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THE 6s5d $^1D_2 \rightarrow$ 6s5d ^3D_J EXCITATION ENERGY TRANSFER IN BARIUM INDUCED BY COLLISIONS WITH He, Ar AND Xe ATOMS

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Dedicated to Professor Mladen Paić on the occasion of his 90$^{\mathrm{th}}$ birthday

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The cross sections for the Ba 6s5d $^1D_2 \rightarrow$ 6s5d ^3D_J excitation energy transfer, induced by collisions with He, Ar and Xe, were measured using laser absorption and fluorescence methods in the steady-state regime. The populations of the barium metastable 6s5d $^1D_2$ and Ba 6s5d ^3D_J states were created by subsequent radiative and collisional relaxation of the optically excited 6s6p $^3P_1^0$ level. The four-level model, comprising 6s^2 $^1S_0$, 6s6p $^3P_1^0$, 6s5d $^1D_2$ and 6s5d ^3D_J states, is proposed for the description of the population and depopulation processes of the Ba metastable states in noble gas atmosphere. The analysis of the experimental results, within the assumed model, yields the following cross-section values for the investigated processes: $\sigma_{\mathrm{He}} = 1.5 \times 10^{-20}$ m^2, $\sigma_{\mathrm{Ar}} = 2 \times 10^{-22}$ m^2 and $\sigma_{\mathrm{Xe}} = 8 \times 10^{-21}$ m^2, with an accuracy of $\pm 50\%$.

1. Introduction

During the last decade, the excitation energy transfer in barium occurring due to collisions with noble gas atoms was studied extensively. Because of its unique electronic configuration, barium represents a very interesting and instructive subject for investigation of collisional processes. The first excited states in barium are the 6s5d $^1D_2$ and 6s5d ^3D_J metastable states which are characterized by extremely long radiative lifetimes, because their radiative relaxation to the ground state is dipole forbidden and they are of the same parity as the ground $6s^2$ $^1S_0$ state. The reported calculated radiative lifetime values of barium metastable levels [1] are in the range of seconds.

The barium metastable states can be populated by optical excitation of the higher lying states and their subsequent radiative relaxation. If barium atoms undergo collisions, the relaxation of the higher–lying states is collisionally enhanced, and the population of the metastable levels can be very efficient. In this manner, as shown in Ref. 2, a very large fraction of the ground state barium atoms can be transferred into the metastable states, making the barium vapours act as a storage of excitation energy.

Recently, collisions involving barium 6s5d $^1D_2$ and 6s5d ^3D_J metastables in noble gas atmosphere have been studied using two different techniques, the tunable pulsed laser excitation with time–resolved analysis [3] and the steady state measurements with tunable cw lasers [4]. Regarding particularly the 6s5d $^1D_2 \rightarrow$ 6s5d ^3D_J excitation energy transfer, in Ref. 3 the results are given for He, Ar and Xe as perturbers while in Ref. 4 the extensive quantitative study has been done only for Ar. For argon as a perturber, the results of these two experiments are in good mutual agreement. Nevertheless, neither of these experiments confirms the results of the previous investigations [5,6] of the same processes.

Here we present a new approach for quantitative analysis of the measurements performed with He, Ar and Xe perturbers, within a model based upon the recent findings [3,4] on the properties of the collisional mixing between Ba metastable levels.

2. *Experiment*

The schematic diagram of the experimental set–up is shown in Fig. 1. The barium metal was contained in the three-arm stainless–steel cell filled with He, Ar or Xe as the buffer gas. The cell was resistively heated up to a temperature of about 750 K. The generated metal vapour was optically excited by a frequency stabilized, temperature and current tuned single–mode diode laser (Hitachi HL7851, maximum power: 50 mW). The frequency of the diode laser was adjusted to the center of the 791.3 nm intercombination line which corresponds to the $6s^2$ $^1S_0 \rightarrow$ 6s6p $^3P_1^0$ transition. After expansion and collimation, the diode laser beam passed a circular aperture (diameter: 2 mm) which cut its central part. Therefore, behind the aperture the beam had nearly homogeneous power distribution. The power of the beam was reduced using the neutral density filters and its value ranged up to maximum 300 μW. The absorption on the optical path $L \approx 5$ cm was measured simultaneously with the fluorescence from the centre of the 791.3 nm line.

