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Linewidth Studies on the Ar^+ 476.5 nm and 480.6 nm Lines Excited in a Helium–Argon Hollow Cathode Discharge

L. Csillag and M. Jánossy

Central Research Institute for Physics, P.O.B. 49, H-1525 Budapest 114, Hungary (Fax: +361/169-5380)

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Abstract. The spectral line shapes of the Ar^+ 476.5 nm and 480.6 nm lines, excited in a He–Ar hollow cathode (HC) discharge, were measured using the Fabry-Perot technique. The collisional and Doppler linewidths were determined for the two lines. The collisional broadening constants are estimated to be (5 ± 3) MHz/mbar and (6 ± 3) MHz/mbar, respectively. The temperature obtained from the two Ar ion transitions was found to be 260 K higher than that expected for the rest of the gas mixture from earlier measurements. The possibility is discussed, that this excess temperature is caused by Ar ions partially created in the HC discharge by charge transfer collisions with He_2^+ molecules.

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In hollow cathode (HC) excited noble gas mixtures, cw laser oscillation has been observed at several ionic transitions. As typical examples the He–Kr and He–Ar systems can be mentioned where the Kr^+ 469.4 nm and Ar^+ 476.5 nm lines are the strongest laser transitions. In both cases the upper laser levels are excited selectively by second kind collisions between metastable He atoms and ground state Kr or Ar ions [1] while the ground state noble gas ions are believed to be created by impact with high energy electrons, which are present in a relatively large number in the HC discharge [2]. An interesting feature of these lasers is that they oscillate in a single axial mode without any optical mode selection. This is attributed to the large homogeneous collisional broadening of the gain curve due to the relatively large filling gas pressure (20–40 mbars) characteristic for this type of lasers [3, 4].

In a previous paper [5], results of linewidth-investigations on the Kr^+ 469.4 nm and 473.9 nm lines were presented. Collisional ($\Delta\nu_c$) and Doppler ($\Delta\nu_D$) linewidths, and from these data the broadening constants α and Doppler-temperatures T_D were determined for the two Kr^+ lines at different exciting currents and gas pressures. It was found that T_D (469 nm) was about 160 K higher than T_D (474 nm). This temperature difference could be explained on the basis of the excitation mechanism of the upper level of the Kr^+ 469.4 nm line, where at the collision process some extra kinetic energy is created:

$$\begin{aligned}\mathrm{He}(2^3S_1)+\mathrm{Kr}^+(4p^{5/2}P_{3/2})&\rightarrow\mathrm{He}(1^1S_0)\\&+\mathrm{Kr}^+(6s^4P_{5/2})+\Delta E,\end{aligned}\qquad(1)$$

where $\Delta E=+0.35$ eV. A part of this excess energy is taken away by the excited Kr^+ ions, causing the higher temperature.

On the other side, the upper level of the Kr^+ 474 nm line (16.6 eV) lies far below the He triplet metastable level (19.82 eV), and it could be rightly assumed, that here the upper level is populated mostly by electron impact and not by second kind collisions of type (1). Therefore, it was concluded that T_D (474 nm) corresponds to the average gas temperature T_g.

It seemed reasonable to make further investigations on a system, where the excitation conditions are similar to (1) but $\Delta E\approx0$. In this case, no difference between the Doppler-temperatures of the ionic lines excited by different mechanisms is expected. Such a system is He–Ar, and results of investigations on this system are presented. Linewidth studies were performed on the spontaneous Ar^+ 476.5 nm (laser) and – for comparison – on the Ar^+ 480.6 nm (non laser) transitions, at a fixed current and pressure value. The result obtained from the present investigations was not exactly what was expected: the Doppler-temperatures proved to be equal for the two lines, but both values were found to lie about 260 K higher than the T_D (474 nm), i.e. the earlier accepted average gas temperature T_g for the He–Kr system, under similar experimental conditions.

