The use of Zeeman effect for increasing the selectivity of laser isotope separation

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Abstract. **It is proposed to use the Zeeman effect for increasing the selectivity of laser isotope separation. It is shown on the basis of the available spectroscopic data that the selectivity of laser separation of the palladium isotope ^{102}Pd can be increased significantly by using the Zeeman effect.**

1. Introduction

Two trends can be singled out in the problems of laser isotope separation (LIS). The first one is aimed at obtaining large amounts of the moderately enriched isotope. For example, a 2 % – 4 % concentration of ^{235}U must be obtained in the production of fuel for nuclear power reactors, while the natural abundance of this isotope is 0.7 %. The second trend involves the production of small quantities of highly enriched isotopes (of the order of a few grams) for medicine. For example, the concentration of the ^{168}Yb isotope required for medical applications should be at least 20 % – 25 %, whereas its concentration in the natural mixture of isotopes is only 0.14 %.

Theoretical and experimental studies made during recent years in Russia (at A.M. Prokhorov General Physics Institute, Russian Academy of Sciences, and the NPF LAD) noticeably stimulated the second field of applications and resulted in the creation of the first setups capable of producing a commercially viable enriched isotope ^{168}Yb by selective photoionisation (see reviews [1 – 3]). It seems quite natural to consider the possibilities of application of the LIS technique to other isotopes by using the experience gained in these investigations.

The spectral overlap of lines corresponding to different isotopes (blending), resulting from the hyperfine splitting of lines for isotopes with nonzero nuclear moments, often hinders the attainment of a high selectivity in the step photoionisation of a rare isotope. In this case, one can try to use the Zeeman effect for shifting the blending lines beyond the width of the laser radiation line and the Doppler broadening of atomic lines. We shall study this possibility

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by considering the specific example of the ^{102}Pd isotope using the data [4] on the isotopic and hyperfine structure of the intermediate $4d^9 5p\,^3P_1$ state of the Pd atom.

2. Spectroscopic parameters of Pd

2.1 Choice of the selective photoionisation scheme for ^{102}Pd

The ground state of palladium is $4d^{10}\,^1S_0$ ($E = 0$). The nearest states are the metastable states with the $4d^9 5s$ configuration: $^3D_3$ ($E = 6564$ cm^{-1}), $^3D_2$ (7755 cm^{-1}), $^3D_1$ (10094 cm^{-1}), and $^1D_2$ (11722 cm^{-1}) (dipole transitions from these states to the ground state are forbidden by parity). At temperatures of a vapour source up to 2000 K (resistive evaporation), the metastable states are weakly populated (over 90% atoms are in the $^1S_0$ state), and hence the ground $^1S_0$ state of palladium should be used as the initial state in the photoionisation scheme.

Note that quadrupole transitions from the ground state to the excited states can hardly be used for ionisation because the probabilities of these transitions are too low. For example, the probability of transition from the ground state to the state with $4d^9 5s\,^1D_2$ configuration estimated from Bates – Damgaard tables is $A \sim 0.05$ s^{-1}. Therefore, one has to use dipole transitions for photoexcitation of palladium atoms.

The $4d^9 5p$ configuration levels $^3P_1$ ($E = 36180.64$ cm^{-1}, $\lambda = 276.4$ nm), $^1P_1$ (40838.8 cm^{-1}, 244.9 nm), and $^3D_1$ (40368.73 cm^{-1}, 247.7 nm) are the levels closest to the ground state, to which dipole transitions can occur (see Ref. [5] for data on the level energies). A frequency-doubled dye laser pumped by a copper laser can excite only the $^3P_1$ level, which was used as the first working level in the step ionisation in Ref. [4].