The counter-propagating laser beam from a single–mode frequency–stabilized ring–dye laser (Spectra Physics 380D; dye: Rh6G) was shone through the zone excited by diode laser beam. The diameter of the dye laser beam was 1 mm and its power was reduced down to 5 μW in order to avoid optical saturation. The absorption of the dye laser beam, which was tuned to the frequencies corresponding to the 6s5d ^{3}D$_J$ $\rightarrow$ 5d6p ^{3}P^0_J or 6s5d ^{1}D$_2$ $\rightarrow$ 5d6p ^{1}P$^0_1$ transitions, was measured in order to determine the metastable 6s5d ^{3}D$_J$ and 6s5d ^{1}D$_2$ populations created by radiative transitions from the 6s6p ^{3}P$^0_1$ level, as well as collisions with noble gas atoms.

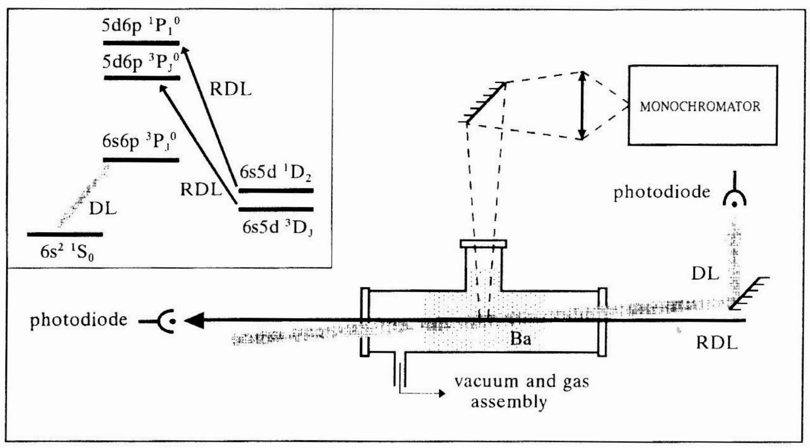


Fig. 1. Experimental set-up; DL: diode laser beam; RDL: ring-dye laser beam. The inset shows the partial term diagram of the barium, indicating the pumping step and the transitions used for probing the populations of the metastable 6s5d $^1D_2$ and 6s5d ^3D_J states.

The absorption of both diode laser and ring-dye laser beam was measured by photodiodes. The central part of the fluorescence zone was imaged onto the entrance slit of the 1 m McPherson monochromator (slit width: 500 μm; band width: 0.5 nm) and the fluorescence signals were detected by a RCA S20 photomultiplier.

3. Model

The excitation energy transfer processes between the lowest lying Ba levels, due to the collisions with noble gas atoms, in the case when the Ba 6s6p ^{3}P$^0_1$ state is optically excited, can be adequately described within a simple four–level model schematically illustrated in Fig. 2. The relevant spontaneous emission and collisional relaxation rates are denoted by A_{ij} and R_{ij}, respectively, where $i, j = g, p, s, t$. The subscripts g, p, s and t are the respective labels for the 6s^2 ^{1}S$_0$ ground state, 6s6p ^{3}P$^0_1$ state, the metastable singlet 6s5d ^{1}D$_2$ and triplet 6s5d ^{3}D$_J$ states, henceforth referred to as ^{1}S$_0$, ^{3}P$^0_1$, ^{1}D$_2$ and ^{3}D$_J$ states. The optical excitation rate is given by ρB_{gp}, where ρ is the power density of the laser beam and B is the Einstein absorption coefficient. The populations of the corresponding levels are denoted by N_i. In analogy with gas kinetics, the R_{ij} rates are defined as the product $N\sigma v$, where N is the number density of perturbers (noble gas) inducing the excitation transfer, σ is the cross section for the particular transfer process and v is the mean relative velocity of colliding atoms.

