Experimental investigation of the asymmetric charge exchange reaction in the Ar$^+$–Ni system in the afterglow of a pulsed glow discharge

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1. Introduction

Asymmetric charge transfer (ACT) reactions between ground state noble gas ions and metal atoms play an important role in many glow discharge applications, such as in hollow cathode sources [1,2], in different metal ion lasers (e.g. Ne–Cu$^+$, He–Ag$^+$, He–Au$^+$, He–Cu$^+$, He–Zn$^+$, etc.) [3–8], as well as in analytical plasma sources [9–12], both in glow discharge mass spectrometry (GD-MS) [13–15], and glow discharge optical emission spectroscopy (GD-OES) [16]. The plasma sources of GD instruments are mostly operated in argon buffer gas. Detailed understanding of the operation of these plasma sources requires sophisticated numerical modeling of the discharge plasmas, the accuracy of which depends critically on the correctness of the input parameters. To date, the lack of knowledge of ACT rate coefficients has prevented precise modeling of the relative sensitivity factors (RSF) [17–19] in GD-MS and limited the accuracy of the calculated emission spectra in GD-OES.

In the ACT reaction, a ground state metal atom (M) is ionized and excited by an ion (A$^+$) in a simple step:

$$A^+ + M \rightarrow A + M^{++} + \Delta E.$$  \hspace{1cm} (1)

Unlike other ionization processes (like Penning ionization, or electron impact ionization), the ACT between atomic species and atomic ions is a selective (nearly-resonant) mechanism. The process is most efficient for excited metal ion M$^{++}$ levels having an energy $0 \leq \Delta E \leq 1$ eV below the ground state energy of the noble gas ion A$^+$, with highest cross sections belonging to an energy difference $\Delta E \approx 0.1$–0.3 eV [20]. We note that during discharge operation noble gas ions may have significant kinetic energy that makes endoergic charge transfer possible as well [21]. This process cannot take place in the late afterglow.

Earlier rate coefficient measurements of ACT reactions between noble gas ions and metal atoms were mainly carried out with volatile metals, like Hg, Pb, Cd, Zn, or Ti [22–26]. There are very few rate coefficient and cross-section data available for other elements, that are difficult to evaporate, e.g. Cu, Fe, Ti, Ni, Mo, etc. For the Ne$^+$–Cu system, data have been published at ~2000 K [27]. Cross sections for the interaction of Xe$^+$ ions and various metals have been determined for a wide range of ion energies 1 eV $\leq E \leq 5000$ eV [28]. Experimental rate coefficient data for ACT reactions between Ar$^+$ ions and iron atoms, at thermal energies (~300 K), have been derived in our recent work [29], which combined plasma diagnostics methods and a kinetic model of the afterglow plasma, allowing monitoring of the temporal evolution of the densities of different plasma species. In this experiment iron vapor was created inside a discharge cell by cathode sputtering and its density was measured by atomic absorption spectroscopy. The rate coefficient of the reaction was evaluated from the emission intensity decay of Fe$^{++}$ lines pumped by the ACT process in He–Ar–Fe and Ar–Fe afterglow plasmas. This work has shown that the rate of the ACT reaction is an order of magnitude higher than the rate of the Penning ionization, confirming (in agreement with [30]) that the ACT reaction at certain conditions can play a significant role in the ionization balance in GD cells. This observation stresses the need for further studies concerning other elements,
where ACT is expected to be important and, indeed, the aim of the present paper is to investigate the ACT process in the \( \text{Ar}^+ + \text{Ni} \) system.

Experimental (spectroscopic) evidence for the ACT reaction between \( \text{Ar}^+ \) ions and Ni atoms has already been presented in [31–34], however, the rate coefficient of the reaction has not been measured yet, to our best knowledge. As to theoretical efforts, the semi-classical calculations of ACT rate coefficients between these species resulted in a value of \( k = 0.43 \times 10^{-9} \text{ cm}^2 \text{s}^{-1} \) [30].

This paper, as mentioned above, is devoted to experimental investigations on the ACT reactions between argon ions [both \( \text{Ar}^+ (2\text{P}_3/2) \) and \( \text{Ar}^+ (2\text{P}_1/2) \)] and nickel atoms, and the determination of the rate coefficient of these processes. In Section 2 we describe the experimental apparatus and the method of data acquisition. Section 3 presents and discusses the results, while Section 4 summarizes the work.

