titanium-carbide coated graphite at TEXT, for example. When W and Mo were high priority elements a great deal of new data along isoelectronic sequences relevant to them were interpreted. Long isoelectronic extensions into the unknown territories resulted largely from the interests of magnetic fusion. They occur mainly along or near sequences of closed shells: $4f^{14}$ and $4d^{10}$ for interpreting W spectra, $3d^{10}$, and $2p^6$ for Mo. That Mo was a favored element is evident from the energy level compilation of Sugar and Musgrove (1988) that shows results for nearly every stage of ionization. For the $3s^2 3p^n$ sequences of Cu to Mo many magnetic dipole (M1) lines have been identified in tokamak plasmas, mainly by Hinnov and Suckewer and their colleagues at Princeton. These are included in the compilation of M1 lines and A-values by Kaufman and Sugar (1986). Today many electric dipole (E1) lines for nearly all of the ions of this group are accurately measured and securely interpreted. These are probably the first ions for which the classification of M1 lines preceded that of E1 lines. The next region of current interest is the $2p^n$ shell from Cu to Mo. These data are coming from high energy lasers and from the large tokamaks.

The importance of M1 lines of the 2p and 3p shells for plasma diagnostics has been reviewed in many publications, for example by Denne and Hinnov (1987) and by Doschek and Feldman (1976) who first suggested that M1 lines could be observed in a tokamak plasma. M1 lines are prominent in tokamak plasmas because the electron collision rate is about the same as the transition rate in this thin plasma of about $5x10^{13}$ electrons/cm^3. Their wavelengths are frequently longer than 2000 Å and their Doppler profiles are easily measured for determining ion temperatures. The first such line was observed with the PLT tokamak by Suckewer and Hinnov (1978) at 2665 Å originating from Fe XX. The transition is $2s^2 2p^3 (^2D_{5/2} - ^2D_{3/2})$. These M1 lines have had other diagnostic applications. Their Doppler shift has been used to measure the plasma rotation in tokamaks induced by unbalanced neutral beam injection (Suckewer et al., 1979). These lines have also proved convenient for mapping impurity transport in tokamaks (Suckewer et al. 1984). Recently, Wróblewski et al. (1988) measured the poloidal magnetic field in the TEXT tokamak by means of the circular polarization of the M1 line of Ti XVII at 3834 Å. The optics for this experiment requires a line above 2000 Å. To make a similar measurement in a high temperature tokamak may require a much heavier element in order that it not be too highly ionized. Ti in the TFTR would probably be totally stripped.

To assist in the program of M1 line identification Kaufman and I (1984) undertook to predict the wavelengths of all the M1 lines of the 3p-shell from Cu to Mo. This was done by fitting radial energy parameters to the known levels in the Fe period and extrapolating the ratios of these parameters to Hartree-Fock values for use in the heavier elements. The eigenvectors resulting from the matrix diagonalizations for Cu to Mo were then used to calculate the transition probabilities for all the M1 lines. The method was repeated by Biémont and Hansen (1985) who added correlation explicitly to the calculation. In our calculations correlation was absorbed by the scaling of the parameters and by the introduction of the "effective" configuration interaction parameter α. In general the A-values resulting from these two methods agreed to about 3%. These M1 wavelength predictions were sufficiently accurate to help in the discovery of many more lines. We have now refined the wavelength predictions by another method, that I will shortly describe, so that they are nearly as accurate as the measured lines.

I would like to review briefly the main spectroscopic studies that have been carried out in the range of ions of Cu to Mo for the isoelectronic sequences Na-like to K-like. For most of them the wavelength uncertainty is ±0.02 - ±0.05 Å. These estimates are based on comparison with our present measurements on the TEXT tokamak, which have an uncertainty of about ±0.007 Å. High energy laser-generated spectra are notoriously difficult to measure accurately because there are few internal impurities and no low ionization lines that have previously been measured. Five major papers appeared in the 1970's, beginning with Fawcett and Hayes (1975) who identified the strong lines of the elements Cu to Br. The motivation for most of this work was tokamak impurity spectra. Fawcett and Hayes remarked that their data could be used for accurate predictions of wavelengths of Mo.

