THEORETICAL ESTIMATION OF THE SPECTRAL LINE BROADENING CONSTANTS OF COPPER I

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The major effects contributing to the broadening of the spectral lines of Cu I, multiplets 4P—4D and 4P—5D, are theoretically considered in this paper. The force constants are presented in such a fashion as to render the interpretation of experimental results easy. For the rather high values of the quadratic Stark constants possessed by these transitions, the classical impact broadening is considered. As the transitions takes place between the excited states, the quadripole broadening effect is also considered. The foreign gas broadening of the spectral lines arising from the collisions with neutral gas is considered assuming a Van der Waals force law to exist between the perturbing argon gas and the emitting excited state copper atom.

1. Introduction

The idea that the measurement of line profiles supported by adequate theory can be a good diagnostic for luminous plasmas has gained wide-spread acceptance. Various theories have been worked out for the broadening of the spectral lines of hydrogen and isolated lines of many atomic species (see Griem's book [1]). It has been accepted that such calculations yield accurate broadening parameters in the case of the H_β line. However, the calculations in the case of multi-electron atoms are not so accurate. On the measurement side, the limits of experimental accuracy and the inevitable mathematical processing, like Abel's inversion, profile unfolding, *etc.*, that invariably follows the measurement must be considered in evaluating the overall accuracy of the result.

On the application side, line profile methods have been used for the investigation of a variety of plasmas. Next to the refractivity method of measuring electron density, the line profile method stands as the second best. But it should be noted that the line profile method, especially using the half-widths, is comparatively easy as it does not involve absolute intensity measurement. If the plasma is pure then such a measurement is easy but becomes increasingly difficult if spectral lines overlap.

This paper deals with the theoretical broadening constants of the excited states of Cu I under a variety of conditions. Copper is extensively used in the electrical industry and the

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excitation of this metal has been studied in various fields like circuit-breaking, exploding wires, metal-inert gas welding, *etc.* Copper vapour arcs at atmospheric pressure burning in air has been under study in this laboratory for quite some time. The relative intensity of the spectral lines of Cu I at 5105 Å and 5218 Å has been used for the determination of the distribution temperature [2], and quadratic Stark constants of the $4P-4D$ and $4P-5D$ multiplets have been derived in [3]. It is the purpose of this paper to give the pertinent theoretical broadening constants of the above multiplets as a means of evaluating the total electron density inside such an arc. The determination of electron density and the use of the Saha equation will immediately lead to the relative density of the metal vapour and other components. But the validity of local thermodynamic equilibrium in low current arcs, even at high pressures, has been seriously questioned by many researchers (see Kolesnikov's review article [4]). However, these objections being based on experiments conducted under poorly defined conditions, (problems of arc instability, presence of smoke, inhomogeneity, *etc.*) are of questionable tenability. Hence it becomes necessary to check the validity of local thermodynamic equilibrium before applying the Saha equation. It is believed that the theoretical broadening constants given in this paper will be useful in the interpretation of experiments connected with the thermodynamic and radiative properties of copper vapour arcs.

2. Pressure broadening of the spectral lines of Cu I

Pressure broadening is an effect of the interaction of the emitting atoms with surrounding particles. It is further divided into: (1) Stark broadening — due to charged perturbers, (2) Resonance broadening — due to perturbers similar to the emitter and (3) Van der Waals or foreign gas broadening — due to neutral perturbers of a kind different from that of the emitting atom. Although it is generally understood that the Stark broadening is the predominant broadening mechanism when there is evidence of even slight ionization, there are cases in which Van der Waals broadening could assume importance, for example in electric discharges [5] and shock-tube experiments [6]. Also, the Stark and temperature dependent Doppler broadening mechanisms could compete with each other, necessitating a mathematical "unfolding" process to recover the Doppler and Stark widths.

2.1 (a). Stark broadening

This broadening should be considered in two parts, namely, the interaction of the radiating atom and the relatively static ionic field and then the collision interaction of electrons and ions with the radiating particles. In this paper, only the electron-collision broadening under impact approximation is considered since it is the most important effect contributing to the broadening. The interaction is considered to be of the inverse 4^{th} power law leading to quadratic Stark broadening. According to Lindholm's theory [7], Weisskopf's radius for such an interaction can be written as,

$$\varrho_w = \left(\frac{\pi C_4}{2v}\right)^{1/3} \tag{1}$$

where C_4 =quadratic Stark constant (sec^{-1} . cm^4), v = relative velocity ($sec^{-1} \cdot cm$), which leads to an half-width given by

$$\Delta\lambda_S = 11 \cdot 37 C_4^{2/3} v^{1/3} N_e \frac{\lambda^2}{2\pi c} \times 10^8 \tag{2}$$