2. Experimental

The scheme of the experiments is displayed in Fig. 1. The discharge cell is situated in a chamber connected to a vacuum and gas filling system. The base pressure of the system is below \( 5 \times 10^{-6} \text{ mbar} \). We use 6.0 purity argon and helium gases, which are further purified using liquid nitrogen traps and a VICI P100-2 purifier [29].

The discharge cell has two plane and two hollow cathode electrodes, made of nickel of purity 99.9% (supplied by Goodfellow Ltd.). This electrode configuration provides proper conditions for the experiments for a wide range of the charge transfer reaction rate, which is not known prior to the experiments. At a low charge transfer rate establishing a high metal vapor density, using the hollow cathodes, is advantageous. At a high rate the charge transfer reaction can already take place within the hollow cathode cavities, and a low density of ground state metal vapor reaches the center of the reaction cell. Under these conditions the plane cathodes provide a higher metal atom density in the center. Data acquired during the exploration phase of our measurements indicated that using the plane cathodes is the better choice. These plane cathodes have an active surface of 50 mm (length) \( \times 5 \) mm (width). The inner diameter and the length of the anode cavity are 15 and 70 mm, respectively. Discharge pulses of 1.8 ms length are established by a high-voltage power supply, at a repetition rate between 2 Hz and 15 Hz, to keep the temperature of the discharge cell (measured by a K-type thermocouple) constant at different currents.

The rate coefficient of the ACT reactions is measured in a stationary afterglow experiment in the following way. (1) Nickel vapor is generated by sputtering the cathodes situated in the discharge cell, and its density, \([\text{Ni}]\), is measured in a time-resolved manner using atomic absorption spectroscopy (AAS). (2) The decay rate of the \( \text{Ar}^+ \) ion density is determined by emission spectroscopy; the intensities of ACT-excited spectral lines are acquired during the afterglow period. (3) The ACT reaction rate is determined from a simple mathematical model considering additional processes influencing the ion density.

2.1. Absorption and emission spectroscopy

The Ni vapor density inside the cell is determined by atomic absorption spectroscopy (AAS), using a 2 m focal length Zeiss PGS-2 spectrometer equipped with a 650 grooves/mm grating and a Hamamatsu (H7732P-11) photomultiplier tube. The signal from the tube is recorded in a time-resolved photon counting mode by an AMETEK multi channel scaler PCI-card. As a light source we use a nickel HC lamp (model Hamamatsu L253–28NO), operated at a current of 5 mA. The light of the lamp is collimated by Lens A and focused on the entrance slit of the spectrometer by Lens C, as shown in Fig. 1 (Lens B is not used in this measurement).

The ground electronic state of Ni I (a\(^2\)F) consists of \( J = 4, 3 \) and 2 sublevels with energies 0, 0.165 and 0.275 eV, and there is also a metastable state (a\(^2\)D) with \( J = 3, 2 \) and 1 sublevels at energies of 0.0254, 0.109 and 0.212 eV, respectively. As all these states can lead to ACT reactions with argon ions, one needs to account for the total density of Ni atoms at these levels. This can be accomplished following two different approaches. The first possibility is to carry out absorption measurements to determine the populations of each of these levels independently. This approach suffers from the low intensity and low absorbance of some of the transitions in the investigated spectral region. The other approach is based on the theoretical consideration that the populations of the levels are linked via respective statistical weights \( 2J + 1 \) and Boltzmann factors \( e^{-E/k_BT} \) (where \( E \) is the energy of the “initial” state and \( T \) is 300 K for our conditions). This theoretical prediction gives the following ratios for the populations of the different states: \([a^2F_4][a^2F_3][a^2F_2][a^2D_3][a^2D_2][a^2D_1]=1.001:10^{-2}:0.291:0.008:10^{-4}\). To test this theoretical prediction we have experimentally checked the ratio between the populations of the \( a^2F_4 \) and \( a^2D_3 \) states. The density of the \( a^2F_4 \) state was derived from absorption on the 232.003 nm and 228.998 nm lines (with oscillator