The $^3P_1^0$ level is radiatively depopulated due to the $^3P_1^0 \to {}^1S_0$ and $^3P_1^0 \to {}^3D_J$ transitions, representing the only allowed radiative transitions present in this model. Additionally, in the presence of a noble gas, the $^3P_1^0$ level is collisionally depopulated exclusively through the $^3P_1^0 \to {}^1D_2$ channel [3, 4]. The $^3P_1^0 \to {}^3D_J$ collisional process has not been observed and therefore it has been neglected in the present model.

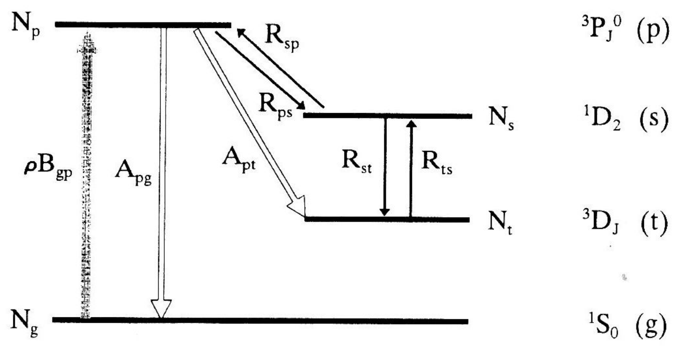


Fig. 2. Schematic diagram of the barium levels relevant for the model applied (see Section 3); ρB – pumping rate; A – spontaneous emission rates; R – collisional mixing rates; N – population density of the particular level; indices: g – ground state, p – optically excited state, s – singlet metastable state, t – triplet metastable state.

As mentioned in the Introduction the radiative lifetimes of the metastable states are very long. Thus the dominant mechanism for the depopulation of both the $^1D_2$ and ^3D_J states is collisional transfer. In the case of the $^1D_2$ state, it comprises the $^1D_2 \to {}^3P_1^0$ and $^1D_2 \to {}^3D_J$ channels, while the depopulation of the ^3D_J state is realized through the $^3D_J \to {}^1D_2$ channel. In general, both metastable levels are depopulated also by collisional transitions to the ground state, but these quenching processes were found [4] to be at least five orders of magnitude weaker in comparison with the ones mentioned. They have been neglected in the present analysis.

According to the presented model, we consider the balance between the population and depopulation processes within the excitation volume. Since the radiative lifetimes of the metastable barium atoms are very long, the diffusion of the metastable atoms out of the laser excitation volume should be taken into account, too. Under typical experimental conditions (noble gas pressures above 1 mbar = 100 Pa), the relaxation rates of Ba $^3P_1^0$ and $^1D_2$ states are considerably greater than the diffusion losses [4]. Therefore, the Ba $^3P_1^0$– and $^1D_2$–atoms are primarily confined within the laser excitation volume. On the other hand, collisional relaxation rates for ^3D_J atoms are of the same order of magnitude as the diffusion rates for Ba metastable atoms in a noble gas atmosphere [7]. As a consequence, when the depopulation rates of the ^3D_J level in excitation volume are considered, the diffusion effect should be included. Therefore, the steady–state rate equations for the p, s and t levels in the excitation zone are given by:

$$\frac{\mathrm{d}N_p}{\mathrm{d}t} = -(A_{pg} + A_{pt} + R_{ps})N_p + \rho B_{gp} N_g + R_{sp} N_s = 0 \tag{1}$$

$$\frac{\mathrm{d}N_s}{\mathrm{d}t} = -(R_{st} + R_{sp})N_s + R_{ps} N_p + R_{ts} N_t = 0 \tag{2}$$

$$\frac{\mathrm{d}N_t}{\mathrm{d}t} = -(R_{ts} + W_D)N_t + A_{pt} N_p + R_{st} N_s = 0. \tag{3}$$

The quantity W_D in the Eq. (3) is the removal rate caused by the diffusion of the ^3D_J atoms out of the excitation volume.

