Calculation of broadening of several Ar I spectral lines by neutral atoms

Magdalena Christova

Department of Applied Physics, Technical University-Sofia, BG-1000 Sofia, Bulgaria

e-mail: mchristo@tu-sofia.bg

Abstract. Calculations of broadening of nine Ar I spectral lines due to collisions with neutral argon atoms are presented. The semi-classical impact broadening theory has been used. The interaction of an excited Ar atom with Ar atom in the ground state has been treated using the Kaulakys potential and a comparison with other potentials has been performed. The influence of the Maxwellian averaging and the scattering length on the broadening cross section has been studied.

1. Introduction

Pressure broadening is a general term that describes any broadening and shift of a spectral line produced by fields generated by a background gas or plasma. Neutral atom broadening indicates neutral atomic perturbers. The interactions between emitters and neutral atomic particles are significant in plasmas with a low degree of ionization being the dominant mechanism of broadening and shifting of the spectral lines.

In the previous work [1], results of the broadening of argon lines by neutral atoms using van der Waals, Lennard-Jones and Kaulakys potentials without Maxwellian averaging of the broadening cross section have been reported. The case of emitters in intermediate Rydberg states with effective quantum number $n^* (5 < n^* < 15)$ has been reconsidered by Omont [2]. On the basis of this treatment Kaulakys [3] obtained expressions for the Rydberg level broadening and shift cross-sections due to the elastic collisions of Rydberg atoms with ground state noble-gas atoms.

The purpose of the present work is to study the broadening of Ar I spectral lines caused by the neutral atoms in pure argon using Kaulakys potential and performing Maxwellian averaging. The study is of interest for research of surface wave-sustained discharges (SWDs) [4, 5]. One of the first works dealing with the experimental and calculated values of pressure broadening and shift of argon spectral lines emitted in SWDs is presented in [6].

2. Theory

Considering an atom in a certain energy level with energy spread $\Delta E$ and lifetime $\Delta t$, the Heisenberg uncertainty principle states that:

$$\Delta E \Delta t = \hbar.$$  \hspace{1cm} (1)

The lifetime of an atom in its ground state is very long and hence the energy level is quite sharp. For an excited state, its stability against decay is much less and hence the energy spread is much larger. Therefore although each quantum emitted in a transition $i \rightarrow f$ has a precise energy $E = \hbar \omega$, where $\omega$ is the circular frequency, the observed line profile produced by many such transitions will have a finite
width (natural damping width). For each atomic level, the effective quantum number \( n^* \) can be obtained from the hydrogenic approximation:

\[
(n^*)^2 = \frac{E_{n}^{\text{ion}}}{E_{n}^{\text{ion}} - E_{\text{exc}}},
\]

(2)

where \( E_{n}^{\text{ion}} \) and \( E_{n}^{\text{ion}} \) are the ionization energy of hydrogen and argon atoms, respectively, and \( E_{\text{exc}} \) is the excitation energy of the argon level under consideration.

From the other side, the wave train of radiation is interrupted by collisions between the radiator and other atoms in its environment. According to the impact theory, the intensity distribution of the line corresponding to a transition between two levels is given by the Lorentzian profile. The width \( \gamma \) of the line can be written [7] as:

\[
\gamma = 2N \left\langle \sigma' \nu \right\rangle = \beta N, \tag{3}
\]

where \( N \) is the perturber density, \( \sigma' \) is the effective cross section for the impact broadening of the line and \( \beta \) is the broadening coefficient. Here the symbols \( \left\langle \ldots \right\rangle \) denote the thermal average over a Maxwellian distribution of the relative velocities of the interacting atoms.

In most theoretical interpretations of experimental data the Maxwellian averaging of the broadening cross section is omitted and the broadening coefficient in equation (3) is approximated in [8–10] by:

\[
\beta = 2\left\langle \sigma' \nu \right\rangle = 2N \left\langle \sigma' \nu \right\rangle, \tag{4}
\]

where

\[
\nu = \left( \frac{8kT_g}{\pi\mu} \right)^{1/2} \tag{5}
\]

is the mean relative velocity between the radiator and the perturber, \( T_g \) is the gas temperature, \( \mu \) is the reduced mass of radiator-perturber system, and \( k \) is the Boltzmann constant.