![Fig. 1. Schematic view of the reaction cell and the optical setup. The X-X section is perpendicular to the optical axis.](image-url)
strengths $f = 0.68$ and $f = 0.13$ respectively [35]). To determine the density of the $\text{a}^3\text{D}_3$ state absorption measurements on the transitions with the metastable lower level with $J = 3$ (using the 230.078 nm line, with oscillator strength $f = 0.06$ [35] and $E_0 = 0.0254$ eV) were carried out. For different discharge pulse currents we observed a ratio $1:0.3$ ($\pm 0.05$) in the afterglow period, in good agreement with the theoretical ratio $1:0.291$. Using this second approach the measurement of the density of the Ni $1\text{a}^3\text{P}_4$ state is sufficient (for which we continue to use the 232.003 nm and 228.998 nm lines), the total Ni atom density contributing to ACT processes can be estimated as $1.33$ times this density value.

For the emission spectroscopy measurements we use the Lens B + Lens C configuration (see Fig. 1) to collect light from the discharge center. Fig. 2 shows the 226 nm–230.5 nm range of the emission spectrum in the afterglow (integrated between 0.4 ms and 10 ms, with respect to switching the discharge off). This spectrum was recorded in the second order of the PG5-2 spectrometer. To block interference from the first spectral order we use an Edmund optics type 68336 805-01 bandpass filter, transmitting in a $\pm 15$ nm wavelength range around 228 nm. Several strong Ni-II lines show up in the spectrum, of which the time-dependent intensity is measured during the experiments. The signal to noise ratio is improved by averaging data taken after 4000 to 10000 discharge pulses. During the measurements we set the diaphragm (‘7’ in Fig. 1) at 10 mm diameter (to cut light emission originating near the electrode surfaces, placed at a distance of 15 mm), and set the slits of the spectrometer to 50 $\mu$m, which gives an $\approx 0.02$ nm full width at half maximum (FWHM) of the spectral lines. The diaphragm has the same diameter in the absorption measurements.

We note that we have tested the sensitivity of the absorption and emission spectroscopy results on several experimental parameters: (i) setting of the slit of the spectrometer in the 25–50 $\mu$m domain, (ii) adjusting the current of the HC lamp to any values below 7 mA, (iii) choosing a size of the diaphragm between 3 mm and 10 mm, had no observable effect on the results. More details of the plasma diagnostics methods (Langmuir probe measurements, absorption and emission spectroscopy) have already been described in [29].

2.2. Determination of the rate coefficient

The basic processes relevant to our measurements have already been discussed in [29] based on a kinetic model. This model has shown that the ACT rate coefficient can be determined both in pure argon and in helium–argon mixtures. The model also shed light on the optimum timing of the measurements: in pure argon taking data between 0.2 ms and 1.0 ms is advantageous, while in helium–argon mixture taking data beyond 0.5 ms is preferable (for more details see [29]). In both cases the balance equation for $[\text{Ar}^+]$ in the afterglow can be written in the following form:

$$\frac{d[\text{Ar}^+]}{dt} = -k_{CT} [\text{Ar}^+] [\text{Ni}] - \frac{D}{\Lambda} [\text{Ar}^+] \cdot$$

(2)

where the first term on the right hand side represents the ACT reaction between $\text{Ar}^+$ ions and Ni atoms with a rate coefficient $k_{CT}$, the second term is the ambipolar diffusion to the wall with a diffusion constant $D$ and a characteristic diffusion length $\Lambda$. Assuming a constant nickel number density $[\text{Ni}]$ – which is a reasonable approximation for short ($\leq 1$ ms) time periods – the solution of Eq. (2) can be written as:

$$[\text{Ar}^+] = \left[\text{Ar}^+\right]_0 e^{-\frac{t}{\tau}}$$

(3)

where

$$\frac{1}{\tau} = \frac{D}{\Lambda} + k_{CT} [\text{Ni}] = \frac{1}{\tau_D} + \frac{1}{\tau_{CT}}.$$