where C_4 = quadratic Stark constant of the spectral line ($sec^{-1} \cdot cm^4$), N_e = electron density (number of electrons $\cdot$ cm^{-3}), λ = wave length (cm) c = velocity of light ($sec^{-1} \cdot cm$) and v = relative velocity ($sec^{-1} \cdot cm$). The C_4 constants have been derived by the authors [3] and in the case when the magnetic sub-levels are not split one can find the Stark constant for an unsplit line as a function of the quadratic Stark constant of the split lines and their relative intensities according to [8] as follows,

$$C_4(\text{unsplit}) = \sum_k C_{4p} \cdot p_k \tag{3}$$

C_{4k} is the quadratic Stark constant of component k whose relative intensity is p_k. The relative intensities can be taken from the tables of Lochte-Holtgreven [9]. The quadratic

TABLE I

Quadratic Stark constants of the $4P-4D$ and $4P-5D$ transitions in Cu I

Wawe length Å	$C_4 \times 10^{-15}$ cm^{-1} sec^4
4062.641	1626.26
4063.238	1222.64
4022.629	1282.59
5218.202	16.058
5220.07	20.398
5153.235	28.638

Stark constants of the unsplit lines of the $4P-4D$ and $4P-5D$ transitions are given in Table I. The relatively heavy ions contribute a negligible amount to the collisional half-width.

2.1(b). Quadripole Broadening

In addition to the dipolar broadening mentioned in 2.1 (a), there could be quadripole broadening, since the excited states, $4P-4D$ and $4P-5D$ are considered. Brechot and Van Regermorter [10] have shown that this quadrupole interaction — an inverse 3rd power law, can contribute considerably to the broadening of the lines. Basing on their results, one can define an interaction constant,

$$C_3 = \frac{e^2 a_0^2 \beta}{\hbar} \tag{4}$$

where e, a_0 and $\hbar$ are atomic constants and β is defined by

$$\beta = [4/15(2l+1)\ C_{l2l}^{2}]^{1/2} \cdot \bar{r}^2 \tag{5}$$

with $(2l+1)\ C_{l2l} = 4/5$ for P states and $4/7$ for D states. $\bar{r}^2$ can be approximated by the expression,

$$\bar{r}^2 = \frac{n^2}{2Z^2}[5n^2+1-3l(l+1)] \tag{6}$$

then, one can calculate the half-width γ_q ($\sec^{-1}$) through the relation,

$$\gamma_q = 6.05\times10^{-8}N_e(\beta_i-\beta_f) \tag{7}$$

i and f stand for the initial and final states of the transition and N_e is the electron density. Using the effective quantum numbers of the $4P$, $4D$ and $5D$ states, the β constants of the transitions considered are derived and shown in Table II.

TABLE II

Quadripole force constants β of the $4P$, $4D$ and $5D$ states of Cu I, in atomic units

State	Force constant
$4P$	9.828
$4D$	46.622
$5D$	192.134

2.2. Van der Waals Broadening

This broadening is attributed to the collision of the radiating atom with a neutral atom of the gas in which the radiating atom is present. The width of the line will be affected by the temperature of the environment, the neutral gas pressure and the atomic constants characterising the collision process. If an inverse 6^{th} power law is assumed to describe the interacting potential then following Lenz, Weisskopf and others, the optical cross-section ϱ_0 can be written as

$$\varrho_0 = \left(\frac{12\cdot 1C_6}{v}\right)^{1/5} \tag{8}$$

C_6 = an atomic constant and v in the relative velocity of the collision members. With this, the number of broadening collisions can be written as,

$$\frac{1}{\tau_0} = \pi\varrho_0^2 N_{\text{neu}} v \tag{9}$$

N_{neu} = number of neutral gas atoms $\cdot$ cm^{-3}, τ_0 = effective life time of the level. The half-width of the resulting broadened line can be written as,

$$\Delta\lambda_v = \frac{1}{\pi\tau_0}\left(\frac{\lambda^2}{\text{velocity of light}}\right). \tag{10}$$

The theoretical estimates of the Van der Waals constants between the excited states of Cu, namely the $4P$, $4D$ and $5D$ states and the neutral gas are necessary in order to determine $\Delta\lambda_v$.