In the classical straight-path approximation, the broadening cross section can be expressed as

\[
\sigma' = 2\pi \int_0^\infty \left[ 1 - \cos \eta(\rho) \right] \rho d\rho, \tag{6}
\]

where \( \rho \) is the impact parameter and \( \eta(\rho) \) is the phase-shift due to the total interaction \( V(R) \) between the perturber and radiating atom in its upper and lower state

\[
\eta(\rho) = \frac{2}{\nu h} \int \frac{V(R) R dR}{\rho \sqrt{R^2 - \rho^2}}, \tag{7}
\]

where \( R \) is the distance between the interacting atoms. Equations (1) – (7) are in CGS units.

For spectral lines involving low-excited levels the purely attractive van der Waals or empirical Lennard-Jones potentials were applied in many interpretations of experimental results. In the case of interaction between an atom in a highly excited state and neutral atomic particle the Fermi model was used. The potential of the interaction between a Rydberg atom and the rare-gas atoms proposed by Kaulakys [3] consists of the polarisation attractions and short-range interaction between the Rydberg electron and perturber. The polarisation interaction is given by:

\[
V_{\text{pol}}(\vec{R}, \vec{r}) = -\frac{\alpha}{2R^4} + \frac{R^2 - \vec{R} \cdot \vec{r}}{R^3 \left[ R - r \right]^3} - \frac{\alpha}{2R^4} \left[ R - r \right], \tag{8}
\]

where \( \vec{r} \) is the location of the Rydberg electron, \( r_0 \) is the distance of the short-range interaction between the electron and the perturber and \( \alpha \) is the polarisability of the perturber. The first term in the right part is the polarisation attraction between the perturber and the core of the Rydberg atom. The second one describes the interaction between the electron and the dipole induced in the perturber by the atomic core. The potential of the electron-perturber interaction \( V_e(\vec{r} - \vec{R}) \) consists of the
polarisation attraction \(-\alpha / 2(r - \bar{R})^4\) and short-range interaction. This potential causes the electron-atom scattering cross section and, for an atom with small polarisability, is approximated by a Fermi pseudopotential:

\[
V_{\text{Fermi}}(r - \bar{R}) = 2\pi L \delta(r - \bar{R}),
\]

where \(L\) is the scattering length, \(\delta\) is the Dirac function. Kaulakys [3] has derived expressions for the broadening (\(\sigma'\)) and shift (\(\sigma''\)) cross sections suitable for elastic collisions of ground-state rare-gas atoms with Rydberg atoms. For small \(n^*\) the broadening cross sections are defined by Rydberg-electron-perturber interaction:

\[
\sigma'_e = \begin{cases} 
4\pi (n^*)^4 & \text{if } n^* < n^*_1 \\
8\pi(n^*)^8 & \text{if } n^*_1 < n^* < 0.7n^*_2 \\
8\pi(n^*)^8 & 2(n^*)^8 & \text{if } n^* > 0.7n^*_2 , 
\end{cases}
\]

For larger \(n^*\)

\[
\sigma' = \sigma'_e + \frac{8\pi(n^*)^8}{(n^*)^4} \left[ 1 - \left( \frac{5.7}{\pi} \right) \left( \frac{\alpha}{2V} \right)^{1/3} \frac{1}{2(n^*)^2} \right]
\]

where

\[
\sigma'_e = \left( \frac{\pi}{2} \right)^{5/3} \Gamma \left( \frac{1}{3} \right) \left( \frac{\alpha}{2V} \right)^{2/3} \equiv 5.7 \left( \frac{\alpha}{2V} \right)^{2/3}
\]

is the broadening cross section due to polarization interactions between the perturber and the core of a Rydberg atom; \(n_1^*\) and \(n_2^*\) are critical effective principal quantum numbers defined by:

\[
n_1^* = \left[ \frac{L}{4V} \right]^{1/4}
\]

\[
n_2^* = \left[ \frac{L}{4V^{1/6}V^{-5/6}} \right]^{1/3}.
\]

It should be noted that for \(n^* < n_1^*\) the Kaulakys treatment predicts broadening cross section, which corresponds to the classical geometrical cross section \((\pi r_0^2 = \pi a_0^2 n^*^4)\) of the sphere with radius equal to the Bohr radius \(r_0 = a_0 n^*^2\) for a given \(n^*\). For \(n^* > 0.70n_2^*\) broadening cross section decreases asymptotically approaching the value \(\sigma'_e\). Equations (8) – (13) are in atomic units \((e = m = \hbar = a_0 = 1)\).

### 3. Results

The calculations of the broadening of the studied argon spectral lines have been performed for the values of the gas temperature from 300 to 3000 K in the pressure range 1 – 200 Torr and under atmospheric pressure.