Subsequent excitation can be carried out in two ways (Fig. 1). In the first version, excited palladium atoms from the $4d^9 5p\,^3P_1$ state can be ionised either directly into a continuum using radiation with $\lambda < 322$ nm, or through autoionisation states with the $4d^9 nl$ configuration [6]. The parameters of these photoionisation schemes are determined by the characteristics of the $^3P_1$ level having a lifetime of 7.5 ns [7]. The short lifetime sets a lower limit on the pulse power of ionising radiation (because the ionisation rate must be higher than the spontaneous decay rate) and the synchronisation of exciting and ionising radiation pulses (with an error not exceeding 3 ns). The selectivity of the scheme is determined by the isotopic structure of the $^1S_0 - {}^3P_1$ transition.
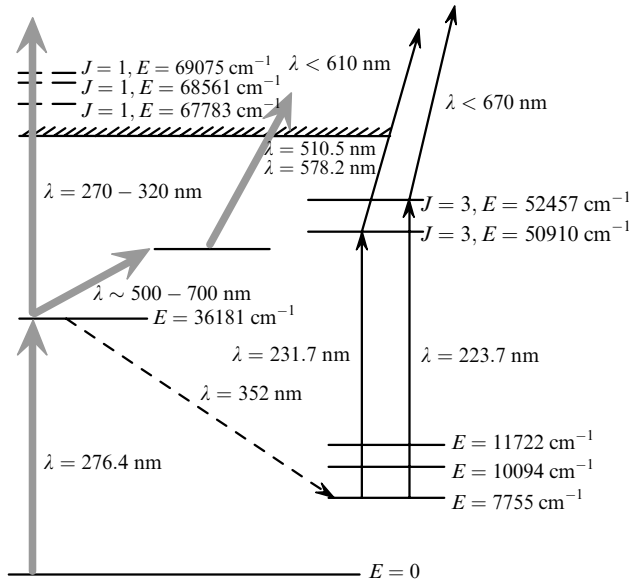
Figure 1. Photoionisation scheme of Pd.

In the second version, one can use the fact that the $4d^9 5p\,^3P_1$ state decays mainly (about 80%) to the $4d^9 5s\,^3D_2$ metastable state. Therefore, a large number of atoms can be accumulated in this state by irradiating vapour at the wavelength of the $^1S_0 - {}^3P_1$ transition; this state can be used subsequently as the lowest level in the ionisation scheme. In this case, the selectivity is determined by the product of the selectivity of photoionisation at the $^1S_0 - {}^3P_1$ transition used for populating the $^3D_2$ level and the selectivity of the first working transition in the scheme. If the second harmonic of a dye laser pumped by a copper vapour laser is used, the first working transition in this scheme may be transitions to the following levels of the $4d^9 5p$ configuration: $^3P_2$ ($2\lambda = 760.05$ nm), $^3P_1$ (703.59), $^3F_3$ (722.12), $^3F_2$ (643.98), $^3D_3$ (674.79), $^3D_2$ (684.44), $^3D_1$ (613.24), $^1F_3$ (622.99), $^1D_2$ (605.76) and $^1P_1$ (604.53).

We will consider the first version, namely, the two-step photoionisation through the $4d^9 5p\,^3P_1$ state.

2.2 Isotopic shift and hyperfine structure of levels

To find the isotopic structure of a level, the information on the isotopic shifts and the hyperfine structure (HFS) is required. While discussing the isotopic structure of the energy levels in the following, we will measure the energy of atomic levels from the ground state. In other words, we assume that the ground states of all isotopes are made coincident on the energy scale (traditionally, it is assumed that the ionisation limits of the levels coincide, but this is not convenient in our case). The energy shifts will be measured in mK (1 mK $= 10^{-3}$ cm$^{-1} = 29.979$ MHz).

The corrections to the level energies due to interaction with magnetic and quadrupole moments of the nuclei (HFS of the levels) can be described with a high degree of accuracy by the formula from the theory of atomic spectra:

$$\Delta E(I, J, F) = \frac{1}{2} A(I, J) C + \frac{3}{8} B(I, J)$$

$$\times \frac{C(C + 1)}{I(2I - 1) J(2J - 1)} + \Delta(I, J), \qquad (1)$$

where $C = F(F + 1) - J(J + 1) - I(I + 1)$; I is the nuclear moment; J is the moment of the atomic state (state of the electron shell of the nucleus); F is the total moment of the atom; $A(I, J)$ and $B(I, J)$ are constants.

The first term in formula (1) (constant A) is related to the splitting of the term with a given J due to the interaction with the nuclear magnetic moment (which is proportional to I), while the second term is related to the splitting caused by the interaction with the quadrupole electric moment of the nucleus. The shift $\Delta(I, J)$ is independent of the total moment F of the atom and is the same for all HFS sublevels of a level with a given value of J. As a rule, the data on HFS available in the literature contain not the measured shifts of the HFS levels with different F, but rather the values of constants A and B for which the measured shifts are in the best agreement with formula (1).