Using Eqs. (2) and (3) with the substitution $\chi = N_s/N_t$, the singlet–to–triplet collisional transfer rate R_{st} can be expressed as:

$$R_{st} = \frac{W_D(R_{ps}/A_{pt}) - \chi R_{sp}}{[1 + (R_{ps}/A_{pt})]\,[\chi - (R_{ts}/R_{st})]}. \tag{4}$$

The principle of the detailed balance requires the rates R_{ts} and R_{st} to be in the ratio $R_{ts}/R_{st} = g_s/g_t \exp[-\Delta E_{st}/kT]$ which, for the temperature in our experiment (750 K), yields $R_{ts}/R_{st} = 0.01$.

The fluorescence intensity I is proportional to the product $A_{pg}N_p$ and it can be expressed in the following way using Eqs. (1), (2) and (3):

$$I \sim A_{pg} \frac{\rho B_{gp}}{X - SR_{sp}Y + \rho B_{gp}(1+Y)} N_0. \tag{5}$$

Here $S = \chi/(1+\chi)$, $X = A_{pg} + A_{pt} + R_{ps}$, $Y = (A_{pt} + R_{ps})/(W_D T + R_{sp} S)$, $T = 1/(1+\chi)$ and the total barium atom number density is $N_0 = N_g + N_p + N_s + N_t$. Note that S and T represent the fractions of the singlet and triplet metastables with respect to the total number of atoms in the metastable complex $^1D_2$ + ^3D_J. The rate labelled with X is actually the total depopulation rate of the $^3P_1^0$ level while Y expresses the total population-to-depopulation rate ratio of the metastable complex $^1D_2$ + ^3D_J.

Applying Eq. (5) to the measured fluorescence intensities $I^{'}$ and $I^{''}$ obtained for two different pump power densities ρ' and ρ'', the diffusion removal rate W_D can be determined according to the relation:

$$W_D = \frac{1}{T}\left\{(A_{pt} + R_{ps})\frac{SR_{sp}(F-1) + \rho' B_{gp}[(\rho''/\rho') - F]}{X(F-1) - \rho' B_{gp}[(\rho''/\rho') - F]} - SR_{sp}\right\} \tag{6}$$

where $F = (I'/I'')(\rho''/\rho')$.

Since for a particular perturber number density the measurements yield the values for the quantities W_D and χ while the values for A_{pt}, σ_{ps} and σ_{sp} are known from the literature [4,8], Eq. (4) allows the determination of the collisional rate for the ^{1}D$_2 \to {}^3$D$_J$ excitation transfer process.

4. *Measurements and results*

In the course of the experiment, the power of the diode laser beam was changed to produce various ^{3}P$_1^0$ populations. For each power applied, the noble gas pressure was changed over a wide range and the populations of all states under consideration were probed.

The temperature of the barium vapour was determined by measuring barium ground state number density and using the vapour pressure curve [4]. The Ba ^{1}S$_0$ number density was evaluated from the absorption of the optically thin 791.3 nm line. In order to avoid the depletion of the ground state, the measurement was performed at low noble gas pressures and using a weak (5 μW) diode laser beam (for details see Ref. 4). The obtained value for Ba ground state number density was 1×10^{11} cm^{-3}, corresponding to the temperature $T = 750$ K.

Under the specific experimental conditions the profiles, of the measured barium lines were generally of the Voigt type, i.e., the convolution of a Gaussian (Doppler broadening) and a Lorentzian function (pressure and natural broadening). In this case, the absorption coefficient k_{ij}^0 in the center of $i \to j$ transition is given by the well–known expression:

$$k_{ij}^0 = N_i \frac{g_i}{g_j} \frac{\lambda_{ij}^3}{8\pi^{3/2}} A_{ij} \sqrt{\frac{M}{2kT}} H^0(a). \tag{7}$$

Here $H^0(a)$ is the Voigt function [9] for the line center with the parameter $a = \Gamma_\nu/(2\Delta\nu_D)$, where Γ_ν is the Lorentzian full-width-at-half-maximum and $\Delta\nu_D = (\nu_{ij}/c)(2kT/M)^{1/2}$ is the Doppler constant. The quantity Γ_ν is defined as the product of the perturber number density N and the broadening parameter γ_ν. For the barium lines of interest in this work, the noble gas pressure broadening parameters were taken from the literature [2,10] and the corresponding values for the $H^0(a)$ were calculated for each particular noble gas pressure. Since the temperature was known,the relevant number densities N_i were determined from the measured absorption coefficients.