Hinnov (1976) identified resonance lines of Na-like, Mg-like, Cu-like and Zn-like Kr and Mo in a tokamak plasma with an uncertainty of ±0.05 Å. Burkhalter et al. (1977) gave a fairly extensive spectrum of Na-like Mo and some lines of Mg-like with an uncertainty of ±0.06 Å. Mansfield et al. (1978) attempted to classify many lines of Mo, measured with an uncertainty of ±0.06 Å, from a large number of ionization stages. Kononov et al. (1979) renewed isoelectronic sequence studies with Na-like Cu to Br and with wavelength measurement uncertainties of ±0.01 Å. The 1980's brought a greatly increased flow of papers that continue to the present, making use of high powered lasers, tokamaks, a Z-pinch machine, and beam foil excitation. The Na sequence was extended to Se by Brown et al. (1986) with a wavelength uncertainty of ±0.04 Å and to Sr by Reader (1986) who achieved a wavelength uncertainty of ±0.005 Å. Kaufman and I measured the n=3-3 transitions of Na-like spectra for Cu to Mo with a wavelength uncertainty of ±0.007 Å. These were incorporated in a study of these transitions for Ar to Sn by Reader et al. (1987) who fit a simple function to the difference between observed and calculated wavelengths and used these fitted differences to obtain an overall accuracy of ±0.007 Å. A study of Al-like spectra for Zn, Ge, Se, Zr, Mo, and Ag was made by Hinnov et al. (1986) with the PLT tokamak. They obtained a wavelength uncertainty of about ±0.05 Å. Several studies of Kr have been made, one by Wyart and the TFR Group (1985) of K to Na-like and another by Stewart et al. (1987) of Al to Na-like, the latter with a Z-pinch device. The TFR Group and Wyart (1988) reported another study of Kr, Sr, Zr, and Rh for K to Na-like spectra. The wavelength uncertainty achieved by these groups was ±0.03 Å. Wyart et al. (1987) measured and interpreted 40 lines of Mg-like Sr. Using laser excitation they obtained the spectrum with a wavelength uncertainty of ±0.05 Å.

Beam-foil excitation was used by Hutton et al. (1987) to obtain the spectrum of P-like Cu with an uncertainty of ±0.03 Å. With a similar device, Träbert et al. (1988) observed intersystem transitions in Al-like and Si-like Cu and Zn and established the $3s3p^2\ ^4P$ term and the $3s3p^3\ ^5S$ term, respectively, of these sequences. Their average measurement uncertainty is about ±0.04 Å.

Kaufman, Rowan, and I observed all the elements from Cu to Mo (except for Rb and Sr) with the TEXT tokamak at the University of Texas, Austin using a 2.2m grazing incidence spectrograph with a 1200 line/mm grating and photographic detection. These were supplemented by laser-generated plasmas of Cu to As, photographed at NIST with a 10.7m grazing incidence spectrograph. These light sources are complementary in some respects. Wavelengths of Fe and Ti suitable for standards were present in the TEXT exposures as impurities, so no wavelength shifts between standards and sample lines were present. Furthermore the lines observed in TEXT were sharp due to the low density of the plasma. These factors combined to provide accurate wavelengths from the tokamak exposures. The rms deviations of the standard lines from the dispersion curves were about ±0.005 Å. Thus we estimate the wavelength measurement uncertainty to be ±0.007 Å. The spectra obtained from the laser-generated plasmas, on the other hand, contained very few impurity or low ionization lines with which to detect shifts of the spectra from the standard wavelengths. Standards were exposed on a second track and from a different light source, usually a spark. However, measurements from TEXT served as internal standards for the laser spectra.

A drawback of the low electron density of TEXT is that it does not maintain the population of high-lying configurations, so that one is limited to observing mostly resonance lines and low configurations. However, M1 lines and strongly spin-forbidden transitions are not quenched. Laser-plasmas, on the other hand, provide more fully developed spectra but have the disadvantage of a lack of internal reference lines. A combination of the two light sources is ideal.

To interpret these data we used the methods successfully employed by Edlén in his analysis of the data for the n=2 shell in the Fe period (1984). We follow a transition along its isoelectronic sequence, each step of the way comparing it with its calculated value and plotting the difference. These plots are smooth and slowly varying with atomic number. The change per element is usually less than 0.1 Å and frequently only a few hundredths. This allows for an accurate prediction of the next unknown line in the sequence.

The first isoelectronic study incorporating our new data was on the Na sequence (Reader et al. 1987). Edlén (1978) treated the data of this sequence from S to Mo in a similar manner. For elements Cu to Mo the wavelength data available to him had measurement errors of ±0.05 Å. With our new data for Cu to Mo, with Y to Pd data from a 100 GW laser at Los Alamos, and with Ru to Sn from the 24 beam 2 TW OMEGA laser facility at Rochester we derived improved wavelengths for Ar to Sn with an uncertainty of ±0.007Å. Theoretical values were calculated with the Dirac-Fock code of Grant. The difference between measured and calculated wavenumbers was fit to the formula $\Delta\sigma = a + bZ + c(Z+d)^{-1}$ with a, b, c, and d as adjustable parameters.

We next carried out a study of the Al sequence (Sugar et al., 1988). Calculated wavelengths were published by Huang, who used the Dirac-Fock code of Desclaux. An earlier study of this sequence was carried out by Hinnov et al. (1986) for selected elements. Our improved wavelengths with an uncertainty of ±0.007 Å permitted a well defined observed-minus-calculated (O-C) curve to be fit to the new data. Interpolated values for the missing points were obtained with an uncertainty of ±0.01 Å. The energy levels of the ground configuration $3s^2 3p$ and the excited configurations $3s3p^2$ and $3s^2 3d$ were derived from the wavelength data.