Specific values of the isotopic shifts at the $4d^9 5p\,^3P_1 \rightarrow 4d^{10}\,^1S_0$ transition are not available in the literature. In Ref. [4] only a diagram of the isotopic structure of this transition is presented without any reference to the data on which it is based. We estimated isotopic shifts from this diagram (which coincide approximately with the shifts measured for other transitions in Refs [8–10]) and used them in Fig. 2 in the present work. The HFS of the $4d^9 5p\,^3P_1$ level in the ^{105}Pd isotope was determined in Refs [7, 10]. The values of the constants A and B measured in these works are almost identical. Fig. 2 was constructed by using the more recent data obtained in Ref. [10]: $A = -130$ MHz and $B = 140$ MHz.
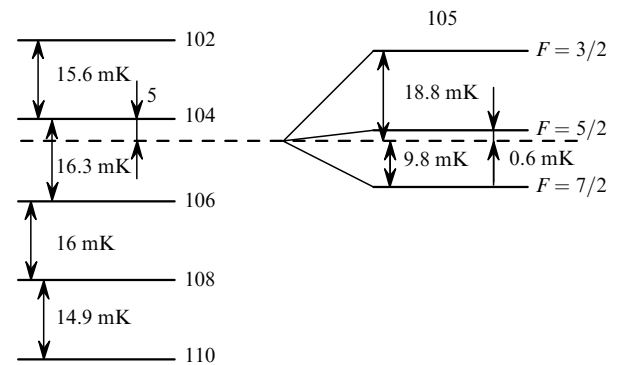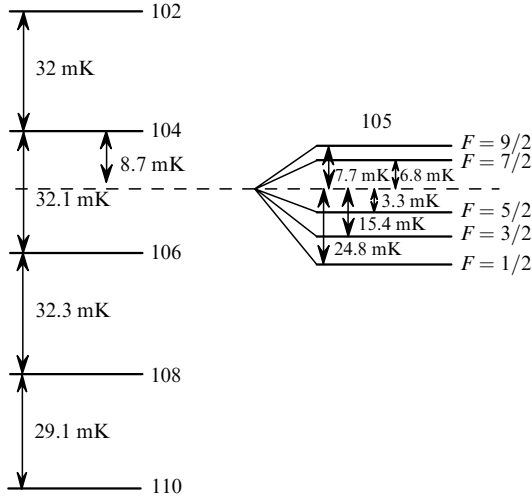

Figure 2. Shifts and HFS of the $4d^9 5p\,^3P_1$ level in Pd I. The numbers at the levels indicate the mass numbers of isotopes, the dashed line shows the centre of gravity of HFS for the ^{105}Pd isotope.

The HFS of the $4d^9 5s\,^3D_2$ level was calculated by using the most precise values of the constants available in the literature: $A = 66$ MHz and $B = -400$ MHz [9]. No information is available on the isotopic shifts of this level. The shifts were reconstructed from the isotopic shifts of the $4d^9 5p\,^3P_1$ level (Fig. 4) and the data from Ref. [8] on the isotopic shifts for the lines at 340.5 and 357.1 nm (i.e., transitions between the levels that are closest to the required levels $^3P_1$ and $^3D_2$ on the energy scale among all the levels for which measurements were made). The isotopic structure thus obtained is presented in Fig. 3.

2.3 Radiative transition probabilities

Very few publications have been devoted to the transition probabilities in Pd I or to the isotopic structure of levels. The oscillator srengths and transition probabilities for a

Figure 3. Shifts and HFS of the $4d^9 5s\,^3D_2$ level in Pd I. The notation is as in Fig. 2.

number of Pd I levels, including transitions between the lowest working levels required by us are given in monograph [11] (these data were obtained from the measurements of intensities of lines in an arc). The absolute error in the data presented in [11] is comparatively low, about a factor of two (according to the estimates of the authors). The relative error is determined by the error of measurement of the ratios of line intensities and is much smaller (just a few percent). Note that the probabilities given in Ref. [11] pertain to transitions in even isotopes (^{102}Pd, ^{104}Pd, etc.).

The oscillator strength f for the $4d^9 5p\,^3P_1 \rightarrow 4d^{10}\,^1S_0$ transition was measured experimentally in Ref. [12]. The value of this strength ($f = 0.036$) was found to be about half that given in Ref. [11] ($f = 0.071$). The lifetime τ of the $4d^9 5p\,^3P_1$ state was measured in a recent experiment [10], and was found to be equal to 7.46 ns, which is about double the lifetime calculated from the data given in Ref. [11]. The experimental results presented in Refs [10] and [12] are nearly identical with an error of about 5%. Note that the lifetime τ was also measured in an earlier work [7] and was found to be 8.9 ns, which led to more significant discrepancies in transition probabilities.