1 The Excitation of Ar^+ Lines

At HC excitation of the He–Ar mixture, the basic excitation process for the Ar^+ 476.5 nm transition

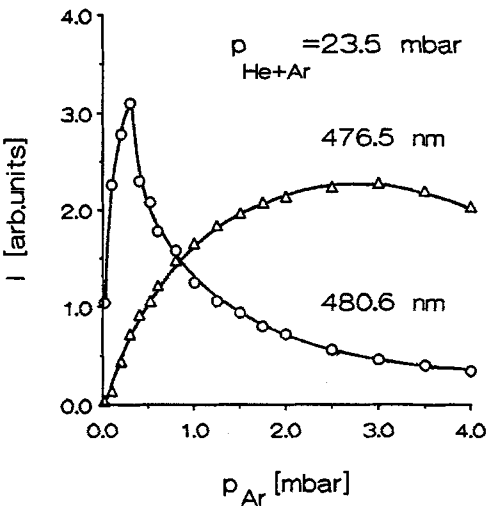

Fig. 1. Relative intensities of the Ar^+ 476.5 nm and 480.6 nm lines, measured at different argon partial pressures. Total (He+Ar) pressure: 23.5 mbar; discharge current: 200 mA

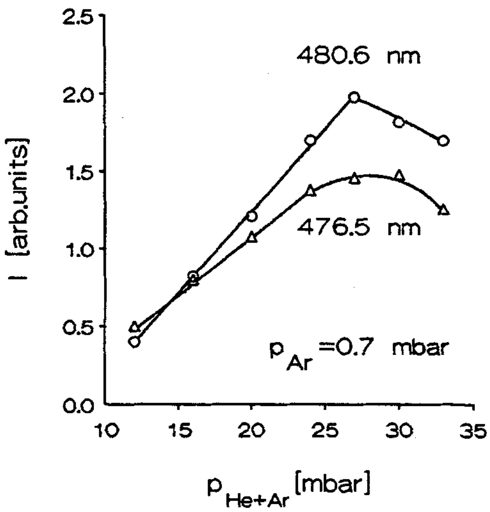

Fig. 2. Relative intensities of the Ar^+ 476.5 nm and 480.6 nm lines, measured at different total (He+Ar) pressures. Argon partial pressure: 0.7 mbar; discharge current: 200 mA. The dark hole appears above 25 mbar

$(4s^2P_{1/2} \leftarrow 4p^2P^0_{3/2})$ is quite similar to that of the Kr^+ 469.4 nm line in the He–Kr system [6]:

$$\mathrm{He}(2^3S_1) + \mathrm{Ar}^+(3p^{5/2}P_{3/2}) \rightarrow \mathrm{He}(1^1S_0) + \mathrm{Ar}^+(4p^2P^0_{3/2}) + \Delta E\,. \tag{2}$$

The only difference compared to (1) is, that here $\Delta E = -0.05$ eV, i.e. there is practically no energy difference between the two excited levels.

For the Ar^+ 480.6 nm transition $(4s^4P_{5/2} \leftarrow 4p^4P^0_{5/2})$ the upper level (19.22 eV) lies 0.60 eV lower than the He metastable level (19.82 eV), and therefore it can be assumed, that in the excitation of this line process (2) has no significant contribution. This assumption is supported by the fact that the intensity of the two Ar^+ lines change with the Ar partial pressure in a quite different manner: at 23 mbar total pressure and 200 mA current, the Ar^+ 480.6 nm line has a sharp optimum at $p_{Ar} \approx 0.3$ mbar, while for the Ar^+ 476.5 nm line there is a rather broad optimum at about $P_{Ar} = 3$ mbar (Fig. 1). It is believed that the upper level of the Ar^+ 480.6 nm line – like that of the Kr^+ 473.9 nm – is populated mostly by electron impact.

2 Experimental Setup and Evaluation Method

The light source, measuring system and evaluation method were the same as described in [5]. The HC discharge tube had a structure similar to that which was applied for lasers, with a cathode length of 3 cm. The middle of the 3 mm-∅ discharge area was observed "end on".

Both Ar^+ lines were not very strong. Therefore, the linewidth measurements were carried out only at the most favourable conditions. As the intensities increased nearly linearly with He pressure (Fig. 2), 23 mbar was chosen; above this pressure value, saturation sets in. (The "saturation" is due to formation of a dark hole in the middle of the discharge.) For the argon partial pressure $P_{Ar} = 0.7$ mbar was chosen. Here the intensities of the two lines were nearly equal (Fig. 1).

Measurements were carried out after careful evacuation, with one gas filling for several hours. During this period no contamination could be detected in the spectrum. It is mentioned, however, that after filling the gas about one hour was needed for homogeneous mixing of the two components.