The Van der Waals interaction is the long range attractive potential C_6/r^6 between neutral copper atoms or molecules. The C_6 constants for the excited states of copper atom and noble gas (argon in this paper) system can be calculated making assumptions similar to that of Mahan [11] and expanding C_6 in the form of a series. The basic formula for the Van der Waals interaction can be written as

$$C_6 = e^4 \sum_{n,m} \left\{ \frac{(\chi_n \cdot \varphi(R) \cdot \chi_m)^2}{E_n + E_m} \right\} \tag{11}$$

where $\varphi = 1 - 3\hat{R}\hat{R}$, E_n and E_m are excited relative energies of the noble gas and copper atom respectively, χ_n and χ_m are the matrix elements for these transition. The denominator can be expanded as follows,

$$1/E_n + E_m = 1/E_n - [E_m/E_n]^2 + - \ldots \quad \text{if } E_m \ll E_n \tag{12}$$

This is valid for the system under consideration in view of the fact that the excitation energies of the noble gases are much larger than those of the copper atom. Only the first two terms in the series expansion $C_6 = \sum_n C_6^{(n)}$ are of significance and it can be shown that the second term is independent of the emitting atom and its state of excitation. In fact $C_6^{(1)}$ turns out to be a small negative correction to the first term and dependent only on the noble gas.

The first term $C_6^{(0)}$ according to Dalgarno and Kingston [12] is

$$C_6^{(0)}(m_l, l) = 1/2 e^2 a_\beta^2 a_0 n^{*2} \frac{[5n^{*2} + 1 - 3l(l+1)][5l(l+1) - 3(m_l^2 + 1)]}{(2l+3)(2l+1)} \tag{13}$$

where n^* is the effective quantum number of the copper valence electron, (l, m_l) are angular quantum numbers, a_β is the radius of the first Bohr's orbit. Coulomb potential is assumed for the central field of the emitter. It may be noticed that $C_6^{(0)}(l, m_l) = C_6^{(0)}(l, -m_l)$. Effective quantum numbers can be evaluated from the equation $n^* = (109737 \cdot 2/\text{term value})^{1/2}$ and knowing the polarizability of the noble gas atom, equation (13) can be evaluated.

For S states ($l = 0$, $m_l = 0$) the value is obtained directly from Eq. (13), but not for the P and D states. A state with a given value of (j, m_j) is a linear combination of states with different (l, m_l) and can be represented as follows using transformation formulae for vector amplitudes [13].

^2D term

$$j = 3/2;\ C_6^{(0)}(3/2; 3/2) = 1/5\ C_6^{(0)}(2; 1) + 4/5\ C_6^{(0)}(2; 2) \tag{14a}$$

$$C_6^{(0)}(3/2; 1/2) = 2/5\ C_6^{(0)}(2; 0) + 3/5\ C_6^{(0)}(2; 1) \tag{14b}$$

$$j = 5/2;\ C_6^{(0)}(j; m_j) = C_6^{(0)}(5/2; 5/2) = C_6^{(0)}(2; 2) = C_6^{(0)}(l, m_l) \tag{14c}$$

$$C_6^{(0)}(5/2; 3/2) = 4/5\ C_6^{(0)}(2; 1) + 1/5\ C_6^{(0)}(2; 2) \tag{14d}$$

$$C_6^{(0)}(5/2; 1/2) = 3/5 C_6^{(0)}(2; 0) + 2/5\ C_6^{(0)}(2; 1) \tag{14e}$$

^2P term

$$j = 1/2;\ C_6^{(0)}(1/2;\,1/2) = 1/3\ C_6^{(0)}(1;\,0) + 2/3\ C_6^{(0)}(1;\,1) \tag{14f}$$

$$j = 3/2;\ C_6^{(0)}(3/2;\,3/2) = C_6^{(0)}(1;\,1) \tag{14g}$$

$$C_6^{(0)}(3/2;\,1/2) = 1/3\ C_6^{(0)}(1;\,1) + 2/3\ C_6^{(0)}(1;\,0) \tag{14h}$$

and through Eq. (13), relations like,

$$\begin{aligned} C_6^{(0)}(1;\,1) &= 4/7\ C_6^{(0)}(1;\,0) \\ C_6^{(0)}(2;\,2) &= 5/8\ C_6^{(0)}(2;\,1) \\ C_6^{(0)}(2;\,2) &= 5/9\ C_6^{(0)}(2;\,0) \end{aligned} \tag{15}$$

can be derived. These will be helpful in evaluating the Eqs (14) and reduce Eq (14) to the following

$$\begin{aligned} C_6^{(0)}(5/2;\,3/2) &= 37/25\ C_6^{(0)}(5/2;\,5/2) \\ C_6^{(0)}(5/2;\,1/2) &= 43/25\ C_6^{(0)}(5/2;\,5/2) \\ C_6^{(0)}(3/2;\,3/2) &= 28/25\ C_6^{(0)}(5/2;\,5/2) \\ C_6^{(0)}(3/2;\,1/2) &= 42/25\ C_6^{(0)}(5/2;\,5/2) = 3/2\ C_6^{(0)}(3/2;\,3/2) \\ C_6^{(0)}(1/2;\,1/2) &= 5/4\ C_6^{(0)}(3/2;\,3/2) \end{aligned} \tag{16}$$

Dalgarno and Kingston's [14] polarizability values for argon and Moore's [15] energy values were used and the Eq. (16) was evaluated for the $4P$, $4D$ and $5D$ states of a copper atom perturbed by argon at 1 atm. The results are shown in Table III.