In order to obtain the singlet-to-triplet ratio χ, the peak optical depths $k_{ij}^0 L$ of the 582.7 nm, 611.2 nm, 597.3 nm and 602.1 nm lines were measured. The 582.7 nm line corresponds to the ^{1}D$_2 \to$ 5d6p ^{1}P$_1^0$ transition and yields the data for the population N_s of the singlet metastable state, while the remaining lines (^{3}D$_J \to$ 5d6p ^{3}P$_J^0$ multiplet transitions) supply the data for the population N_t of the triplet metastable states. The values for the transition probabilities A_{ij} were taken from [11].

The dependence of the ratio χ on the buffer–gas pressure (Fig. 3), shows very different behaviour depending on the noble gas species. On the other hand, we found that χ does not depend on the pumping power.

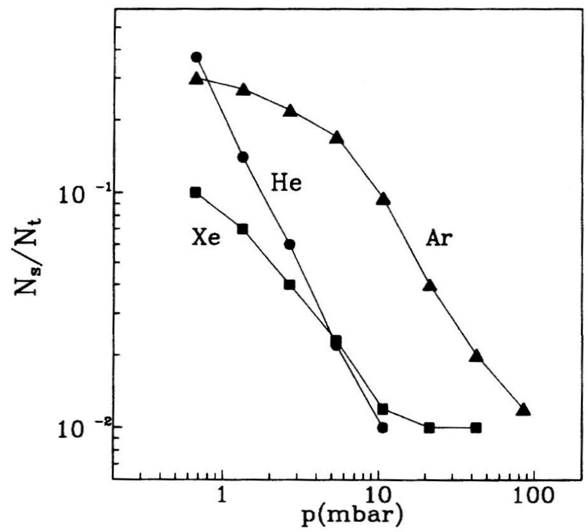


Fig. 3. The ratio of the singlet-to-triplet metastable number densities as a function of He, Ar *or* Xe *pressure.*

In order to determine the diffusion rates W_D the peak optical depth $K = k^0_{791.3}L$ and the peak fluorescence intensity I of the 791.3 nm line were measured as functions of the buffer gas pressure and the pump power. The results obtained for Xe are shown in Fig. 4. The data for He and Ar, not shown explicitly, exhibit similar behaviour. The optical depth K decreases with increasing pump power, indicating strong depletion of the ground state. The cause for this depletion is the transfer of the ground state atoms to the metastable states mainly through collisional relaxation of the $^3P^0_1$ level. The other possible reason for this depletion could be optical saturation. As shown below, this effect was negligible in our experiment.

The pump power ρB_{gp} of the laser beam having the power P and the cross section q can be calculated using the following expression:

$$\rho B_{gp} = \frac{1}{8\pi^{3/2}} \frac{\lambda^3_{gp} A_{pg}}{hc\Delta\nu_D} \frac{g_p}{g_g} \frac{P}{q} H^0(a). \tag{8}$$

With typical value $P = 100$ μW one obtains $\rho B_{gp} = 4H^0(a) \times 10^3$ s^{-1}. The value of $H^0(a)$ changes from 1 to 0.7 in the range of noble gas pressures covered by the measurements. Since $A_{pg} = 3 \times 10^5$ s^{-1}, the applied pump rates were always much smaller than the spontaneous emission rate, which means that the optical saturation was negligible.

The results for the W_D, evaluated according to Eq. (6), and plotted against noble gas pressure, are shown in Fig. 5 for He, Ar and Xe. In the evaluation of the W_D we used the χ data displayed in Fig. 3 and the respective fluorescence intensities (Fig. 4b), corrected for the corresponding absorption (Fig. 4a).