The transition probabilities presented below were obtained as follows. It was assumed that the relative probabilities of transitions from the $4d^9 5p\,^3P_1$ level to all other levels correspond to the data given in Ref. [11]. These probabilities were then normalised in such a way that the lifetime for the $^3P_1$ state was equal to 7.46 ns, i.e., the measured value from Ref. [10].

The transition probabilities in the odd ^{105}Pd isotope were recalculated by using the formula for intensities of the hyperfine structure components:

$$A(JIFM \rightarrow J'IF'M';\mu)$$

$$= A_0 (2F'+1)\langle F'M'1\mu|FM\rangle^2 \begin{Bmatrix} J' & F' & I \\ F & J & 1 \end{Bmatrix}^2,$$

where $A_0 = (2J+1)A(J \rightarrow J')$; $I = 5/2$ for the ^{105}Pd isotope; $\langle F'M'1\mu|FM\rangle$ is the Clebsch–Gordan coefficient; $\{:::\}$ is the 6j-symbol; and $\mu = 0$ and ± 1 for linear and

circular polarisations of radiation, respectively. The obtained transition probabilities are presented in Tables 1 and 2. Note that, according to the data available in the literature, the probabilities of $4d^9 5p\,^3P_1 \rightarrow 4d^8 5s^2\,^3F_{2,3,4}$ transitions, which are missing in the tables, are negligibly small compared to the values given in them. The transition probabilities for the odd isotope are given only for transitions from the sublevels of the $^3P_1$ level to the sublevels of the $^3D_2$ level. There is no need to recalculate all the remaining probabilities since transitions to the other levels lead to decay, and the decay rate of the $JIFM$ sublevel due to transitions to the $J'IF'M'$ sublevels (the total decay rate over $M'F'$) is simply equal to the probability of the $J \rightarrow J'$ transition in an even isotope. The probabilities given in Tables 1 and 2 were used in calculations presented below.

Table 1. Transition probabilities in even isotopes of Pd I.

Transition	$A/10^6\,\text{s}^{-1}$
$4d^9 5p\,^3P_1 \rightarrow 4d^{10}\,^1S_0$	10.3
$4d^9 5p\,^3P_1 \rightarrow 4d^9 5s\,^3D_2$	106
$4d^9 5p\,^3P_1 \rightarrow 4d^9 5s\,^3D_1$	14.2
$4d^9 5p\,^3P_1 \rightarrow 4d^9 5s\,^1D_2$	2.98

**Table 2.** Probabilities of transitions between HFS sublevels in ^{105}Pd.

Transition	$A/10^7\,\text{s}^{-1}$
$4d^9 5p\,^3P_1(F=3/2) \rightarrow 4d^{10}\,^1S_0(F=5/2)$	1.03
$4d^9 5p\,^3P_1(F=5/2) \rightarrow 4d^{10}\,^1S_0(F=5/2)$	1.03
$4d^9 5p\,^3P_1(F=7/2) \rightarrow 4d^{10}\,^1S_0(F=5/2)$	1.03
$4d^9 5p\,^3P_1(F=3/2) \rightarrow 4d^9 5s\,^3D_2(F=1/2)$	3.18
$4d^9 5p\,^3P_1(F=3/2) \rightarrow 4d^9 5s\,^3D_2(F=3/2)$	4.45
$4d^9 5p\,^3P_1(F=3/2) \rightarrow 4d^9 5s\,^3D_2(F=5/2)$	2.96
$4d^9 5p\,^3P_1(F=5/2) \rightarrow 4d^9 5s\,^3D_2(F=3/2)$	1.27
$4d^9 5p\,^3P_1(F=5/2) \rightarrow 4d^9 5s\,^3D_2(F=5/2)$	3.87
$4d^9 5p\,^3P_1(F=5/2) \rightarrow 4d^9 5s\,^3D_2(F=7/2)$	5.45
$4d^9 5p\,^3P_1(F=7/2) \rightarrow 4d^9 5s\,^3D_2(F=5/2)$	0.378
$4d^9 5p\,^3P_1(F=7/2) \rightarrow 4d^9 5s\,^3D_2(F=7/2)$	2.27
$4d^9 5p\,^3P_1(F=7/2) \rightarrow 4d^9 5s\,^3D_2(F=9/2)$	7.94

