Investigation of the interactions of long-lived excited atoms in the afterglow of gas discharge plasma

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Abstract. When an electric discharge is fired in a gas consisting of atoms or molecules with long-lived excited states there are several inelastic processes releasing fast electrons in the afterglow plasma after the end of the current pulse. Most common among them are the chemi-ionization and de-excitation electron–atom collisions. Here these processes are investigated by measurements of the reactant particle densities at the entrance and at the exit channels of the reactions. In this way the rate coefficients of the ionising collisions of the couples Ne 3P2−Ne 3P2, Ar 3P2−Ar 3P2, Kr 3P2−Kr 3P2, Xe 3P2−Xe 3P2 as well as the rate coefficients for chemi-ionization of the ground state mercury atoms by collision with Ne 3P2 and Ar 4P2 atoms were obtained. By similar measurements the rate coefficients for super elastic collisions between electrons and excited heavy rare gases atoms as well as mercury atoms in the electron temperature range 500 – 2000 K were obtained. By monitoring the decay of the excited atom’s density and electron’s density and temperature the rate coefficients of electron impact induced transfer of excitation between the levels of configuration np(n+1)s in Ne, Kr and Xe were determined. In the same way were derived the rate coefficients of the transfer of excitation between Cd 6P2,0 levels induced by collisions with ground state cadmium and neon atoms. The diffusion coefficients of magnesium atoms in rare gases and their reflection coefficients from the vessel metallic wall are determined. Besides, the diffusion coefficients of metastable Cd 6P2,0 atoms in neon are also determined.

Key words: afterglow plasma, metastable atoms, rate coefficients, chemi-ionization, superelastic collisions, level mixing, diffusion, reflection from wall

1. Introduction.
The data for rate coefficients of various plasma particle interactions are scarce and insufficient in the literature. Despite the large quantity of results obtained so far many more investigations are required in order to have a more or less complete database for these coefficients since they are of vital importance for the modeling of plasma used in different devices. Especially interesting for the numerous applications such as light sources, gas lasers, spectro-chemical analyses, etc. are the properties of the...
long-lived excited atoms and molecules. For example it is difficult to imagine the present day laser physics without metastable atoms. That is why so many works in the literature are dedicated to measurements and calculations of the cross sections and rate coefficients of the inelastic interactions in which these excited species take part. Two main types of experiments are used for this aim: beam methods and afterglow plasma methods. Both types of investigations have specific advantages and drawbacks as well and a specific area of application. Thus it is quite difficult to accomplish an experiment with two crossing beams of excited atoms. Therefore it is not easy to obtain results for ionizing collisions between two excited particles by the conventional beam method of Penning electron spectroscopy while this is possible in the decaying plasma due to the substantial density of such atoms and molecules existing in the afterglow phase. Another example is the collisional transfer of excitation between the energy sublevels of one electron configuration – so called “level mixing” where the afterglow plasma methods are superior due to the small energy gap between the levels. Since this reaction is predominantly responsible for the creation of the so called “block” or “lumped states” the adequate description of respective plasma media needs correct values of the rate coefficients for “mixing”. At low pressures the main losses of the particles are due to the diffusion. Therefore the diffusion coefficients both of excited and of normal atoms are also quite important for the plasma models. The present work briefly describes the experimental methods used and the results of determination of the above-mentioned rate coefficients by measurements in the afterglow plasma.

2. Investigation of the fast electrons appearing in the afterglow plasma.

2.1. Theoretical consideration
After the switching off of the field sustaining the plasma a rapid relaxation of the electron energy is going on. In a few tens of microseconds the electron energy distribution (EED) becomes a Maxwellian one with an average temperature of 0.1 eV. It was mentioned in the introduction that the fast electrons arise in the decay of the low temperature plasma in reactions involving excited atoms such as:

\[ A^* + A^* \rightarrow A^+ + A + e(\varepsilon_p), \]  

\[ A^* + A^* \rightarrow A^* + e(\varepsilon_p) \]  

\[ A^* + B \rightarrow A + B^* + e(\varepsilon_p) \]  

\[ A^* + e \rightarrow A + e(\varepsilon_1), \]  

Here A and B are reacting atoms, \( \varepsilon_p \) and \( \varepsilon_1 \) are the energies acquired by the fast electrons in Penning or associative ionization or in superelastic collisions. The fast electron density is several orders of magnitude less than the density of the bulk electrons. However it turns out that in some cases it is possible to detect their distribution [1]. In order to make it clear we will discuss the kinetic problem.