Seven lines of the K-like transition array $3p^6 3d$ - $3p^5 3d^2$ were identified for Zn XII to Mo XXIV (Kaufman et al., 1989). This sequence illustrates a problem encountered in complicated cases where there are many levels and the eigenvectors for some of them change rapidly along the sequence. Kaufman et al. give two O-C curves. One of them shows a transition from a level that maintains its identity and the intensity of the transition throughout the sequence. The other represents a transition from a level whose designation is shifting to a new level along the sequence, as is the calculated intensity of the transition. The latter required the start of a new O-C curve after the theoretical crossing at Kr.

Our work on the Mg I isoelectronic sequence (Sugar et al., 1989) from Cu XVIII to Mo XXXI showed the great disparity between the amount of data that may be observed with a laser plasma compared with a tokamak plasma. For Cu to As obtained with a laser we observed transitions among the configurations 3s3p, 3s3d, $3p^2$, 3p3d and $3d^2$ with at most 53 lines of Zn XIX classified. With the tokamak the 3p3d and $3d^2$ configurations were not found and only 8 lines were observed in Se XXIII. For the theoretical wavelengths we carried out Dirac-Fock calculations. The resulting O-C curves showed a scatter of the experimental data of about 20 cm^{-1}, or well within our ±0.007 Å uncertainty estimate. Values for Rb and Sr were read from the curves and have an estimated uncertainty of ±0.01 Å. For the spin-forbidden resonance line $3s^2\ ^1S_0$ - $3s3p\ ^3P_1$ the first points, Cu and Zn, are deduced from our E1 measurements. From As to Mo they were observed with TEXT.

For the Cl I isoelectronic sequence the $3s^23p^5\ ^2P$ ground term splitting is known from observed M1 lines for the elements Cu to Se, Kr, Y, Zr, and Mo (see Kaufman and Sugar, 1986). Those of Br, Rb, Sr, and Nb were determined by Kaufman et al. (1989) from a plot of observed minus calculated values. Several transitions to the ^2P term from levels of the $3s^23p^43d$ configuration were also reported by them.

The remaining sequences S, P, and Si are much more complicated cases having $3p^4$, $3p^3$, and $3p^2$ ground configurations. The first step in treating them was to determine the energy levels of these ground configurations. Employing the method of the O-C curves we were able to derive these levels for Cu to Mo from the known M1 lines. For calculated values we used the Dirac-Fock calculations by Saloman and Kim (1988) for S, and by Huang (1984, 1985) for P and Si. The M1 data was taken from Kaufman and Sugar (1986).

Table 1 summarizes the new M1 predictions for the Si sequence. The starred values are the new predictions with indicated uncertainties about equal to the those of the observed data. Table 2 is a similar table for the S sequence. A large number of predicted values from the compilation are revised with much improved uncertainties. A table for the P sequence is in preparation. With these results all the levels of the ground configurations for the $3p^n$ sequences from Cu to Mo are now known.

Several applications of these data have been found. When the Na work was underway calculations were made with both the Desclaux and Grant Dirac-Fock codes and compared with the observed data (Reader et al., 1988). There was a significant difference; the Desclaux results were found to diverge from the observed values of the $3s\ ^2S_{1/2}$-$3p\ ^2P_{1/2}$ transition with increasing Z but the Grant code did not. The latter contained an approximation for the QED effects for the n=3 shell, namely $1/n^3$ scaling of the n=2 calculations. Kim et al. (1988) did the same test with the Al sequence data by calculating the ground term ^2P splitting with and without this correction. The difference between the observed splitting and the calculated value without n=3 shell QED diverges rapidly whereas with the QED correction for the n=3

Table 1. Complete M1 line-list (in Å) for transitions within the $3s^23p^2$ ground configuration of Si-like Fe through Mo. Wavelengths > 2000 Å are values in air. Newly predicted values are preceded by the symbol "*". The rest are observed values.

