

SELECTIVE PHOTOIONIZATION OF RARE-EARTH ELEMENT ISOTOPES

A. G. Zhidkov and B. B. Krynetskii

1. INTRODUCTION

The problem of laser separation of isotopes arose primarily as applied to the technology of enriching elements with large isotopic shifts (U, Pu) [1]. Although the problems encountered in the realization of this program have already been overcome, the degree to which the method is competitive is still under discussion. At the same time, the question of applying these methods to obtain rare isotopes, whose world market price exceeds \$10,000 per gram with low enrichment, has been under consideration since the middle seventies [2].

The difficulty of laser separation of rare-earth isotopes has both physical and commercial causes. In fact, in contrast to uranium isotopes, electronic transitions in rare-earth atoms have low isotopic shifts (1-2 GHz), which inhibit achievement of high selectivity on account of field broadening which takes place already at relatively low (peak) laser power densities, $\leq 100 \text{ W/cm}^2$. As a result, the low content of the required isotope in the natural mixture (0.1-1%) lowers drastically the efficiency of excitation of the first step, and hence the productivity. Finally, the existence of a technology for electromagnetic separation of rare-earth isotopes toughens the demands on the cost and productivity of laser-separation methods.

The specific feature of rare-earth elements (REE) – the absence of volatile molecular compounds, has determined the form of the laser technology: separation of isotopes from a flux of neutral atoms (atomic vapor laser separation – AVLIS) and the result of the laser action – electronic transitions of the atoms.

Electronic transitions of REE atoms have a rich spectrum in the visible region, necessitating the choice of laser systems causing selective excitation and ionization. These conditions are satisfied by tunable lasers using organic dyes, color centers, titanium ions in sapphire, or chromium ions in beryllium with coherent pumping.

In contrast to elements of the uranium group, metals of the rare-earth group have low isotopic shifts, 1-2 GHz. Table 1 lists data on the isotopic shifts in certain lines of ytterbium and gadolinium, and for comparison the isotopic shifts for uranium.

As a rule, elements of rare-earth metals have resonant transitions in the yellow-red wavelength range and ionization potentials 5.5-6.5 eV. This makes it possible to use a three-step scheme for selective photoionization of the isotopes.

The three-step selective photoionization scheme consists of the following. A directed stream of atoms is produced in a resistive or electron-beam evaporator and is irradiated by a multifrequency laser beam. Dye lasers excite the atom twice in succession. The third excitation is effected in an autoionization state having a lifetime 1 psec. An approximate scheme of the process is shown in Fig. 1. The charged particles resulting from the photoionization are separated from the gas stream by an electromagnetic extractor.

The present paper is devoted to calculations of the selectivity of three-step photoionization of rare-earth element isotopes with isotopic shifts not exceeding 2 GHz.

2. SELECTIVE PHOTOIONIZATION OF ISOTOPES

Consider the dependence of the degree of selectivity of the photoionization on the parameters of the laser emission. By degree of selectivity we mean the ratio of the densities of the different isotopes produced as a result of selective photoionization

Translated from a preprint (manuscript) of the Lebedev Physics Institute, Russian Academy of Sciences, Moscow.

TABLE 1. Isotopic Shifts for Certain Transitions of Rare-Earth Atoms (Gd, Yb) and Uranium

Element	Wavelength	Isotope	Isotopic shift in GHz
Gadolinium	528.3	152 - 154	3.66
	561.8	152 - 154	3.3
Ytterbium	555.6	168 - 170	1.35
		168 - 171, 173	0.128
Uranium	591.5	235 - 238	8.46
	635.9	235 - 238	6.3
	682.7	235 - 238	11.4

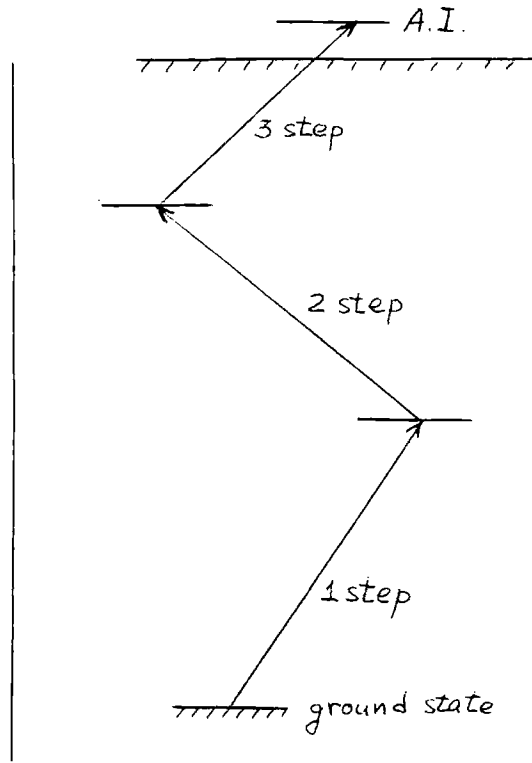


Fig. 1. Model scheme of the three-step selective photoionization process.