(4)

where $[\text{Ni}]$ denotes time dependence. The first term on the right side of Eq. (4), $1/\tau_D$, is a constant at a given pressure (and buffer gas composition). Thus, the plot of $1/\tau$ versus the nickel number density, $[\text{Ni}]$, is expected to be a straight line, the slope of which is given by the rate coefficient $k_{CT}$. The absolute value of the nickel atom number density, needed for the evaluation of $k_{CT}$, is provided by the atomic absorption measurements. On the other hand, we do not need the absolute density of argon ions, the characteristic decay time $\tau$ can be obtained from relative values. In our experiment the relative number density of argon ions is determined from the intensity ($I_{CT}$) of Ni-II lines pumped by the ACT reaction between $\text{Ar}^+$ ions and Ni atoms. The intensity of these lines is directly proportional to $[\text{Ar}^+][\text{Ni}]$. It follows, that the relative $\text{Ar}^+$ ion density decay can be obtained from the ratio of $I_{CT}/[\text{Ni}]$, or $k_{CT}/A$, where $A$ is the measured absorbance of Ni atoms. Fitting the time evolution of this ratio by an exponential decay gives us the value of $\tau$. For the evaluation of $k_{CT}$ the obtained $\tau$ is assigned to the nickel density averaged over the time interval of the exponential fit.
3. Results and discussion

In a thermal afterglow argon ions can exist in two different states: the Ar$^+$ (3P$^2_1/2$) “ground state” with an energy of 15.760 eV and the “metastable” state Ar$^+$ (3P$^2_3/2$) with an energy of 15.937 eV. Under such conditions ACT excitation of a group of spectral lines of which the upper level is below the energy of the Ar$^+$ (3P$^2_1/2$) ions may originate both from reactions involving Ar$^+$ (3P$^2_3/2$) ions or Ar$^+$ (3P$^2_1/2$) ions. For another group of lines with upper state energy between those of these two ionic states ACT can occur from Ar$^+$ (3P$^2_1/2$) ions only. The lines belonging to the same group have the same relative decay in the afterglow, as it was indeed confirmed by our measurements at identical discharge conditions (pressure, current, etc.). This is illustrated in Fig. 3, which shows the time-dependent intensities of three Ni II lines. Two of these lines (227.877 nm and 229.828 nm) are efficiently excited via ACT with Ar$^+$ (3P$^2_1/2$) ions. The third line (230.009 nm) is excited by the metastable Ar$^+$ (3P$^2_3/2$) ions. Thus, for the determination of the rate coefficient any of these lines can be used, we have selected lines with the highest intensity.

In the determination of the ACT rate coefficient we consider lines with upper levels lying below the energy of the ion ground state [Ar$^+$ (3P$^2_3/2$)], and assume that excitation of these lines originates from reactions with the Ar$^+$ (3P$^2_1/2$) ions only. This [neglecting the presence of the Ar$^+$ (3P$^2_3/2$) ions] is justified by the following three arguments: (i) due to the different statistical weights Ar$^+$ (3P$^2_1/2$) ions should be dominant, (ii) due to the fact that excitation (at these energy levels) with a smaller $\Delta E$ should be more significant, and (iii) the faster decay of the 230.009 nm line (Fig. 3), which is excited by the metastable Ar$^+$ (3P$^2_1/2$) ions, is an indication of quenching processes (see Discussion below).

To determine the rate coefficient we have carried out experiments in pure argon (at $p =$ 220 Pa) and in helium-argon mixture (at 1500 Pa and 1100 Pa pressures, with 2% Ar). We applied different currents in the range 10–70 mA, and adjusted the repetition rate of the pulses to keep the temperature in the cell at a nearly constant, room temperature value, $300 \pm 3$ K.

Fig. 4 shows the inverse decay times, $1/\tau_{CT}$, for all our measurements. Note that the first term on the right hand side of Eq. (4) has been subtracted from the measured inverse decay times, so the points are expected to fall on the same line and intersect the vertical axis at zero. Our measured data from the different series of measurements indeed show this behavior, with reasonable scattering. Data sets acquired on different lines, on different days, with different buffer gases (Ar/He–2%Ar) show similar slopes, with an uncertainty of 20%. Taking into account uncertainties in the determination of the Ni atom density, a rate coefficient of $k_{CT} = 2.3(\pm 0.9) \times 10^{-7}$ cm$^3$ s$^{-1}$ cm is derived from the data shown in Fig. 4.