$3s^23p^2$ Spectrum	$(^3P_0 - {}^3P_1)$	$(^3P_1 - {}^3P_2)$	$(^3P_1 - {}^1D_1)$	$(^3P_2 - {}^1D_2)$	$(^3P_1 - {}^1S_0)$
Fe XIII	10746.8(4)	10797.9(4)	2578.77(1)	3388.5(4)	1216.43(1)
Co XIV	*8440.8(4.0)	*9242.2(9.0)	2320.4(1.0)	3099.2(2.0)	*1120.6(3)
Ni XV	6701.7(4)	8024.1(4)	2085.51(5)	*2818.0(5)	*1033.2(3)
Cu XVI	5375.8(3)	*7067.7(5.0)	1871.2(2)	2544.7(5)	952.8(3)
Zn XVII	4355.0(3)	*6298.3(5.0)	1676.9(2)	2284.6(1)	* 878.7(3)
Ga XVIII	*3559.4(1.0)	*5676.1(4.0)	*1500.0(4)	*2038.4(1.0)	* 810.2(3)
Ge XIX	2933.7(2)	5170.3(3)	*1340.7(4)	1810.4(5)	746.9(3)
As XX	2438.0(3)	*4746.6(2.0)	*1197.6(4)	*1602.3(5)	* 688.2(3)
Se XXI	2042.3(3)	4396.5(3)	1069.2(5)	1414.2(5)	* 633.8(3)
Br XXII	*1722.4(3)	*4096.1(2.0)	* 955.5(5)	*1246.5(5)	583.6(1)
Kr XXIII	1462.65(3)	3840.9(3)	853.8(1.0)	*1098.5(5)	* 537.2(3)
Rb XXIV	*1249.8(3)	*3294.6(1.0)	* 764.0(4)	* 968.6(5)	* 494.4(3)
Sr XXV	*1074.5(3)	*3426.1(1.0)	* 684.3(3)	* 855.2(5)	* 455.3(3)
Y XXVI	* 928.9(3)	3254.8(1.0)	* 613.7(3)	* 756.4(3)	* 418.6(3)
Zr XXVII	807.1(3)	3101.1(3)	551.3(3)	670.8(3)	* 385.1(3)
Nb XXVIII	* 705.0(3)	*3055.7(1.0)	* 496.0(3)	* 595.6(3)	* 354.4(3)
Mo XXIX	618.5(3)	2841.1(2)	446.9(2)	530.3(3)	* 326.3(3)[k]

Table 2. Complete M1 line-list (in Å except where otherwise indicated) for transitions within the $3s^2 3p^4$ ground configuration of S-like Cu through Mo. Wavelength between 2000 Å and 5 μm are values in air. Newly predicted values are preceded by the symbol "*". The remainder are observed values.

$3s^2 3p^4$ Spectrum	$(^3P_0-^3P_1)$	$(^3P_2-^3P_1)$	$(^3P_1-^1D_2)$	$(^3P_2-^1D_2)$	$(^3P_1-^1S_0)$
Cu XIV	*14.18(12)μm	4183.4(3)	*3490.3(9)	*1903.3(4)	1190.4(5)
Zn XV	* 4.010(10)μm	3450.4(2)	*3360.0(8)	1702.8(2)	*1108.2(5)
Ga XVI	* 2.014(10)μm	*2870.7(5)	*3241.1(9)	*1522.8(3)	*1029.0(3)
Ge XVII	*12125(15)	2406.9(3)	3131.3(3)	*1361.3(3)	952.9(3)
As XVIII	* 8020(9)	2032.6(3)	*3030.8(1.3)	*1216.8(3)	* 880.0(3)
Se XIX	56450(3)	1727.7(3)	2935.8(3)	*1087.8(3)	810.3(3)
Br XX	* 4146(4)	*1477.8(4)	*2847(2)	* 973.0(3)	* 744.7(5)
Kr XXI	* 3147(3)	*1271.1(3)	*2765(2)	* 870.9(3)	* 682.9(5)
Rb XXII	* 2451(2)	*1099.3(3)	*2687(2)	* 780.2(3)	* 625.2(5)
Sr XXII	* 1950(2)	* 955.4(3)	*2613(2)	* 699.6(3)	* 571.7(5)
Y XXIV	* 1579.5(1.2)	* 834.3(3)	*2543(2)	* 628.3(3)	* 522.4(5)
Zr XXV	* 1298.4(9)	731.8(2)	2476(2)	564.9(3)	477.1(5)
Nb XXVI	* 1081.3(8)	* 644.5(3)	*2412(2)	* 508.6(3)	* 435.5(5)
Mo XXVII	* 910.9(5)	569.8(1)	2350.8(3)	458.6(2)	397.2(3)

shell it is nearly linear. It is due to the accuracy of the data that this test of the theory may be made.

Na-like spectra occur in many high-energy plasmas, including those generated to obtain Ne-like spectra for x-ray lasers. Eckart et al. (1988) obtained a spectrum of Se with a line focus of a high powered laser beam, looking down the axis of the line-focus where lasing is observed. Distributed among the lasing lines are Na-like lines, which provide wavelength standards to measure the lasing lines. Similar spectra of Ne-like Cu and Ge obtained by Lee et al. (1987) show a similar distribution of Na-like lines, and there is also a strong Mg-like line present. These lines were used by them as wavelength standards to measure the lasing lines. They note that "High precision wavelength measurements for the lasing lines are needed for comparison with theoretical predictions and atomic physics models."

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