$$\eta = p_1 N_1 / p_2 N_2$$

where p_i is the probability of ionizing the i th isotope by action of the laser pulses, N_i is the density of the i th isotope in the mixture. For a three-step photoionization scheme, the probability of ionizing the first isotope is

$$p_i = \langle f(v)[1 - n_1(v) - n_2(v) - n_3(v)] \rangle_{t=T}$$

where f is the distribution functions of the atoms in velocity, n_i is the relative density of the i th state of the atom, and T is the instant when the action of all three laser pulses terminates. The averaging $\langle \dots \rangle$ implies integration over the atom velocities and over the distribution function of the laser-field distribution in frequency.

We consider in this paper the limiting selectivity of three-step photoionization of the isotopes of an element. This means that effects due to the influence of the Doppler broadening and the laser-emission line width are disregarded. We investigate below the dependence of the selectivity only on the intensity of the laser emission and on its durations.

To calculate the atom-level populations it is convenient to use the density-matrix representation

$$i d\rho/dt = [H_0 - \sum DE_k, \rho] + i\Gamma\rho \quad (1)$$

Here H_0 is the Hamiltonian of the unperturbed atom, and DE_k is the matrix element of the interaction of the atom with the k -field.

We assume further that the matrix element of the interaction between the ionizing radiation and the atom is substantially smaller than the width of the autoionization level. For dye lasers pumped by copper lasers this condition is quite well satisfied. In this case the interaction between the ionizing radiation with the atom reduces to inelastic ionization with a cross section

$$\sigma = 4D^2\gamma/[c^2(\Delta\omega^2 + \gamma^2)] \quad (2)$$

where D is the dipole moment of the transition into the autoionization state, γ is the width of the autoionization state, and $\Delta\omega$ is the detuning of the frequency from exact resonance. The ionization frequency is then defined as

Here I is the intensity of the ionizing radiation and ω is the emission frequency.

For a three-level system, Eq. (1) takes in the approximation (2) the form

$$\begin{aligned} \dot{\rho}_{11} &= -i(V_{12}\rho_{21} - V_{21}\rho_{12}) + A_{12}\rho_{22}; \\ \dot{\rho}_{22} &= i(V_{12}\rho_{21} - V_{21}\rho_{12}) - i(V_{23}\rho_{32} - V_{32}\rho_{23}) - A_{12}\rho_{22}; \\ \dot{\rho}_{33} &= i(V_{23}\rho_{32} - V_{32}\rho_{23}) - \nu\rho_{33}; \\ \dot{\rho}_{12} &= -iV_{21}(\rho_{22} - \rho_{11}) + iV_{32}\rho_{13} + (i\Delta\omega_1 - A_{12}/2)\rho_{12}; \\ \dot{\rho}_{13} &= -iV_{12}\rho_{23} + iV_{23}\rho_{12} + i(\Delta\omega_1 + \Delta\omega_2 + i\nu/2)\rho_{13}; \\ \dot{\rho}_{23} &= -iV_{32}(\rho_{33} - \rho_{22}) - iV_{21}\rho_{13} + (i\Delta\omega_2 - \nu/2 - A_{12}/2)\rho_{23}; \end{aligned} \quad (3)$$

$$\rho_{ij} = \rho_{ij}^*, V_{12} = V_{21}^* = -D_{12}E_1/h, V_{23} = V_{32}^* = -D_{23}E_2/h.$$

$\Delta\omega_i$ is the detuning of the frequency of the i th laser emission from resonance. For isotopes of one element, the frequency detunings differ by the values of the isotopic shifts in the transition energy.

The boundary conditions for Eq. (3) are quite obvious:

$$\rho_{11}(t=0) = 1, \rho_{ij}(t=0) = 0.$$

The ionization probability of an atom by the instant T when the action of the laser ceases is determined by the difference

$$p = 1 - \rho_{11} - \rho_{22} - \rho_{33} \quad (4)$$

Note that owing to transitions to the continuum the system (3) is not conservative. The selectivity of the process is determined by the ratio of the ionization probabilities for different isotopes. We disregard below for simplicity the isotope-density difference.