The discharge current was stabilized at 200 mA which corresponds to a current density of about 30 mA/cm^2 on the cathode surface. The Al-cathode was cooled with flowing water. The tube voltage at the given pressure and current amounted to 220–230 V, this value being quite similar to that measured at the He–Kr discharge.

The spectral lineshapes were recorded with a piezoelectrically scanned Fabry-Perot interferometer (triple pass, distance 12 mm, effective finesse better that 35 in the range 450–550 nm). Due to the low intensities, photon counting was applied, with a measuring time of about 15 minutes for one measurement.

At the evaluation of the spectra first the Lorentzian and Gaussian components were determined by deconvolution assuming a Voigt-profile for the line, and then by applying small corrections due to overlapping orders and to the apparatus function of the FPI, the collisional $\Delta\nu_c(\lambda_i)$ and Doppler $\Delta\nu_D(\lambda_i)$ linewidths (full widths at half maxima) and from the latter the Doppler-temperatures $T_D(\lambda_i)$ were deduced.

The collisional broadening constant α was calculated assuming a linear pressure dependence:

$$\Delta\nu_c(p) = \Delta\nu_0 + \alpha p\,. \tag{3}$$

Here, $\Delta\nu_0$ denotes the zero pressure (radiation) linewidth. For $\Delta\nu_0$ numerical data are available: Korolev et al. [7] measured the linewidth of the Ar^+ 476.5 nm line at a negligible small gas pressure. According to their results $\Delta\nu_0 = (500 \pm 50)$ MHz. They also stated that the lower level ($4s^4P_{5/2}$) of the Ar^+480.6 nm transition has a rather long lifetime: τ_{lower} (480.6 nm) = 460 ns; while the average lifetime of the upper level ($4p^4P_{5/2}$) of this line was measured by Fink et al. [8]: τ_{upper}(480.6 nm) = 7.0 ns. From these data $\Delta\nu_0$ (480.6 nm) = (23 ± 6) MHz.

3 Results and Discussion

Results on the Ar^+ lines are summarized in Table 1. For comparison, earlier results on the Kr^+ lines at the given pressure and current values and the zero pressure linewidths are also presented in the table.

The linewidth data for Ar^+ were determined from six measurements, the standard deviations for the mean values being ±20 MHz.

The errors for $\Delta\nu_c$, $\Delta\nu_D$ and T_D given in Table 1 are estimated ones, taking into account the possible systematic errors due to the evaluation process. The α values for the Ar^+ lines should be treated only as estimations due to the large uncertainties in the $\Delta\nu_0$ values.

From the results the following conclusions can be drawn:

1. Collisional linewidths for the Ar^+ 476.5 nm and Kr^+ 469.4 nm laser lines are nearly equal at the given pressure; their origins differ significantly from each other, however. At the Kr^+ laser the small radiation linewidth is connected with a large pressure broadening constant, while at the Ar^+ laser the situation is the opposite: the radiation linewidth is large and the pressure broadening constant is small. Consequently, the earlier argumentation in explaining the single mode behaviour of HC noble gas mixture lasers should be corrected: especially for the Ar^+ 476.5 nm laser, single-mode operation is not due to the large filling pressure but due to the short lower level lifetime.

2. The small linewidth of the Ar^+ 480.6 nm line originates both from the small radiation linewidth and from the small pressure broadening constant.

3. The Doppler-temperatures for the two Ar^+ lines are practically equal, as it was expected.

4. The actual T_D values, however – in contrast to the expectation – are about 260 K higher for the Ar^+ lines than that for the Kr^+ 473.9 nm line, which was accepted earlier as the average gas temperature. This result has to be discussed in more detail.

There is no obvious reason, that average gas temperatures should differ significantly in the He–Ar and He–Kr mixtures. To obtain more information on this problem, we made linewidth measurements on the He 501.6 nm line, too. The situation is complicated here by the fact that the lower level of this line (He 2^1S_0) is metastable and at our experimental conditions (large pressure, large current and thick plasma) significant deformation of the line profile can be expected. In spite of this, as the profile was found to be nearly Voigt-type, we made the deconvolution. The Lorentzian component proved to be about two times larger than that calculated by extrapolating the data of Vaughan [9] based on a low current, low pressure and thin plasma measurement. The Doppler-temperatures, however, deduced from the Gaussian components, gave nearly the same T_D values for He–Ar, He–Kr mixtures and for pure He, too. Their average value $\bar{T}_D$(501.6 nm) = (563 ± 50) K lies quite near the T_D value deduced from the Kr^+ 473.9 nm line: T_D(473.9 nm) = (545 ± 50) K (i.e. to the earlier accepted value of the average gas temperature).