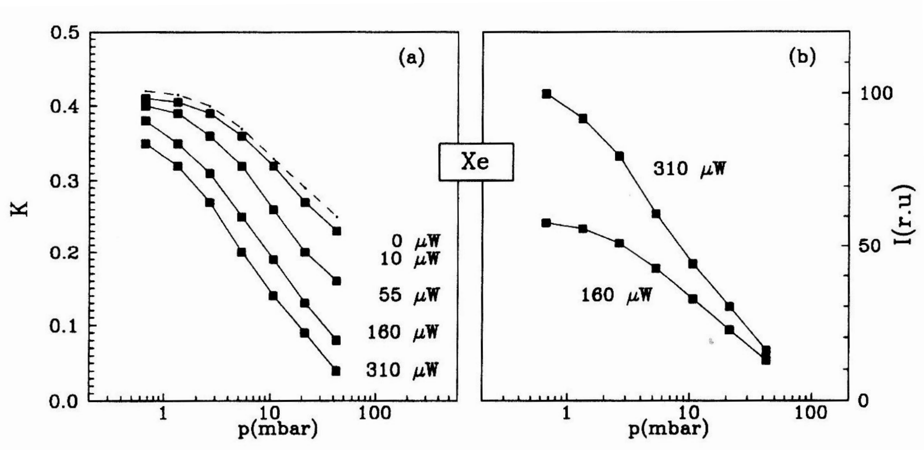


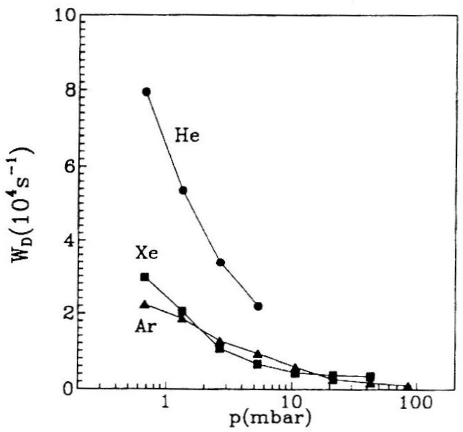
Fig. 4. (a) Plot of the optical depths $K = k^0_{791.3}L$ of the barium 791.3 nm line vs. xenon pressure in dependence on the laser beam power. The dashed line represents the extrapolation to zero power (1 bar = 10^5 Pa). (b) The relative fluorescence intensity of the barium 791.3 nm line as a function of the xenon pressure, obtained for the two different pumping powers.

TABLE 1.

Cross sections for the $^1D_2 \to {}^3D_J$ excitation transfer in barium induced by collisions with noble gases, compared to other investigations; a: [3], $T = 775$ K; b: [4], $T = 760$ K; c: [5], $T = 1000$ K; d: [6], $T = 1100$. The values of the cross sections are given in 10^{-20} m^2.

	This work	Other authors			
		a	b	c	d
σ_{He}	1.5 ± 0.7	5.3 ± 0.5	–	0.12 ± 0.03	0.1 ± 0.06
σ_{Ar}	0.02 ± 0.01	0.037 ± 0.005	0.015 ± 0.010	–	0.5 ± 0.3
σ_{Xe}	0.8 ± 0.4	0.62 ± 0.04	–	–	–

Using the W_D data shown in Fig. 5 and the results for singlet-to-triplet population ratio χ displayed in Fig. 3, the corresponding collisional rates R_{st} were determined according to Eq. (4). The obtained values for R_{st} plotted versus the noble gas pressure are shown in Fig. 6. The straight lines represent least square fits through the measured data. The cross sections for the $^1D_2 \to {}^3D_J$ excitation transfer in barium induced by collisions with He, Ar and Xe atoms, as listed in Table 1, were determined from the slopes of the straight lines shown in Fig. 6 and the mean Maxwellian relative velocities. The statistical accuracy of the cross sections is ±10%, while the overall error of the presented values is estimated to ±50%, comprising the quoted uncertainties of those quantities used in the calculation, values of which were taken from the literature.



