1
Laser Isotope Separation in Atomic Vapors

1.1
Introduction

For the last 30 years, the investigations and developments aimed at creation of new highly efficient, alternative methods for separating isotopes of chemical elements were actively performed in some countries and attempts were made for their industrial employment. Among those methods, isotope separation with the help of laser radiation is of particular interest. The methods of atomic (AVLIS process—photoionization method) and molecular (MLIS process) isotope separation are well known and developed.

Since the early 1980s, the further development of AVLIS process was additionally stimulated and brought up to a qualitatively new level due to achievements in laser spectroscopy, and plasma physics and technique. The acceleration in this period is mainly explained by the fact that in the USA the photoionization method of isotope separation was chosen after thorough study and comparison of the above-mentioned methods from the point of view of the highest accessible efficiency for uranium isotope separation.

Throughout 1980s, Lawrence Livermore National Laboratory (USA) in cooperation with some large companies extensively developed, updated, and demonstrated the elementary basis of AVLIS. Up to the late 1980s, the noticeable success in all directions of the program was achieved. In 1989, it became possible to start with specifying the date of the development of AVLIS technology for full-scale industrial production.

On January 1990, the USA Department of Energy presented to Congress a detailed program on AVLIS technology that included the order, conditions, and the date of demonstrating equipment in operating modes as well as the date of assignment of the developed technology and of setting into operation a powerful optical factory for uranium laser separation and concentration. This program was

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approved by the Congress, and creation of new experimental demonstration equipment, a large-scale prototype of optical mill, started in Livermore.

Specialists of Lawrence Livermore National Lab had to create, demonstrate, and bring the new technology into commercial practice. The period from 1990 to 1995 was devoted to intensive preparation and carrying out a final series of demonstration tests of equipment, aimed at specifying the performance data and cost of the AVLIS process as a whole, which was needed for substantiating the full-scale production. The final strategic goal of the AVLIS program was to reduce the cost of uranium concentration via realizing new competitive technology.

During 1992–1993, an important development stage was accomplished and new-generation equipment was created. This equipment, including high-power laser systems and industrial-scale separators capable of providing the required efficiency of uranium concentration and production volumes, was subjected to complex demonstration tests. Some economical and technical problems concerning industrial production were eliminated in the course of the tests. The Department of Energy has thus come to a decision to build an optical mill.

For more than 10 years, the annual financing amounted to $150 million, because the AVLIS process was considered the cheapest technology for uranium enrichment to the level (the ratio of ^{235}U and ^{238}U isotopes) sufficient for using it as fission material.

The progress in realizing the AVLIS process in the early 1990s made it possible for the USA to start a new program on developing and demonstrating a technological basis for plutonium enrichment via the AVLIS process as the basic component capable of obtaining isotopically reach plutonium for military purposes.

Nuclear power plants in Japan make the basis of national power engineering. Apparently, it is believed that the difficulties inherent in nuclear power engineering are less risky than the dependence on oil import. Thus, in 1990–1995 the research and developments of the new, distinct from classical (centrifugal and gas-diffusion separation), technology of uranium isotope laser separation in atomic vapors, had got an additional acceleration. The corresponding investments to the development of the AVLIS process amounted to hundreds of millions dollars. The Japan national program devoted to solving this problem is also termed AVLIS. Ideally, the new technology of uranium enrichment should be a technology of 21st century, that is, compact, highly automated, and the safest one. In view of Japan territorial specificity, the radiation safety is of particular importance. A load on environment and the probability of radiation and chemical damage of population by concentrator wastes should be minimized.

In Japan, the works concerning the AVLIS process started at University of Osaka and Japan Energy Research Institute. Presently, the most active center succeeded in investigations and development of AVLIS technology is Laser Atomic Separation Engineering Research Association of Japan (LASER-J) in Tokyo. It is a joint industrial–government organization founded in April 1987 by nine electrotechnical companies, Japan Atomic Power Company, Japan Nuclear Fuel Industries Company, and Central Research Institute of the Electric Power Industry.

Presently, financing of the AVLIS program is of the order of $154 million (two third of this sum is provided by government budget) for creating an industrial AVLIS prototype within the next 4–5 years.

The corresponding European program is called SILVA. The most important components for laser isotope separation (LIS) are developed in France (Jilas Alcatel) and England (Oxford Lasers). In recent years, high investigation and development activity in this field has also been observed in China (Shanghai University) and Israel (Beer Shiva University).

1.2
Brief Description of the AVLIS Process as Applied to Uranium

In the beginning, LIS ideas in physical and industrial aspects were developed in the framework of national AVLIS programs on uranium enrichment. Some key steps and stages of this process are published in [64–67].

Let us briefly describe the AVLIS process as applied to uranium.

It is known that uranium conversion to appropriate fission fuel necessitates the concentration of ^{235}U from 0.7% (the natural contents of isotope in a mixture with ^{238}U) to 3%. In AVLIS technology, atomic vapor that is a natural uranium isotope mixture is obtained by electron–vacuum evaporation in a special high-vacuum technological unit. Then vapor passes from the evaporation unit to flow former, where it is shaped to a required, for example, leaf-like form. Then it comes to an interaction zone with light beams produced by a dye laser system. The dye laser system is pumped by another high-power system of copper-vapor lasers. The ionization potential for uranium is $U_{\text{ion}} = 6$ eV; the isotopic shift of uranium levels amounts to 0.08 cm^{-1}. Then uranium atomic vapor is photoionized in the interaction zone via a three-step excitation process. The spectral width of radiation, the operating wavelengths λ_1, λ_2, λ_3, and the average power of dye laser beams are matched in such a way that after absorbing three sequential quanta of light at specified uranium atom transitions, only the required isotopes would be excited in cascade and photoionization processes. The operating levels of uranium atom are schematically shown in Fig. 1.1. Quanta of energy for each transition are near 2 eV. The choice of particular levels is a rather complicated spectroscopic problem. Uranium possesses a branched system of atomic levels and has many valence electrons. The wavelengths of possible laser sources are also shown in Fig. 1.1 [27].