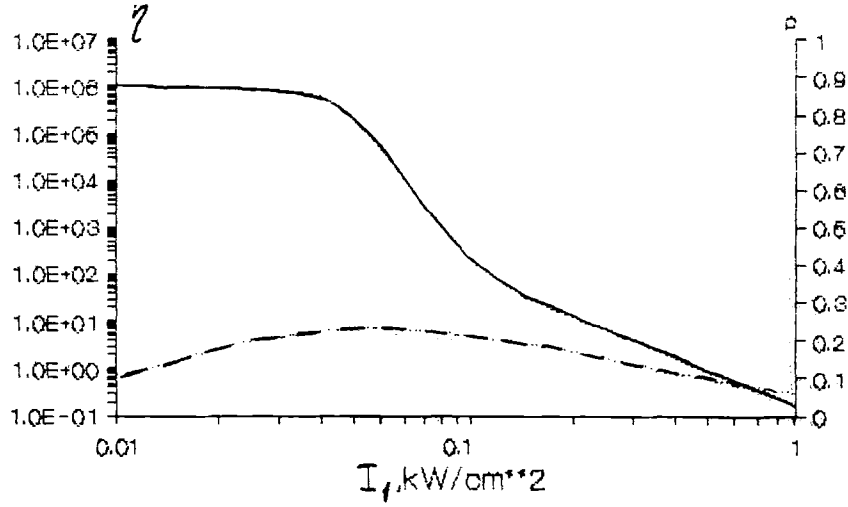


Fig. 2. Dependence of the selectivity and ionization probability on the emission intensity of the first excitation step. The intensity of the second step is $I_2 = 300 \text{ W/cm}^2$.

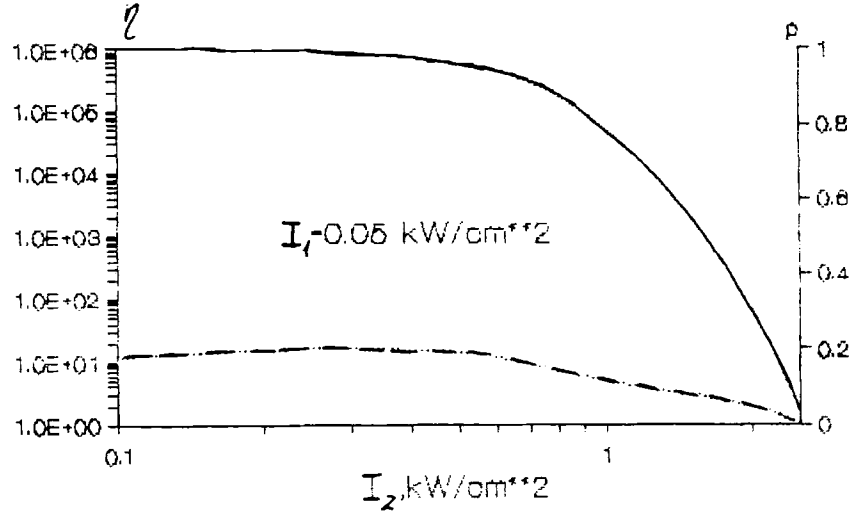


Fig. 3. Dependence of the selectivity and the ionization probability on the emission intensity of the second step at $I_1 = 50 \text{ W/cm}^2$.

3. CALCULATION RESULTS

The system (3) is transformed into

$$\begin{aligned}
 \dot{n}_1 &= 2V_1 t_{12} + An_2; \\
 \dot{n}_2 &= -2V_1 t_{12} + 2V_2 t_{23} - An_2; \\
 \dot{n}_3 &= -2V_2 t_{23} - \nu n_3; \\
 \dot{t}_{12} &= V_1(n_2 - n_1) - V_2 S_{13} + \Delta\omega_1 S_{12} - At_{12}/2; \\
 \dot{t}_{13} &= V_1 S_{23} - V_2 S_{12} + (\Delta\omega_1 + \Delta\omega_2) S_{13} - \nu t_{13}/2; \\
 \dot{t}_{23} &= V_2(n_3 - n_2) + V_1 S_{13} + \Delta\omega_2 S_{23} - (\nu/2 + A/2)t_{23}; \\
 \dot{S}_{12} &= V_2 t_{13} - \Delta\omega_1 t_{12} - At_{12}/2; \\
 \dot{S}_{13} &= -V_1 t_{23} + V_2 t_{12} - (\Delta\omega_1 + \Delta\omega_2)t_{13} - \nu t_{13}/2; \\
 \dot{S}_{23} &= -V_1 t_{13} - \Delta\omega_2 t_{23} - (\nu/2 + A/2)S_{23}.
 \end{aligned} \tag{5}$$