To determine the rate coefficient between the metastable Ar$^+$ (3P$^2_1/2$) ions and nickel, $k_{CT}$, the 230.009 nm line populated only by this metastable state is considered next. The measurements on this line in pure argon show a faster decay compared to the other lines predominantly populated by the ground state Ar$^+$ (3P$^2_3/2$) ions. If we follow Eq. (4), which assumes that there are no other processes than charge exchange and diffusion, from our measured data we obtain $1/\tau_{Q0}$ values about a factor of $-2$ higher than expected for the diffusion of Ar$^+$ in Ar. This indicates that additional processes involving the Ar$^+$ (3P$^2_3/2$) ions only may play a role, like (i) collisional quenching of metastable argon ions with neutrals, Ar$^+$ (3P$^2_3/2$) + X → Ar$^+$ (3P$^2_3/2$) + X + 0.18 eV, where X is Ar [36] or/and impurities such as N$_2$, H$_2$, O$_2$, etc., which have an especially high rate [37–40], and (ii) electron impact quenching Ar$^+$ (3P$^2_3/2$) + e$^-$ → Ar$^+$ (3P$^2_3/2$) + e$^-$ + 0.18 eV.

To account for the processes Eq. (4) has to be extended by two additional terms:

$$\frac{1}{\tau} = \frac{1}{\tau_D} + \frac{1}{\tau_{CT}} + \frac{1}{\tau_{Q0}} + \frac{1}{\tau_{Q2}}. $$

As the buffer gas pressure, the temperature and the purity of the vacuum system (monitored by Langmuir probe, for more detailed information see Ref. [29]) are maintained at very nearly steady values during all the experiments, the decay time, $\tau_{Q0}$, due to the quenching of Ar$^+$ (3P$^2_3/2$) with the neutrals can be taken as a constant. On the other hand we observed a linear dependence of $1/\tau$ on the electron density determined during short time intervals where $1/\tau$ and $n_e$ can be considered as constants. This behavior is attributed to a quenching process for which $1/\tau_{Q0} = k_{Q0}n_e$. This statement is supported by the facts that: (i) no such term was necessary to consider in the case of Ar$^+$ (3P$^2_1/2$), and (ii) binary recombination reactions can be ruled out by the electron density decay curves measured by the Langmuir probe inserted inside the discharge cell.

There is no experimental data available for the rate coefficient $k_{Q2}$ of this quenching process. An estimate for the lower bound, $k_{Q2} \geq 8 \times 10^{-11}$ cm$^3$ s$^{-1}$, was given in [41]. Nevertheless, Eq. (5) still allows an accurate determination of the ACT rate coefficient provided that the $1/\tau_{Q2}$ term can be kept at a low value, and/or (nearly) constant. This condition can be met in He–Ar mixtures, as the electron density in the afterglow, for
different discharge currents, is not high and does not vary significantly (at a time \( t \sim 0.5 \) ms in the afterglow \( n_e \) is in the range \( 5 \times 10^{10} \text{ cm}^{-3} \)). In contrast with this, in pure argon \( n_e \) is an order of magnitude higher and depends considerably on the discharge current (at a time \( t \sim 0.5 \) ms in the afterglow \( n_e \) is in the range \( 1 \times 10^{11} \text{ cm}^{-3} \)). The behavior in helium-argon can be explained by collisional radiative recombination CRR (\( \text{Ar}^+ + e^- \rightarrow \text{Ar} + e^- \)) [42,43], the rate of which has a strong dependence on the electron temperature. The electron temperature values, measured by Langmuir probe, for Ar and He–Ar afterglow are \( \approx 800 \) (\( \pm 100 \) K) and \( \approx 300 \) K, respectively. The line intensities in the He–Ar mixture are not as strong as in Ar plasma and the measurements would have required exceedingly long measurement times to determine accurate values of the rate coefficients \( k_{\text{R}} \) and \( k_{\text{T}} \). Within the limits of our experiments only upper bounds for these reactions were possible to obtain: \( k_{\text{R}} \leq 1.3 \times 10^{-8} \text{ cm}^3 \text{s}^{-1} \) and \( k_{\text{T}} \leq 3.3 \times 10^{-8} \text{ cm}^3 \text{s}^{-1} \).