TABLE III

$C_6^{(0)}$, the first term in the expansion of the Van der Waals interaction constant $C_6 = \sum_n C_6^{(n)}$, in units of 10^{-58} erg. cm^6 where $-C_6^{(1)} = 0.23 \times 10^{-58}$ erg. cm^6. (Perturber is argon gas)

State	n^*	$j;m_j$	first term
$4P$	1.8582	1/2;1/2	2.214
$4P$	1.8655	3/2;3/2	1.805
		3/2;1/2	2.707
$4D$	2.9770	3/2;3/2	10.123
		3/2;1/2	15.185
$4D$	2.9779	5/2;5/2	9.053
		5/2;3/2	13.398
		5/2;1/2	15.571
$5D$	3.9795	3/2;3/2	41.183
		3/2;1/2	61.775
$5D$	3.9809	5/2;5/2	36.836
		5/2;3/2	54.052
		5/2;1/2	63.340

It may be noticed that the dispersive force is different for a Cu atom in the $j = 5/2$, $j = 3/2$ and $j = 1/2$ states. The $j = 5/2$ state splits into 3 and $j = 3/2$ into 2 sub-groups. For the ^2P term, the relation for the ratios of Van der Waals energies is $^2P^{|3/2|}_{3/2}$: $^2P^{|1/2|}_{1/2}$: $^2P^{|1/2|}_{3/2}$ $= 4 : 5 : 6$, which is the same as the one given by Takeo and Chen [16].

The Van der Waals constants are obtained by the simple expedient of adding $C_6^{(0)}$ and $C_6^{(1)}$. As long as the energies of the m_j level are not split by an external perturbation, it is reasonable to take an average over the values of m_j, namely $\langle C_6(j)\rangle = 1/2\,j+1\,(\sum_{m_j} C_6(j \cdot m_j))$ and further in calculating the Van der Waals breadths of optical lines the $C_6\langle j\rangle$ constants for both the lower and upper levels must be considered. These constants can be used in assessing the Van der Waals widths. However, the accuracy can be improved by considering the repulsive part of the potential.

3. Discussion

The quadratic shift constants have not been experimentally measured by the authors. Prof. Vujnovic of the University of Zagreb has kindly intimated that the value of the constant for the line at 4022.7 Å compares well with the experimental value determined in an underwater arc. Acinger *et al.* [17] have used the constant for the line at 5153 Å in evaluating the electron density in a MIG arc. A highly stable copper vapour arc[1] with excellent emission characteristics has been built in this laboratory. A careful investigation of the arc in this device is expected to make way for the confirmation of the theoretical results.

The present calculation encompasses only the pressure broadening mechanism and the estimation of the temperature dependent Doppler broadening is simply carried out using the expression

$$\Delta\lambda_D = 7 \cdot 16 \times 10^{-7} \lambda \left(\frac{T}{\mu}\right)^{1/2} \qquad \mu = 63 \cdot 4 \quad \text{for} \quad \text{Cu.} \tag{17}$$

where $\Delta\lambda_D$ is the half-width of the Doppler broadened line, λ is the wave length of the spectral line under consideration, T is the gas temperature or Doppler temperature in degrees Kelvin and μ is the atomic or molecular weight of the emitter.

The classical theory of Lindholm is quite valid if the quadratic Stark constants are high as in this case. If the Stark constants are low as in the case of resonance transitions or low-level transitions a more rigorous quantum mechanical calculation would be necessary. According to Lindholm's formalism, the half-width calculated would be valid for those transitions for which $N_e \varrho_W^3 \ll 1$, where ϱ_W is the Weisskopf's radius. This means that the half-width of the $4P-5D$ will be valid for densities up to $10^{19}/\text{cm}^3$ and for still higher densities in the case of $4P-4D$ transitions. Also, the shifts calculated using the ion field distribution are many orders smaller than the electron-collision shifts using the quadratic Stark constants.

It is believed that the constants derived in this paper would be useful in the interpre-

[1] Miyachi and Jaya Ram, *A Stabilized Metal Vapour Arc Device*, (to be published).

tation of line broadening studies and will lead to a more detailed knowledge of some of the interesting phenomena mentioned in the introduction.

The investigations of this laboratory on a stabilized metal-vapour arc will be the subject of a future communication.

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Note added In proof: The details of the Stabilized metal vapour arc device are published in [A]. The results ef spectroscopic measurements performed on this device are available in [B] and [C].

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