Table 1. Measured collisional and Doppler-linewidths $\Delta\nu_c$ and $\Delta\nu_D$ (full widths at half maxima), broadening constants α and Doppler-temperatures T_D for the lines Kr^+ 469.4 nm, Kr^+ 474.0 nm, Ar^+ 476.5 nm, and Ar^+ 480.6 nm. The zero pressure (radiation) linewidths $\Delta\nu_0$ are taken from [7, 8] and [14]

Ion	Kr^+ [5]		Ar^+	
λ [nm]	469.4	473.9	476.5	480.6
$\Delta\nu_0$ [MHz]	43 ± 3 [14]	200 ± 50 [7]	500 ± 50 [7]	23 ± 6 [8]
$\Delta\nu_c$ [MHz]	560	500	620	170
$\Delta\nu_D$ [MHz]	1330	1160	1990	1980
α [MHz/mbar]	23	12	5	6
T_D [K]	710	545	780	785

Errors: $\Delta\nu_c$ and $\Delta\nu_D$: ±50 MHz;
α: ±1 MHz (Kr^+), ±3 MHz (Ar^+)

Trivial sources for the observed temperature difference like changes in the electric input or in the spatial intensity distribution of the lines can be excluded, according to our measurements.

Consequently it can be accepted that the Ar ions have a higher temperature than that of the rest of the He–Ar gas mixture, or that of the He–Kr mixture.

One possible mechanism resulting in the excess heating of the Ar ions could be the accelerating action of the residual electric fields inside the cathode hollow [10]. The field distributions and ion acceleration rates can differ significantly for the Ar and Kr ions.

Another possibility is, that this excess energy is connected with the creation of the Ar ions. It was believed up to now, that in the HC discharge Kr and Ar ions are created mainly by collisions with high energy electrons [2, 6]. As this type of ionisation does not result in any significant change of the energy of the atomic particles, it may be assumed that – in the He–Ar HC discharge – other ionisation processes can also contribute to the ionisation or even dominate it. Such a process can be the charge transfer ionisation by collisions with He_2^+ molecules. It is known, that in He discharges at higher pressures the He_2^+ concentration can be rather high [11]. Due to charge transfer collisions of He_2^+ molecules with foreign atoms, which are present in small concentration in the He gas, two ground-state neutral He atoms and an ionized atom are created, the latter being in the ionic ground state or in an excited state depending on the energy conditions. The energy gain at the dissociation of the (excited) He_2^+ molecule is 18.3–20.3 eV [12].

In our case the reaction is:

$$He_2^+ + Ar \rightarrow He + He + Ar^+(3p^{5/2}P^0_{1/2-3/2}) + (2.5\text{–}4.5)\,\text{eV}\,; \qquad (4)$$

i.e. of the total energy 15.8 eV is needed for the ionisation of the Ar atom, while the residual energy is taken away as kinetic energy by the resulting He atoms and the ground state Ar ion, respectively.

The process (3) has a non-resonant character, and its cross-section can be quite high [12, 13]. So, if at least a part of the Ar ions are created in the discharge by process (3), this process can be responsible for the temperature difference observed in the He–Ar mixture.

As for the He–Kr system, the ionisation potential for Kr is only 14.0 eV, and the electron impact ionisation rate can be significantly higher than it is in the He–Ar system. On the other hand, the rate constant for charge transfer ionisation of Kr by collisions with He_2^+ is known to be an order of magnitude smaller than that for Ar [13]. Therefore, the contribution of the reaction type (3) in ionisation of Kr should be significantly smaller than that in the case of Ar, and in this way it can be explained, why the temperature rise due to reaction (3) does not appear at the Kr^+ 474 nm line.

Further investigations are needed to clarify in detail the origin of the observed difference in the Doppler-temperatures of the Kr^+ and Ar^+ lines.

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