The electron Boltzmann equation for the fast part of the energy distribution should take into account the sources, losses and relaxation of the fast electrons. This equation for the isotropic part of the distribution, \( f_0(\varepsilon, r) \) at energies \( \varepsilon >> kT_e \), in the cylinder coordinate system is [2]:

\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r v \frac{\partial f_0}{\partial \varepsilon} \right) + \frac{\partial}{\partial \varepsilon} \left( D_\varepsilon \frac{\partial f_0}{\partial \varepsilon} + V_\varepsilon f_0 \right) + \beta_\varepsilon N_e N_m R_\varepsilon(w) v + \beta_m N_m^2 R_m(w) v = 0
\]  

(5)

In this expression \( D_\varepsilon = \lambda_e \varepsilon / 3 \) is the coefficient of free diffusion of an electron, \( D_\varepsilon \) and \( V_\varepsilon \) are the diffusion and friction coefficients in the energy space, \( \varepsilon = \varepsilon \varphi(r) + w \) is the total energy, \( \varphi(r) \) being the radial potential, \( R(w) \) is the energy spectra of the appearing electrons in reactions (1) – (4), \( N_m \) and \( N_e \) are the densities of the excited atoms and the slow electrons respectively.

The boundary condition of EED on the tube wall, \( r = R \) at energies \( \varepsilon >> kT_e \) in the cylinder coordinate system is [2]:

\[
f_0(\varepsilon, R) = 0
\]  

The function \( f_0(\varepsilon, r) \) is very sensitive from the relaxation parameter:

\[
K(\varepsilon) = (v_0 + \delta v_0) \tau_{df},
\]  

(6)

where \( \tau_{df} = \Lambda^J / D_\varepsilon \) is the time for a free diffusion of an electron, \( \Lambda \) and \( v_0 \) and \( v_\varepsilon \) are the frequencies of the elastic electron-atom and electron-electron collisions, \( \delta = 2 m_e / M_a \).
At $K(\varepsilon) >> 1$ the energy distribution is in the form of “steps”, while at $K(\varepsilon) < 1$, the relaxation processes are weak and the appearing electrons go to the tube walls without substantial changes of their energy. In this case the EED reproduces the initial energy spectra of electrons appearing from the reactions (1) – (4). That is why the recording of the electron energy distribution in similar conditions was called plasma electron spectroscopy [3]. So if we integrate the kinetic equation within the energy intervals where fast electrons appear, the second term in the equation is cancelled. The next integration by $r$, using the boundary conditions for the density $S_e$ of the fast electrons

$$\frac{dS_e}{dr} |_{r=0} = 0; S_e (R) = 0,$$

gives immediately

$$S_e^0 (r) = \frac{\beta_j}{D_e (w)} \int_0^r N_m (r^*) N_j (r^*) r^* dr^*.$$

(7)

It is seen from this expression that in order to determine the respective rate coefficients $\beta_j$ it is necessary:

- to find $S_e^0$ from the measurements of the EED at the tube axis in the absolute scale;
- to calculate the free diffusion coefficients $D_e (w)$ of the fast electrons;
- to measure the radial profile of the densities of excited atoms and slow electrons.

2.2. Experimental methods

2.2.1. Determination of electron energy distribution.

The measurements of EED in the decay plasma are based on the well known Dryuvestein relation. $I''$ is derived by probe current modulation.

$$f (\varepsilon) |_{\varepsilon=U} = \frac{m^2}{2\pi e} \frac{d^2 I_e}{dU^2}; \quad I_e = I_e (U + \Delta U),$$

(8)

where $S$ is the probe area, $U$ is the probe bias potential with respect to the plasma potential, $\Delta U$ is a small alternative addenda, $I_e$ is the electron probe current. In this work $\Delta U$ were used as modulation signals:

$$\Delta U = 2U \cos \omega t \Delta U_0 = \sqrt{2} U_0 (1 + \sin \Omega t) \sin \omega t.$$

(9)

The output signal on the exit of the selective filter is [4]:

$$I_{2\omega, \Omega} = U_0^2 \int_0^\infty \left[ I'' (U') A_{1,2} (U, U') dU' \right] \equiv U_0^2 \left[ I'' * A_{1,2} \right].$$

(10)

Here $A_{1,2}$ are the corresponding instrumental functions of the modulation method chosen.