The value of \( k_{\text{CT}} \) obtained in the present experiment for ACT between \( \text{Ar}^+ (2p_{3/2}) \) and nickel atoms does not agree well with the theoretically predicted value of \( 0.43 \times 10^{-8} \text{ cm}^3 \text{s}^{-1} \) [30]. This can be explained by the fact that in this calculation only two Ni II ion levels, at 0.844 eV and 0.870 eV below the \( \text{Ar}^+ (2p_{3/2}) \) ionic level, were taken into account. During the spectroscopic measurements in the afterglow (see Fig. 2) we have observed ACT-exited lines not only from these two levels (e.g. 227.877 nm and 229.828 nm lines) but also from lower lying levels. Taking into consideration the transition probabilities [44,45,31], \( \gamma \langle \text{A}\rangle \), of the identified lines of Ni II, the relative population of the Ni II levels is plotted. It is evident from Fig. 5 that asymmetric charge transfer reaction occurs even for energy differences up to \( \approx 1.6 \) eV between \( \text{Ar}^+ (2p_{3/2}) \) and Ni II ionic levels.

Based on the approach presented in [30] the rate coefficient for ACT reactions can be calculated as:

\[
k_{\text{CT}} = k_{\text{R}} \sum_{n=1}^{N} e^{-G_n} (1 - e^{-G_n}),
\]

where \( G \) is a parameter, which depends on the energy difference \( \Delta \) between the gas ion and metal ion levels available for asymmetric charge transfer, \( N \) denotes the number of these levels, and \( k_{\text{R}} = \langle \text{AR} \rangle \) is the G-independent part of the rate coefficient, specific for the given metal (for details see [30]). For nickel, \( k_{\text{R}} = 2.392 \times 10^{-9} \text{ cm}^3 \text{s}^{-1} \) [30]. The \( G(\Delta) \) function used previously for the determination of ACT rate coefficients \( k_{\text{CT}} \) is shown in Fig. 6 (black full line) — as mentioned previously only two levels of Ni II have been considered in this calculation [30]. To take into account all the Ni II levels populated by ACT, as observed in our experiments (see Fig. 5), we extrapolate the \( G(\Delta) \) function linearly up to energy difference of \( \Delta = 1.6 \) eV (blue dashed line). This energy range covers 19 levels of Ni II that can contribute to the charge transfer. Using Eq. (6) and obtaining \( G_n \) for \( N = 19 \) levels, we obtain a rate coefficient

\[
k_{\text{CT}} = 1.8 \times 10^{-8} \text{ cm}^3 \text{s}^{-1},
\]

which is in very good agreement with the measured value \( k_{\text{CT}} = 2.3 (\pm 0.9) \times 10^{-8} \text{ cm}^3 \text{s}^{-1} \).

4. Summary

We have carried out spectroscopic measurements in the afterglow of pulsed glow discharges in Ar and in He–Ar mixtures to investigate elementary processes between \( \text{Ar}^+ \) ions and Ni atoms. Numerous Ni II lines showed an efficient pumping by asymmetric charge transfer (ACT) reactions. The rate coefficient for the \( \text{Ar}^+ (2p_{3/2}) + \text{Ni I} \) reaction was determined to be \( k_{\text{ACT}} = 2.3 (\pm 0.9) \times 10^{-9} \text{ cm}^3 \text{s}^{-1} \), for room temperature, \( T = 300 \) K, conditions. This rate coefficient is about an order of magnitude higher than the rate of Penning ionization, making the ACT process an important ionization channel for certain discharge conditions. The measurements concerning the \( \text{Ar}^+ (2p_{3/2}) + \text{Ni I} \) reaction allowed us to give an upper bound for the reaction rate only, \( k_{\text{CT}} < 3.3 (\pm 1.6) \times 10^{-8} \text{ cm}^3 \text{s}^{-1} \), due to the presence of quenching processes. For the rate of the superelastic scattering of electrons with \( \text{Ar}^+ (2p_{3/2}) \) ions we also obtained an upper bound for the reaction rate, \( k_{\text{CT}} < 1.3 (\pm 0.8) \times 10^{-9} \text{ cm}^3 \text{s}^{-1} \).

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