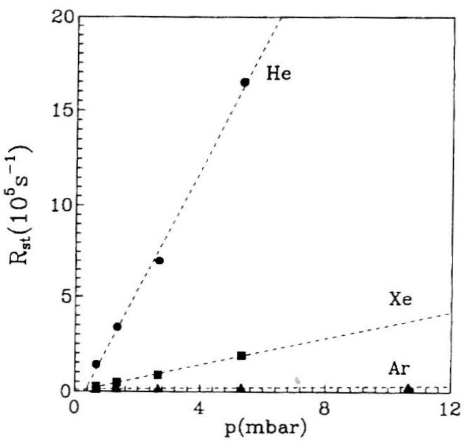


*Fig. 5. Plot of the diffusion removal rate W_D versus the noble gas (*He, Ar *or* Xe*) pressure.*

Fig. 6. The collisional rates R_{st} for the $^1D_2 \to {}^3D_J$ excitation transfer in barium induced by collisions with He, Ar *and* Xe *atoms, plotted against noble gas pressure. The dashed lines are the least squares fits through the experimental data (right).*

5. *Discussion and conclusion*

The cross sections for the 6s5d $^1D_2 \to$ 6s5d ^3D_J excitation energy transfer in barium, induced by collisions with He, Ar and Xe, have been measured and the following values have been obtained: $\sigma_{He} = 1.5 \times 10^{-20}$ m^2, $\sigma_{Ar} = 2 \times 10^{-22}$ m^2 and $\sigma_{Xe} = 8 \times 10^{-21}$ m^2. Up to our knowledge, there are four references in the literature related to this subject [3-6]. The measurements in Refs. 3, 5 and 6 were performed using pulsed lasers and time–resolved analysis. Similar to Ref. 4, the measurements in the present work were performed in the steady state regime, but the applied method is different. In contrast to Ref. 4, where the diffusion distributions of the metastable barium atoms outside the excitation zone were measured, the measurements in the present investigation are related only to the laser beam excitation zone.

As can be seen in Table 1, the results obtained in this work are in satisfactory agreement with those reported in Refs. 3 and 4. However, in the case of helium, our result is three times smaller than the one reported in Ref. 3, but still more than one order of magnitude greater than the value obtained by Refs. 5 and 6. In contrast to the present experiment as well as to experiments in Ref. 3 and 4, where 6s6p $^3P_1^0$ state was excited, the measurements in Refs. 5 and 6 were performed by excitation of higher–lying 6s6p $^1P_1^0$ level. In case of such an excitation, the number of involved states and relevant transitions is greater. Therefore, the modeling and the evaluation is more complicated than in the case of 6s6p $^3P_1^0$ level being excited. Furthermore, the applied laser powers in experiments [5, 6] were high, thus producing additional effects which required complicated analysis. Bearing in mind the above discussion, we believe that the results reported here as well as those in Refs. 3 and 4 are more reliable.

The cross sections reported here confirm the conclusions drawn in Refs. 3 and 4 regarding the interaction potentials between the barium metastable atoms and various noble gas atoms. These potentials depend strongly on the kind of noble gas, therefore, the corresponding cross sections differ in value significantly. We hope that recent experiments will initiate more thorough theoretical investigations of these processes.

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PRIJENOS ENERGIJE POBUDE IZMEĐU 6s5d $^1D_2$ I 6s5d ^3D_J STANJA BARIJA U SUDARIMA S ATOMIMA HELIJA, ARGONA I KSENONA

Metodom laserske apsorpcije i fluorescencije određeni su udarni presjeci za prijenos energije pobude u procesu Ba 6s5d $^1D_2 \rightarrow$ 6s5d ^3D_J uzrokovanom sudarima s atomima helija, argona i ksenona. Metastabilni nivoi 6s5d $^1D_2$ i 6s5d ^3D_J napučivani su radijativnom i sudarnom relaksacijom optički pobuđenog 6s6p $^3P_1^0$ stanja. U okviru predloženog modela sa četiri nivoa, koji uključuje 6s^2 $^1S_0$, 6s6p $^3P_1^0$, 6s5d $^1D_2$ i 6s5d ^3D_J stanja, opisani su procesi napučivanja i pražnjenja barijevih metastabila u atmosferi plemenitog plina. Analiza eksperimentalnih rezultata daje slijedeće udarne presjeke za istraživane procese: $\sigma_{He} = 1.5 \times 10^{-20}$ m^2, $\sigma_{Ar} = 2 \times 10^{-22}$ m^2 $\sigma_{Xe} = 8 \times 10^{-21}$ m^2, s točnošću od $\pm 50\%$