Figure 1. Experimental setup.
Figure 1 presents schematically the whole setup with the optical and probe measuring devices. Similar setups have been in use for a long period [3]. The master generator imposes triggering pulses to other units controlling in this way the operation of the whole system. Usually the afterglow plasma is created by DC pulses with a duration of several tens of µs with a repetition rate of several KHz. In the case of diffusion studies of ground magnesium atoms the pulses are several ms and the repetition rate is in the 0.1 – 10 Hz range. At present computer based schemes are employed [5] The fast part of the EEDF shown bellow is recorded with such equipment.

![Figure 2](image_url)

**Figure 2.** EED in the decay plasma of hollow cathode discharge in He (p= 0.25 Torr). Pulse current 100 mA; repetition rate 2.2 kHz; delay 70 µs; modulating signal \( \Delta U_1 = 0.37 \cos vt \) (V)

It is seen that in this energy spectrum the contributions of the different chemi-ionization reactions: \( \text{He}_2^{2}S_1 + \text{He}_2^{3}S_1 \); \( \text{He}_2^{2}S_1 + \text{He}_2^{3}S_0 \) and \( \text{He}_2^{2}S_0 + \text{He}_2^{3}S_0 \) are separated in the energy range 14eV – 16eV. It is expedient to introduce the energy resolving power of the probe measurements: \( \text{Res} = \varepsilon / \delta \varepsilon \), where \( \delta \varepsilon \) is the Rayleigh limit of the energy resolution between two mono energetic EED. The half width of the electron lines obtained in our experiments is ~ 0.7 eV. The maximum appearing in the chemi-ionization of \( \text{N}_2 \) by \( \text{He}(2^3S_1) \) has a width ~ 0.5 eV (see [3]). Therefore the resolution of the plasma electron spectroscopy method at present is about 30. It is known that the experimental EED is a convolution of the real distribution and the instrumental function [4]. The distortion of the real distribution cannot be minimized since the output signal is proportional to the square of the modulating signal voltage. For this reason the integral equation (relation (10)) connecting the experimental EDF, the corresponding instrumental function and the real distribution should be worked out when a better energy resolution is required. Such an example is shown on figure 3. The time resolution of the method (2 –3 µs) [6], determines the possible excited species which can be examined by this technique. Besides metastable states these can be radiative states with optical transitions to the ground or other heavily populated levels. In this case the trapping of radiation will create a high enough effective life time of these ensembles to allow the measurements. Another possibility, not yet tried, is to create (for example by laser) an excessive density of a radiative level in the afterglow plasma and to investigate its decay via channels (1) – (4) by this method.

The electron temperature was determined from the curve of the probe current second derivative \( I_e'' \), measured in the range 0.3 – 1.5 eV. At that the systematic error in \( T_e \) value did not exceed 10 per cent.

The electron density \( N_e \) in decay plasma was determined by the plasma conductivity measurement. Two versions of the method were used: 1. In a chosen moment of the afterglow period an additional
weak pulse is applied on the discharge tube electrodes [7]. The conductivity is measured during the
time of pulse action. 2. The conductivity and therefore the plasma density is measured in the discharge
active phase and then a calculation of the \( N_e(t) \) evolution in the afterglow is completed. The accuracy
of \( N_e \) determination by the last method is about 30 per cent.

The excited atom’s density is measured in the decaying plasma by a standard absorption method.
The errors of this method are in the range between 15 – 30 % depending on the examined atoms. The
main contribution in this error come from the uncertainties of the oscillators strength values.

3. Experimental results.

3.1. Chemi-ionization in heavy rare gases

Comparing the results of measurements of the densities of the reactants and products of the
processes (1) – (4) the corresponding rate coefficients can be determined. Below are presented the
results for the binary symmetric collisions of the np\(^5\)(n+1)s\(^3\)P\(_2\) metastable states in heavy rare gases.
This state is most heavily populated in the afterglow plasma, therefore the data obtained have minimal
error. Besides these results in works [8] – [10] are shown the rate coefficients values of interactions
with participation of \(^3\)P\(_0\) and \(^3\)P\(_1\) states. It should be noted that at such chemi-ionization collision a
strong interaction occurs between the two excited particles. The ionization probability is near unity
when the particles come close to each other. The close collision is the main type of interaction.
Therefore these experimental data have to be compared with the close collision rate constants.