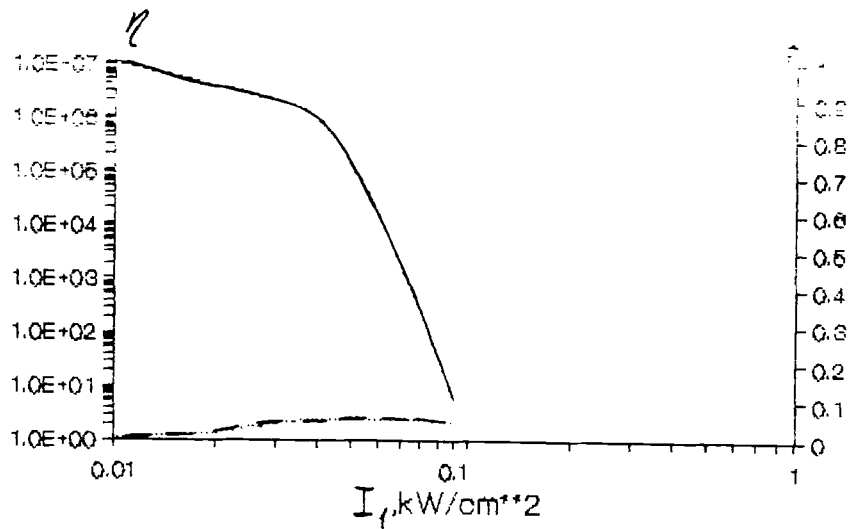


Fig. 4. Dependence of the selectivity and of the ionization probability for pulse delays 10 and 20 nsec, respectively. $I_1 = 50$ and $I_2 = 500$ W/cm².

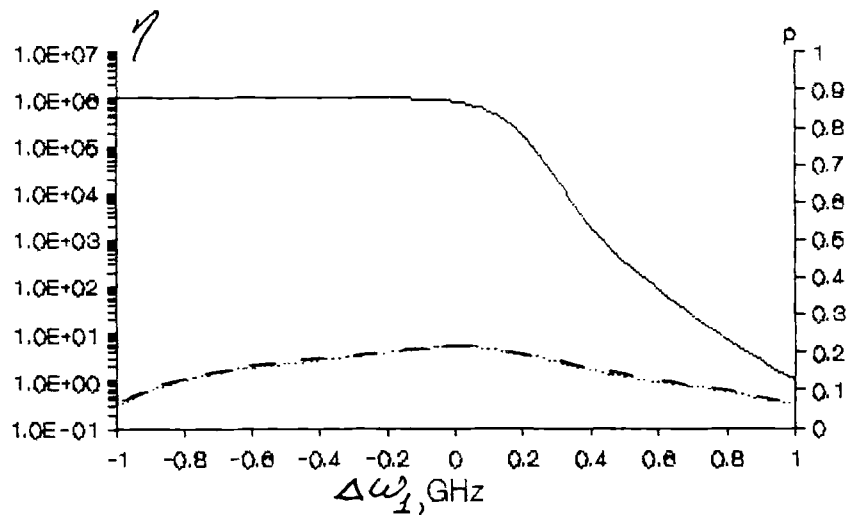


Fig. 5. Dependence of selectivity and ionization probability on the laser frequency detuning of the first degree of excitation.

With initial conditions $n_1(0) = 1$, $n_i(0) = 0$, $t_{ij}(0) = S_{ij}(0) = 0$. The dependences of the matrix elements V_i and of the ionization frequency were specified in the form of Gaussian functions with delay δ and duration τ :

$$f(t) = f_0 \exp[-10(t - \delta)^2 / \tau^2] \quad (6)$$

Equations (5) and (6) were solved numerically using an implicit second-order method.

The calculation results are illustrated in Figs. 2 and 3.