**Table 1.** Wavelength, transition, energy value of upper and lower state, effective quantum number \(n^*\) of the upper state, and symbols in figure 1 for the studied argon lines.

| \(\lambda\) (nm) | Transition | \(E_u\) (cm\(^{-1}\)) | \(E_l\) (cm\(^{-1}\)) | \(n^*\) | Symbol |
|-----------------|------------|-----------------|-----------------|-------|-------|
| 696.5           | 3p\(^4\)4p\(^5\)→3p\(^4\)4s | 107496          | 93144           | 2.28  | *     |
| 737.2           | 3p\(^5\)4d→3p\(^5\)4p     | 119024          | 105463          | 3.68  | △     |
| 641.6           | 3p\(^6\)s→3p\(^5\)4p      | 119683          | 104102          | 3.84  | ⭐    |
| 591.2           | 3p\(^5\)4d→3p\(^5\)4p     | 121012          | 104102          | 3.81  | ⬤    |
| 560.7           | 3p\(^5\)5d→3p\(^5\)4p     | 121933          | 104102          | 4.60  | ×     |
| 603.2           | 3p\(^5\)5d→3p\(^6\)4p     | 122036          | 105463          | 4.65  |      |
| 518.8           | 3p\(^5\)5d→3p\(^5\)4p     | 123373          | 104102          | 4.61  | ○     |
| 549.6           | 3p\(^6\)d→3p\(^5\)4p      | 123653          | 105463          | 5.63  |      |
| 522.1           | 3p\(^7\)d→3p\(^5\)4p      | 124610          | 105463          | 6.62  | —     |
Atomic data for the examined transitions are included in table 1, along with the corresponding symbols used in figure 1. The data for wavelengths and energies are taken from [11].

The broadening of the studied Ar I lines as a function of the gas temperature under atmospheric pressure using Kaulakys potential with Maxwellian averaging of the broadening cross section is presented in figure 1. For spectral lines with $n^* < 5$, $\beta$ increases monotonically with gas temperature. For Ar I 549.6 nm $\beta$ rapidly increases up to 2000 K where it reaches a maximum. The $T_g$-dependence of $\beta$ for Ar I 522.1 nm is completely different. The broadening coefficient slowly increases for small values of $T_g$, reaches a maximum in the interval 500 – 1000 K and then monotonically decreases.

![Figure 1](image1.png)

**Figure 1.** Broadening coefficient of Ar I spectral lines versus the gas temperature under atmospheric pressure, $L = -1.6a_0$. The lines are marked according to table 1.

The influence of Maxwellian averaging on the broadening coefficient is presented in figure 2. The solid circles represent $\beta$ from equation (3) and the open circles - $\beta$ from equation (4). The calculations have been performed for 1600 K under atmospheric pressure with scattering length $L = -1.6a_0$ taken from [3, 12]. The variation in $\beta$ when Maxwellian averaging is performed and when it is omitted is 29% for the first seven lines in the table, 12% for 549 nm, and 7% for 522 nm. The similar flattering effect of the Maxwellian averaging on the $n^*$-dependence curve has been reported in [12] though for lower values of the gas temperature and pressure.

![Figure 2](image2.png)

**Figure 2.** Broadening coefficient versus the effective quantum number ($\bullet$ with Maxwellian averaging of the broadening cross section; $\bigcirc$ without it), $p = 1$ atm, $T_g = 1600$ K, $L = -1.6a_0$.

The influence of the scattering length on the $n^*$-dependence of the broadening coefficient is presented in figure 3 ($\bigcirc L = -1.6a_0$). The results are obtained for gas temperature 1600 K under...
atmospheric pressure using equation (4). The value of scattering length $L = -1.459a_0$ (marked with $\times$ in the figure 3) is taken from [13]. For the spectral lines belonging to the lower transitions, the broadening coefficient does not depend on the scattering length. This indicates that the interaction of an excited atom in $4p$, $6s$, $4d$, or $5d$ state ($n^* < 5$) with a ground state atom is only a superposition of polarization attractions under the examined conditions. The value of $L$ affects considerably the interaction of intermediate Rydberg atom in $6d$ or $7d$ state with neutral atoms, which indicates that the Rydberg electron-perturber short-range interaction is noticeable. There is a difference of 10% for Ar I 522.1 nm and 13% for 549.6 nm between the values of the broadening coefficient for the two scattering lengths.

Figure 3. Broadening coefficient versus the effective quantum number for two values of the scattering length ($\bigcirc L = -1.6a_0$, $\times L = -1.459a_0$), $p = 1$ atm, $T_g = 1600$ K.