| Reaction       | \( \beta_{m2} \) (10\(^{-9}\) cm\(^3\)s\(^{-1}\)) | \( K_m \) (10\(^{-9}\) cm\(^3\)s\(^{-1}\)) | \( \sigma_{exp} \) (10\(^{-15}\) cm\(^2\)) | \( \sigma_{cc} \) (10\(^{-15}\) cm\(^2\)) |
|----------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Ne\(^3\)P\(_2\) + Ne\(^3\)P\(_2\) | 0.38±0.04 | 0.86 | 4.8±0.5 | 10.8 |
| Ar\(^3\)P\(_2\) + Ar\(^3\)P\(_2\) | 1.2±0.2 | 0.81 | 22±4 | 14.4 |
| Kr\(^3\)P\(_2\) + Kr\(^3\)P\(_2\) | 1.1±0.2 | 0.52 | 29±5 | 13.5 |
| Xe\(^3\)P\(_2\) + Xe\(^3\)P\(_2\) | 0.78±0.2 | 0.48 | 23±7 | 15.4 |

Figure 3. Fast part of the electron energy distribution in the afterglow of Ne-Hg discharge
3.2. Mercury.

The chemi-ionization reactions of the ground state mercury atoms by the excited neon Ne \(^3\text{P}_2\) and argon Ar \(^3\text{P}_{2,1,0}\) atoms are investigated. The ionizing collision \(\text{Ne}^{3\text{P}_2} + \text{Hg}^{1\text{S}_0}\) is examined both by the PES method and by studying the variation of the excited atom's density in the afterglow plasma [11]. Figure 3 shows the EED fast part in the decay of a Ne–Hg discharge.

The maximum around 5.3 eV is due to the superelastic electron – Hg \(^3\text{P}_2\) collisions, the maximum at 6.2 eV is due to the Penning ionization of the ground Hg atom by the metastable Ne atom, while the unresolved feature at 6.7 eV can be connected with the associative ionization of the type \(\text{Ne}^{3\text{P}_2} + \text{Hg}^{1\text{S}_0} \rightarrow \text{NeHg}^+ + e\). The solid line is the recovered curve by a deconvolution. The method of kinetic spectroscopy was also used for the Ne–Hg study. The balance equation of the Ne \(^3\text{P}_2\) atoms includes diffusion and chemi-ionization processes. The results of both methods are summarized in Table 2. In the case of Ar – Hg plasma the appearing fast electrons have too low energy. Their contribution is masked by the huge bulk electron peak. In this case the decay of Ar \(^3\text{P}_{2,1,0}\) states are used [12].

### Table 2. Chemi-ionization rate coefficients of mercury atoms by excited Ne \(^3\text{P}_2\) and Ar \(^3\text{P}_{2,1,0}\) atoms; The values without marks are obtained in this work; the values obtained by other authors are denoted.

| Reaction              | \(\beta_{\text{em}}\) \(\times 10^{-10} \text{cm}^3\text{s}^{-1}\) | \(K_{\text{calc}}\) \(\times 10^{-10} \text{cm}^3\text{s}^{-1}\) | \(\sigma_{\text{exp}}\) \(\times 10^{-15} \text{cm}^2\) | \(\sigma_{\text{cc}}\) \(\times 10^{-15} \text{cm}^2\) |
|-----------------------|-------------------------------------------------|---------------------------------|-----------------|-----------------|
| Ne\(^3\text{P}_2\) + Hg \(^1\text{S}_0\) | \(~5\)                                            | 42                              | 8.44            | 15.9            |
|                       | 4.11 [13]                                         | 47 [14]                         | 6.97 [13]       | 15.4 [13]       |
| Ar\(^3\text{P}_2\) + Hg \(^1\text{S}_0\) | 4.3 ± 1.4                                         | 8.16                            | 9.8 ± 3.5       | 18.65           |
|                       | 8.49 [13]                                         | 2.19 [14]                       | 19.4 [13]       | 17.4 [13]       |
| Ar\(^3\text{P}_1\) + Hg \(^1\text{S}_0\) | 4.5 ± 1.6                                         | 8.5                             | 10.3±3.6        | 19.43           |
|                       | 8.49 [13]                                         | 1.24 *                          | 2.84 *          |
| *Ar\(^3\text{P}_0\) + Hg \(^1\text{S}_0\) | 8.4 ± 2.8                                         | 8.04                            | 19.2±6.7        | 18.37           |
|                       | 9.56 [13]                                         | 21.9                            |                 |

*The values marked with * are calculated by the photoionization cross section.*

3.3. Super elastic collisions

The same method was used to determine the rate coefficients of the collisions between slow electrons and excited atoms of the heavy rare gases and mercury as well. The small decrease of \(\beta_{\text{em}}\) of Kr and Xe with the rising of the electron temperature can be seen in [2] and [3].