Figures 2 and 3 show the dependences of the ionization probability and of the selectivity on the parameters of the exciting laser emission, for atom parameters indicative of transitions in ytterbium and gadolinium isotopes. We chose in particular dipole moments $D_1 = 0.33$ a.u. and $D_2 = 0.0515$ a.u., an ionization cross section $\sigma = 6.7 \cdot 10^{-16}$ cm², and isotopic shifts 0.2 GHz on the first excitation step and -1.35 GHz on the second for the photoionization scheme proposed in [2].

Figure 2 shows for zero frequency detunings $\Delta\omega_i = 0$ the calculated selectivity and ionization probability as functions of the emission intensity at the first-excitation wavelength, at a second-step intensity 300 W/cm². Evidently the high degrees of selectivity $\eta > 1000$ are reached at intensities $I < 60$ W/cm² at the maximum of the pulse, and decreases sharply when the peak intensity is increased above 100 W/cm². The ionization probability is small in this case, $p = 0.2$. The pulse durations were assumed in these calculations to be 10 nsec, and the delays were chosen for optimized ionization probability to equal 8 and 12 nsec respectively for the second and third laser pulses.

The high selectivity obtained in the calculations is due to the presence of an excitation resonance in the two-photon transition; it depends weakly on the emission intensity, but for $V_1 \cong V_2$

$$p \cong 4V_1^4 V_2^4 \sin^2[2\sqrt{V_1^2 + V_2^2}]/(V_1^2 + V_2^2)^2$$

is close to unity. Deviation from resonance by more than the magnitude of the matrix elements leads to a drastic decrease of the ionization probability and ensures correspondingly a high selectivity. Since the resonance depends on both matrix elements, the lowest intensity should be that of the field of the first excitation step with the largest dipole moment, and accordingly just this field will determine the productivity of the method.

Figure 3 shows for the same parameters the calculated dependence of the selectivity and ionization probability on the emission intensity of the second excitation step. In this case this intensity is restricted to 500 W/cm² at the emission maximum. Note that the limiting intensity decreases in inverse proportion to the squared dipole moment of the transition.

Figure 4 illustrates the changes in the selectivity and ionization probability for other time delays. It can be seen that a change of the delays leads to a decrease of the ionization probability.

Variation of the frequency detunings, as seen from Fig. 5, makes it possible to increase the radiation intensity of the first step without changing the selectivity. A decrease of the ionization probability, however, does not compensate in this case for this increase from the standpoint of the productivity of the method.

4. SOME ESTIMATES

Small isotopic shifts in the rare-earth-element lines impose stringent requirements on their Doppler broadening and correspondingly on the method of formation of the atomic beam. Thus, for a metal-gas atom temperature $T = 0.1$ eV and for a transition wavelength $\lambda = 550$ nm the Doppler line width

$$\Delta\omega = \omega_0 v/c = \omega_0 \sqrt{kT/Mc^2}$$

(where ω_0 is the transition frequency, $v \cong 3 \cdot 10^4$ cm/sec is the atom velocity, and $M \cong 3 \cdot 10^{-22}$ g is their mass) amounts to $\Delta\omega = 3.5$ GHz, which exceeds substantially the isotopic shifts of the lines. Under certain conditions, by using diaphragms, the Doppler broadening can be decreased apparently to 1-2 GHz. Intradoppler spectroscopic methods [7] can also be used. In this case, when two resonant electromagnetic fields act simultaneously on the atom, the atom-excitation probability contains a sum in the form

$$\omega_1 v n_1/c + \omega_2 v n_2/c$$

The contribution of this sum is considerably offset by choosing the laser-emission propagation directions.

The use of copper lasers and their alternatives to pump the dyes, which have at present no alternatives satisfying the technological requirements, will lead to one more difficulty. The point is that the duration of the copper laser pulse at half-maximum is 10-20 nsec. Assuming the corresponding dye emission duration to be $\tau = 10$ nsec for a pulse of Gaussian shape

TABLE 2

Element	Number of isotope	Percentage in natural mixture
Yb	176	12.73
	174	31.82
	173	16.13
	172	21.82
	171	14.31
	170	3.63
	168	0.14
Gd	160	22.01
	158	24.95
	157	15.64
	156	20.36
	155	14.68
	154	2.16
	152	0.20

$$I(t) \sim \exp(-4t^2/\tau^2)$$

we obtain a diffraction envelope of the form

$$I(\omega) \sim \exp[-(\Delta\omega)^2\tau^2/16]$$

which has at half-maximum a line width $\delta = 8\tau = 0.8$ GHz and is comparable with the isotopic shift in the atomic lines. The amplitude distortions encountered upon amplification of the driving and propagating laser pulse in the atom beam increases the line width additionally. This, clearly, also decreases the possibility of selective ionization of isotopes of rare-earth elements by using commercial copper lasers.