Figure 4. Broadening coefficient versus the effective quantum number using different potentials (Kaulakys potential with Maxwellian averaging, Kaulakys potential without Maxwellian averaging, van der Waals potential, Lennard-Jones potential), $p = 1$ atm, $T_g = 1600$ K, $L = -1.6a_0$.

The broadenings of the examined Ar I spectral lines obtained via different potentials are compared in figure 4. The broadening coefficient is calculated for 1600 K under atmospheric pressure. The $\beta$ values for the Kaulakys potential are greater than those for the van der Waals potential and lower than those for the Lennard-Jones potential. It seems that the Lennard-Jones potential is not appropriate to describe the interaction of an atom in highly excited state with the surrounding ground state atoms. It is in accordance with [12]. From one side, it was found in [9, 14] that the calculated broadenings of the spectral lines using van der Waals potential are 1.2 – 1.5, even 2 times smaller than the experimental
ones. From the other side, dependences of $\beta$ versus $n^*$ similar to those presented in figure 4 have been obtained in [12]. It has been concluded there that in pure argon at 400 K and pressure range 5-18 Torr the Kaulakys potential is more adequate than van der Waals and Lennard-Jones potentials for the intermediate Rydberg states with $n^* > 5$. The above conclusion together with our results obtained at higher temperature and pressure suggests that the Kaulakys potential would be even more appropriate here.

The Ar I 696.5 nm spectral line belongs to the lowest optical transition in this work. The calculations of the width are performed for pressure 1 – 200 Torr and gas temperature 300 – 1000 K using different potentials. The values, corresponding to van der Waals potential are greater than those obtained from Kaulakys and Lennard-Jones potentials. According to [12, 15] the broadenings of argon spectral lines with $n^* < 5$ calculated from the van der Waals potential fit best the experimental results yet are still underestimated [9, 14].

An application of the broadening calculations of argon spectral lines caused by the neutral atoms in the case of SWDs under atmospheric pressure will be published in [16].

4. Conclusion

The gas temperature dependence of the broadening coefficient for nine Ar I lines emitted in pure argon using Kaulakys potential and performing Maxwellian averaging of the broadening cross section has been obtained. The calculations presented here show that the interaction between an excited Ar atom in $4p$, $6s$, $4d$, or $5d$ state with a ground state Ar atom is defined by the polarization attraction of Rydberg-electron-perturber interaction. The interaction of an Ar atom in $6d$ or $7d$ with a ground state atom consists of polarization attraction and Fermi pseudopotential under the conditions of interest. It is better to perform Maxwellian averaging for broadening calculations. The critical value of the scattering length should be used.

Acknowledgments

The author thanks Prof. Dr. N. Allard and Prof. Dr. G. Peach for the useful discussions, Prof. Dr. B. Kaulakys and Prof. Dr. M. S. Dimitrijević for the valuable comments. This work was supported by Technical University-Sofia, Bulgaria, partially financed by projects 795 ПД 10 of TU-Sofia and No1315 of the National Science Fund of Bulgaria.

References

[1] Christova M, Gagov V and Koleva I 2005 Mem. S. A. It. 7 225
[2] Omont A 1977 J. de Physique 38 1343
[3] Kaulakys B 1984 J. Phys. B: At. Mol. Phys. 17 4485
[4] Moisan M and Pelletier J 1992 Microwave Excited Plasmas (New York: Elsevier)
[5] Aliev Y M, Schlüter H and Shivarova A 2000 Guided-Wave-Produced Plasmas (New York: Springer)
[6] Moussounda P S and Ranson P 1987 J. Phys. B: Mol. Opt. Phys. 20 949–96
[7] Sobelman I, Vainshtein L A and Yukov E A 1979 Vozbuzhdenie atomov i ushirenie spektralnyh linii (Moscow: Mir, in Russian)
[8] Hindmarsh W and Farr J 1972 Progress in Quantum Electronics eds Sanders J H and Stenholm S (Oxford: Pergamon)
[9] Peach G 1981 Adv. Phys. 30 367
[10] Al-Saqabi B N I and Peach G 1987 J. Phys. B: At. Mol. Phys. 20 1175
[11] http://www.nist.gov
[12] Wolnikowski J, Bielski A, Trawiński R S and Szudy J 1993 Phys. Scripta 47 186
[13] Petrović Z Lj, O’Malley T F and Crompton R W 1995 J. Phys. B: At. Mol. Opt. Phys. 28 3309
[14] Dimitrijević M S and Peach G 1990 Astron. Astrophys. 236 261
[15] Zagornaev G V and Khakhaev A D 1983 Opt. Spectrosc. (USSR) 54 (4) 346
[16] Christova M and Christov L to be published