3. Zeeman effect for the $4d^9 5p\,^3P_1$ level in Pd I

In order to obtain the energies of sublevels of the level with the moment J and the transition probabilities in an external static magnetic field, we must diagonalise the matrix of perturbation of an atom in a magnetic field, constructed on the basis of unperturbed wave functions:

$$W_{ij} = \langle JF_iM_i|V|JF_jM_j\rangle + \delta_{ij}\varepsilon_i,$$

where $V = g_J\mu_B B\hat{J}$ is the perturbation operator; g_J is the g-factor ($g_J = 1.396$ for the $^3P_1$ level); μ_B is the Bohr magneton; B_0 is the magnetic field strength; $\hat{J}$ is the moment operator for the electron shell; the subscripts i, j number the HFS sublevels of the level with the moment J (with total moments F_i and projections M_i); and ε_i is the energy of the ith HFS level in a zero magnetic field. The energies of the magnetic HFS sublevels of the $4d^9 5p\,^3P_1$ level for palladium isotopes, obtained as a result of
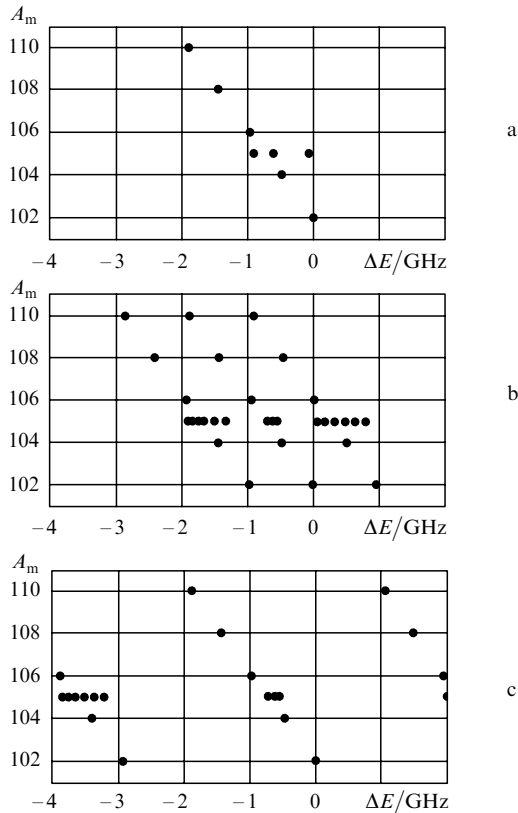
Figure 4. Positions of the magnetic sublevels of the $4d^9 5p\,^3P_1$ level of palladium isotopes with the mass number A_m in a zero magnetic field (a) and in an external magnetic field with $B_0 = 500$ (b) and 1500 G (c). The energy detuning ΔE is measured from the energy of the $4d^9 5p\,^3P_1$ magnetic sublevel of the ^{102}Pd isotope for $M_J = 0$.

of the vapour was assumed to be natural. The laser radiation spectrum could be chosen as Gaussian or Lorentzian (the linewidth and the type of the spectrum were specified). The spectrum of the ionising laser radiation is unimportant for ionisation in the continuum as well as through autoionisation states because of a large width of spectral bands corresponding to these states. The problem was solved in two steps. The influence of the Zeeman effect on palladium isotopes in a magnetic field was studied in the first step. As a result, the energies of all magnetic sublevels of the $4d^9 5p\,^3P_1$ level were determined for all palladium isotopes, and the probabilities of allowed transitions between them were calculated.

The medium (Pd vapour) was characterised by the density and distribution of atoms over the projections of their velocities in the direction of propagation of the laser beams. The atoms of the medium were divided into n groups ($n = 5 - 15$). The balance equations were written for each velocity group (in the given intensity approximation) for the complete system of all sublevels of the $4d^9 5p\,^3P_1$ level for each Pd isotope. The velocity distribution of the atoms was chosen arbitrarily [below, a Maxwellian (Gaussian) distribution was assumed].

The system of balance equations was solved by the standard 4th order Runge–Kutta method. The following processes were taken into account: photoexcitation (deexcitation) of the $^3P_1$ level by laser radiation, decay of this level due to radiative transitions to the states not

diagonalisation of matrices, are shown in Fig. 4 for three values of the magnetic field.

An increase in the magnetic field causes a splitting of the magnetic sublevels of all palladium isotopes. An analysis of Fig. 4 reveals that in magnetic fields exceeding 1500 G, the magnetic sublevels of all undesirable isotopes are displaced by no less than 500 MHz from the working transition frequency, thus ensuring a selectivity of ionisation of the ^{102}Pd isotope.

Note that the presence of a magnetic field imposes certain constraints on the mutual orientation of the linearly polarised laser radiation and the magnetic field: for efficient excitation of the level, the electric vector of the laser beam must be parallel to the magnetic field vector $\boldsymbol{B}_0$, while the beam vector must be perpendicular to $\boldsymbol{B}_0$.