### Table 3. Rate coefficients of superelastic electron–atom collisions

| Reaction              | \(\beta_{\text{em}}\) \(\times 10^{-10} \text{cm}^3\text{s}^{-1}\) | \(T_e\) range (K) |
|-----------------------|-------------------------------------------------|-------------------|
| Ne\(^3\text{P}_2\) + e | 2.7 ± 0.5                                         | 470 – 1600        |
| Ar\(^3\text{P}_2\) + e | 2.8 ± 0.8                                         | 800 – 2800        |
| Kr\(^3\text{P}_2\) + e | 3.4 ± 0.5                                         | 600 – 2500        |
| Xe\(^3\text{P}_2\) + e | 7 ± 2                                             | 600 – 2500        |
| Hg\(^3\text{P}_2\) + e | 290 ± 120                                         | 2000              |

3.4. Impact transfer of excitation.

3.4.1. Transfer of excitation by electron collisions: \(A_i^+ + e \rightarrow A_i^+ + e\)

We studied the electron impact transfer of excitation between the fine structure levels (denoted by \(i\) and \(j\)) of the first excited electron configuration in Ne, Kr and Xe. The rate coefficients are derived by monitoring the decay of the particle densities and solving the balance equations of the respective levels in the afterglow plasma. This method is a variation of so called kinetic spectroscopy. The
balance equations, corresponding to our experimental conditions take into account diffusion losses, transfer of excitation by electron impact as well as by two body and tree body atom-atom collisions. The balance of the resonance level includes radiation losses. In these balance equations we use the measured density of the excited levels and the respective electron temperature and density curves. The solution of the equation system of the connected balances yields the rate coefficients of the transfer of excitation. The table below presents the results for heavy rare atoms. The specific way of measurements and processing of the experimental data used are given in the work [16] dedicated to study in neon.

**Table 4.** Rate coefficients for transfer of excitation between the metastable and resonance states in the heavy rare gases and cadmium atoms by electron impact obtained in this work and by other authors.