The characteristic values of the dipole moments of the transitions in atoms of rare-earth elements can be varied in a wide range, depending on the transition. For resonant transitions without spin change, the dipole moments amount to $D = 1-5$ a.u., and for transitions with "spin change" we have $D \cong 0.5$ a.u. The second transition is characterized by a dipole moment lower by one order, $D \cong 0.1$ a.u. Let us estimate the laser-emission intensity at which the matrix element of the interaction of the radiation with the atom is comparable in the dipole approximation with the isotopic shift $\cong 1$ GHz in the atom. Putting

$$V = DE/h = D\sqrt{4\pi I/c}/h = 10^9,$$

we obtain

$$I_0 = 10^{18}\hbar^2 c/(4\pi D^2)$$

For $D = 1$ a.u. $\cong 2.3 \cdot 10^{-18}$ CGSE, the value of I_0 is 45 W/cm². In this case, assuming an emission-pulse duration $\tau = 10$ nsec and a repetition frequency 10 kHz, we obtain an average power density $W = 4-5$ MW/cm².

In this case one can estimate the maximum productivity of the laser system. Assuming the emission quantum to be equal approximately to 2 eV, we obtain for the number of quanta 10^{16} F/cm²·sec. Multiplying this number by the atom mass we obtain the maximum productivity of the method

$$Q = 3 \mu\text{g}/(\text{cm}^2\cdot\text{sec}).$$

Let us examine one more laser isotope separation problem, connected with the isotope content in natural mixture. Data on the contents of ytterbium and gadolinium are listed in Table 2.

In the case of ytterbium, greatest interest attaches to enrichment of a mixture with the isotope 168, in view of its high cost – \$100,000 per gram at 20% enrichment (Oak-Ridge data). The $6s^2-6s6p^3P$ excitation line of this isotope is completely blanked by the lines of the isotopes 171 and 173, the content of which in the mixture is 300 times higher, and correspondingly the effectiveness of exciting ytterbium 168 is only 0.3% and a maximum possible productivity at a level $10 \text{ ng}/\text{cm}^2\cdot\text{sec}$ when copper lasers are used at pump sources.

5. CONCLUSION

We have shown that the problem of laser isotope separation with an isotopic shift not exceeding 1.5 GHz, a typical value for rare-earth elements, can be solved at a productivity level 1-3 $\mu\text{g}/\text{sec}$. Many questions connected with compensation for Doppler broadening, development of methods of lowering the broadening of laser pulses both in the course of their formations as well in the course of their propagation in a strongly absorbing medium of resonant atoms have not yet been solved.

LITERATURE CITED

1. V. S. Letokhov and B. Mur, "Laser separation of isotopes," *Kvantovaya Élektron. (Moscow)*, **3**, 248 (1976).
2. M. V. Karlov, B. B. Krynetsky, V. A. Mishin, and A. M. Prokhorov, "Laser isotope separation of rare earth elements," *Appl. Opt.*, **17**, 856 (1978).
3. N. A. Lyabin, V. V. Zubov, and A. D. Chursin, "Copper-vapor active element for high-power laser systems of the generator-amplifier type," *Kvantovaya Élektron. (Moscow)*, **17**, 28 (1990).
4. H. Kopferman, L. Kruger, and A. Stuedel, "Über die Isotopieverschiebung im Spectrum des Gadoliniums," *Ann. Physik.*, **B20**, No. 6, 258 (1957).
5. J. H. Broadhurst, H. E. Gage, and D. L. Clark, "High-resolution measurement of isotope shifts and HFS for ytterbium using a CV tunable laser," *J. Phys.*, **B7**, 18, 513 (1974).
6. S. S. Alimpiev, N. V. Karlov, B. B. Krynetskii, and Yu. N. Petrov, "Laser isotope separation," *Itogi Nauki i Tekhniki, VINITI, Moscow* (1980).
7. V. S. Letokhov and V. Chebotaev, *Principles of Nonlinear Laser Spectroscopy [in Russian]*, Nauka, Moscow (1975).
8. ORNL EM Separated Stable Isotopes Price List, Rev. 3/1/1989.
9. B. B. Krynetsky and A. G. Zhidkov, "Laser separation of metal isotopes," *Laser Phys.*, **2**, 3 (1993).