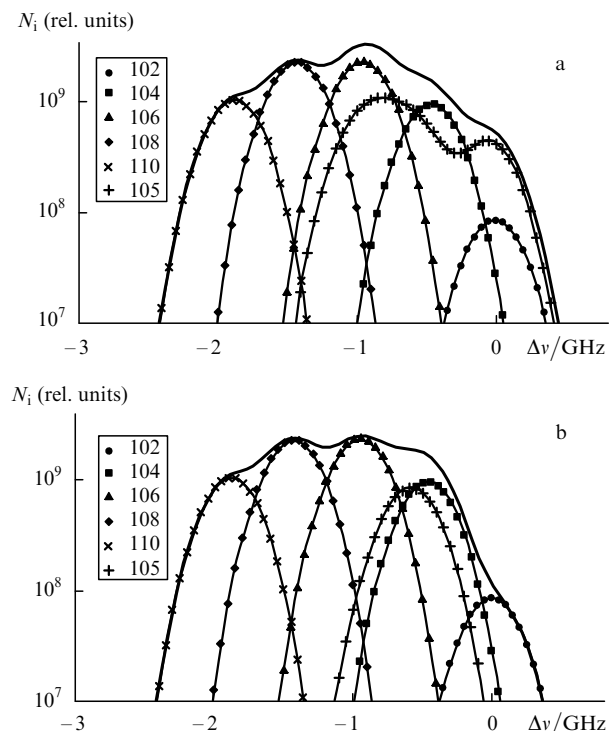## 4. Calculations of the spectral dependence of photocurrent and ionisation efficiencies

To obtain the spectrum of the photocurrent as a function of the laser wavelength exciting the $4d^{10}\,^1S_0 \to 4d^9 5p\,^3P_1$ transition and of the magnetic field strength, a multilevel kinetic model of photoionisation was developed (see references in [1, 2] for details). This model takes into account the simultaneous ionisation of all isotopes excited by the laser, and hence makes it possible to calculate the resulting enrichment upon selective photoionisation.

We considered the problem of photoionisation of an optically thin layer of Pd vapour. The isotopic composition

Figure 5. Dependences of the isotopic composition of the density N_i of ions formed in the selective photoionisation region on the detuning Δv of the selecting laser from the $4d^9 5p\,^3P_1 \to 4d^{10}\,^1S_0$ frequency transition in a zero magnetic field (a) and in a magnetic field with $B_0 = 2000$ G (b). The numbers at the symbols are the mass numbers of isotopes. The solid curve corresponds to the total density of ions. The peak intensity of the selecting and ionising lasers is 10 W cm^{-2} and 100 kW cm^{-2} respectively. The FWHM of the Gaussian atomic and laser lines is 300 MHz; the laser radiation is linearly polarised.

included in the model, and photoionisation to the continuum by exciting and ionising lasers (with a photoionisation cross section $\sigma = 1.2 \times 10^{-16}$ cm^2). Note that because of the orthogonality and completeness relations of the 3jm-symbols, the decay rate is the same for all sublevels of the $^3P_1$ level. It was assumed that laser radiation is a combination of radiation with linear polarisation and left- and right-hand circular polarisations (the fraction of each polarisation was specified in the course of investigations).

Fig. 5 shows two examples of calculated spectral dependence of the photocurrent (for $B_0 = 0$ and 2000 G). The calculations show that it is not possible to attain a high enrichment of the ^{102}Pd isotope in a zero magnetic field because of blending of its line with the line of the ^{105}Pd isotope. In a magnetic field with $B_0 = 2000$ G, a high enrichment can be attained (for an acceptable ionisation efficiency) by tuning the laser in the $0 - 300$-MHz range.

An analysis of the dependences of the ion yield on the peak intensities of the selecting and ionising lasers showed that for a width of laser and atomic lines of the order of 300 MHz, a 40% ionisation efficiency can be attained for a peak intensity of 30 W cm^{-2} and 1 MW cm^{-2} for the first and second lasers, respectively.

5. Conclusions

The spectroscopic data on the isotopic structure of levels and the transition probabilities in Pd available in the literature [4 – 12] suggest that the Zeeman splitting in an external magnetic field can be used for a highly selective step photoionisation of ^{102}Pd. However, the data on hyperfine and spectroscopic structure of the $4d^9 5p\,^3P_1$ level require experimental verification.

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