| Transition                   | $\beta_{ij} \times 10^{-8}$ cm$^3$ s$^{-1}$ | $T_e$ (K) | Authors          |
|-----------------------------|--------------------------------------------|-----------|-----------------|
| Ne$^3$P$_2 \rightarrow$ 3P$_1$ | 12.5 exp(-602/T$_e$)                        | 400 – 4000 | this work       |
| Ne$^3$P$_2$ quenching       | 27.7 exp(-602/T$_e$)(348/T$_e$)$^{0.3}$    | 400 – 14000| Ivanov [25]     |
| Ne$^3$P$_2 \rightarrow$ 3P$_0$ | 3 – 47                                      | 600 – 6000| Bochkova [17]   |
| Ne$^3$P$_2 \rightarrow$ 3P$_0$ | 1.7 exp(-1121/T$_e$)                        | 400 – 4000 | this work       |
| Ne$^3$P$_1 \rightarrow$ 3P$_0$ | 0.82 exp(-1117/T$_e$)                       | 400 – 14000| Ivanov [25]     |
| Ne$^3$P$_1$ quenching       | 4.4 exp(-519/T$_e$)                         | 400 – 4000 | this work       |
| Ne$^3$P$_1 \rightarrow$ 3P$_2$ | 13.2                                        | 400 – 4000 | this work       |
| Ne$^3$P$_1 \rightarrow$ 3P$_2$ | 20.8                                        | 400 – 4000 | this work       |
| Ne$^3$P$_0 \rightarrow$ 3P$_2$ | 8.5                                         | 400 – 4000 | this work       |
| Ne$^3$P$_0 \rightarrow$ 3P$_1$ | 5.6 – 20                                    | 600 – 6000 | Bochkova [17]   |
| Ne$^3$P$_0 \rightarrow$ 3P$_1$ | ~ 100                                       | 400 – 4000 | Phelps [19]     |
| Ne$^3$P$_0 \rightarrow$ 1P$_1$ | 13.2                                        | 600 – 6000 | this work       |
| Ne$^3$P$_0 \rightarrow$ 1P$_1$ | 23 exp(-1543/T$_e$)                         | 400 – 14000| Ivanov [25]     |
| Ar$^3$P$_2 \rightarrow$ 3P$_1$ | 29.7$\cdot$-0.4$\cdot$exp(870/T$_e$)       | 500 – 3000 | Baranov [21]    |
| Ar$^3$P$_0 \rightarrow$ 1P$_1$ | 2970$\cdot$-0.54$\cdot$exp(-1280/T$_e$)     | 500 – 3000 | Baranov [21]    |
| Kr$^3$P$_2 \rightarrow$ 3P$_1$ | 420$\cdot$-0.5$\cdot$exp(-1360/T$_e$)       | 700 – 4500 | this work       |
| Kr$^3$P$_0 \rightarrow$ 3P$_1$ | 5.56$\cdot$exp(-943/T$_e$)                  | 700 – 4500 | Andreev [20]    |
| Kr$^3$P$_0 \rightarrow$ 3P$_1$ | 4.1$\cdot$exp(-1407/T$_e$)                  | 700 – 4500 | Andreev [20]    |
| Xe$^3$P$_2 \rightarrow$ 3P$_1$ | 3.1$\cdot$exp(-1442/T$_e$)                  | 900 – 5500 | this work       |
| Xe$^3$P$_0 \rightarrow$ 1P$_1$ | 3.0$\cdot$exp(-1447/T$_e$)                  | 900 – 5500 | this work       |
| Cd$^3$P$_1 \rightarrow$ 3P$_0$ | 20                                          |            | this work       |
| Cd$^3$P$_0$ \rightarrow$ 3P$_1$ | 30                                          |            | this work       |
In the work [26] the measured cross section for Ar $^3\text{P}_2 \rightarrow ^3\text{P}_1$ transition induced by electron impact is given. The approximation of the experimental points is in the form:

$$\sigma(u) = 4.1 \times 10^{-14} \text{ cm}^2 \frac{u}{u + 2.1} \sqrt{u + 1},$$

where $u = \varepsilon/0.07$; The energy $\varepsilon$ is in eV.

### 3.4.2. Transfer of excitation by atomic collisions $\Lambda^+_i + B \rightarrow \Lambda^+_j + B$

The transitions within the excited electron configuration Cd $5s5p$ by collision with ground state Ne and Cd atoms were studied [27].

The well known expression [15] was used to fit the experimental decay rates of the Cd $^5\text{P}_{2,1,0}$ densities versus the densities of the buffer gas Ne atoms. The variation of the cadmium ground state was accomplished by changing the temperature of the tube.

$$\gamma_2 = \frac{D_{2\exp}}{\Lambda^2} + \beta_{Ne} N_{Ne} + \beta_{Cd} N_{Cd} + v_e$$  \hspace{1cm} (11)

The first term of the right-hand side of the equation gives diffusion losses, the next two terms account for the level mixing by neon and cadmium atom collisions, while the term $v_e$ takes into account other losses. The results derived by solving the system of balance equations are shown below in Table 5.

![Experimental decay rates of the Cd $^5\text{P}_2$ density versus the density of the neon atoms](image)

**Figure 4.** Experimental decay rates of the Cd $^5\text{P}_2$ density versus the density of the neon atoms

### 3.5. Diffusion of metal atoms in rare gases.

#### 3.5.1. Diffusion of cadmium metastable atoms Cd $^5\text{P}_{2,0}$

The decay curves of Cd $5\text{P}2,0$ give the results for the diffusion coefficients of the metastable atoms besides the rate coefficients for excitation transfer listed above.

Temperature dependencies of the diffusion coefficients of Cd $^5\text{P}_2$ and Cd $^5\text{P}_0$ atoms in the range $515 - 568$ K are as follows: $D(\text{P}_2) = (2.1 \pm 0.6). (T/7780)^{1.75} \text{ cm}^2 \text{ s}^{-1}$; $D(\text{P}_0) = (2.2 \pm 0.7). (T/7780)^{1.75} \text{ cm}^2 \text{ s}^{-1}$
3.5.2. Diffusion of magnesium ground-state atoms in rare gases

The diffusion problem can be more complicated if a considerable part of the particles are reflected from the wall. This affects the observed stationary volume density or density decay rate. The reflection coefficients are usually unknown, but they can be measured, or their influence estimated. We use an approach for simultaneous determination of the diffusion coefficients of various species in buffer gases and their reflection coefficients at the container walls. It is based on comparison of the volume density decay rates, measured for various buffer gas pressures, with solutions of the diffusion problem implementing an appropriate boundary condition [31]. Usually this is a boundary condition of the third kind, which depends on both parameters: the diffusion and reflection coefficients.

Table 5. Our results are compared with the data published in [28], [29] and calculations [30]

| Transition | $\beta_s \times 10^{14} \text{ cm}^2 \text{s}^{-1}$ | $T_s$ (K) | $\sigma_{\text{exp}} \times 10^{19} \text{ cm}^2$ |
|------------|---------------------------------|----------|-------------------------------|
| $\text{Cd} \ ^3P_0 + \text{Ne} \ ^1S_0 \rightarrow \text{Cd} \ ^3P_1 + \text{Ne}$ | $(3.2 \pm 1)$ | $515 - 570$ | $(3.9 \pm 1.4)$ |
| $\text{Cd} \ ^3P_1 + \text{Ne} \ ^1S_0 \rightarrow \text{Cd} \ ^3P_0 + \text{Ne}$ | $(4.5 \pm 1.3)$ | $515 - 570$ | $(5.5 \pm 1)$ |
| $\text{Cd} \ ^3P_1 + \text{other rare gases atoms}$ | $\sim 1$ | $515 - 570$ | $0.3$ [28] |
| $\text{Cd} \ ^3P_2 + \text{Ne} \ ^1S_0 \rightarrow \text{Cd} \ ^3P_{1,0} + \text{Ne}$ | $(4.3 \pm 1.6)$ | $515 - 570$ | $(5.2 \pm 1.8)$ |
| $\text{Cd} \ ^3P_0 + \text{Cd} \ ^1S_0 \rightarrow \text{Cd} \ ^3P_1 + \text{Cd} \ ^1S_0$ | $(1.8 \pm 0.7) \times 10^3$ | $515 - 570$ | $(3.9 \pm 1.4) \times 10^3$ |
| $\text{Cd} \ ^3P_1 + \text{Cd} \ ^1S_0 \rightarrow \text{Cd} \ ^3P_0 + \text{Cd} \ ^1S_0$ | $(2.6 \pm 0.9)$ | $515 - 570$ | $(3.9 \pm 1.4)$; $(3 \pm 2)$ [29]; $9.4$ [30] |
| $\text{Cd} \ ^3P_2 + \text{Cd} \ ^1S_0 \rightarrow \text{Cd} \ ^3P_{1,0} + \text{Cd} \ ^1S_0$ | $(7.8 \pm 2.7)$ | $515 - 570$ | $(5.5 \pm 1.9)$ |

Figure 5. Decay curves of ground-state Mg atoms' density in krypton as a buffer gas at 297 K temperature for three gas pressures: 1, 0.25 Torr; 2, 0.6 Torr; 3, 1.2 Torr.

Figure 6. Graphical method for simultaneous determination of the diffusion and reflection coefficients based on experimental diffusion lifetimes determined from the decays given in Figure 5.
Table 6. Diffusion coefficients of ground-state Mg atoms in rare gases and their reflection coefficients at the surface of a magnesium cathode

| Buffer gas | Diffusion coefficient at 1 Torr pressure, $D_0$ (cm$^2$s$^{-1}$) | Reflection coefficient, $R$ |
|------------|-------------------------------------------------|-------------------------|
| $^3$He     | $390 \pm 60/50$ (at T=295K)                      | $[0; 0.9]$              |
| $^4$He     | $340 \pm 27$ (at T=300K)                        | —                      |
| Ne         | $185 \pm 20$ (at T=300K)                        | $0.82_{-0.27}^{+0.08}$ |
| Ar         | $155 \pm 22$ (at T=300K)                        | $0.78_{-0.28}^{+0.08}$ |
| Kr         | $98 \pm 15$ (at T=297K)                         | $[0; 0.9]$              |

References

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