When a copper-vapor laser pumps dye lasers, all three wavelengths of the dye lasers are chosen in the red spectral range because a uranium atom has allowed transitions between levels suitable for efficient cascade excitation in this range (590–600 nm). In the three-step scheme, an atom at the upper autoionization

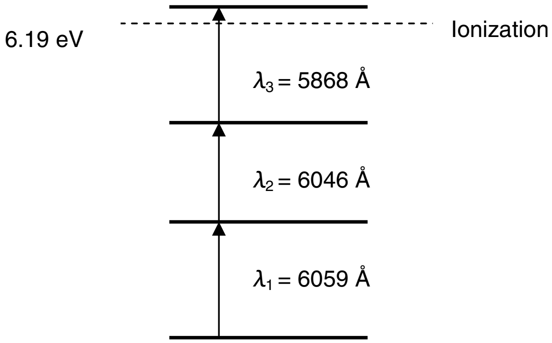

Fig. 1.1 Photoionization of a uranium atom.

level decays into electrons and ions, that is, it is ionized. High selectivity of the preferred ionization for the desired isotope is obtained at all cascade-excitation steps due to fine matching between the frequencies of tunable lasers and the energy levels of the uranium atom. ^{235}U isotopes ionized in this way are extracted from the interaction zone by an electric field and are directed to collector plates where they are neutralized and condensed as the final product of separation.

1.3
General Description of the AVLIS Process

The method of isotope separation considered above has a long history (more than 30 years). The list of papers devoted to the description of this method would make dozens of pages. In this section, we consider only principal features of the AVLIS method. A more detailed description can be found in [20]. A detailed consideration of the method applied, in particular, to ytterbium isotope separation is given in review [19].

The AVLIS method is based on multistep isotope-selective ionization of atom. Generally speaking, the upper excited level can be ionized in different ways. Conventionally, a laser radiation is used. Isotope-selective excitation of atom became possible by means of a frequency-tunable laser radiation with the spectral line width less than the specific frequency differences between the absorption lines of isotopes under consideration.

One important problem with the method considered is the choice of a photoionization scheme. It may be a two-level, three-level (see Fig. 1.2), or four-level scheme. The choice is mainly determined by the laser source. Most of the atoms have such a structure of energy levels that the first-transition radiation (with the wavelength λ_1 in Fig. 1.2) should lie in the visible or UV spectral range. For the second transition, the IR radiation may be used. The corresponding lifetimes are

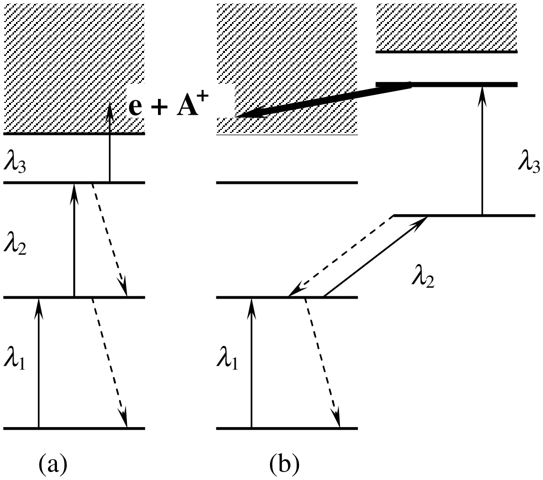

Fig. 1.2 Stepwise ionization: (a) direct photoionization; (b) ionization via the autoionization state (heavy line). The dotted lines designate the radiation decay channels for levels; the thick arrow refers to the decay of the autoionization state into electrons and ions.

usually not very long and lie in the range 3–200 ns (we do not consider excitation of metastable or Rydberg levels).

To avoid losses to spontaneous emission one should employ pulse-periodic sources of laser radiation with the pulse duration lying in the range mentioned.

The characteristic excitation time for a level is determined by the formula $\tau = (\sigma\Phi)^{-1}$, where σ is the absorption cross-section and Φ is the quantum flux. The energy of the pulse per unit area is $W = h\nu\Phi\tau = h\nu/\sigma$. The magnitude of σ is at least 10^{-15} cm^{-3} even in the case of Doppler broadening. For the characteristic quantum energy of 1 eV we have $W \simeq 160$ μJ cm^{-2}. At the pulse repetition frequency of 10 kHz (the typical frequency for pumping pulses) we obtain that the required power is in the range 1–2 W cm^{-2}. The radiation power of modern laser sources noticeably exceeds this value in UV, visible, and IR spectral ranges.

Energy levels are excited by moderate energy, whereas direct photoionization necessitates energy a few orders higher. This is explained by the small cross-section of photoionization, which is 10^{-17}–10^{-18} cm^2. Under the above-mentioned conditions, the average power of the ionizing radiation is estimated as 100–1000 W. The low cross-section of direct photoionization results in a weak absorption of the ionizing radiation. Hence, the optical density is a few orders lower than the corresponding value for the radiation exciting atomic levels. A serious problem of matching optical paths arises at various steps of photoionization. The photoionizing process will mainly determine the energetics of isotope selection.

Ionization via the decay of autoionization levels can be used instead of direct photoionization (see Fig. 1.2b). Such levels lie higher than the first ionization potential. Emission lines from autoionization states are observed in most of chemical elements. Presently, identification of autoionization levels, and refinement of their positions and lifetimes are a subject of intensive investigations. The cross-section of such levels may amount to 10^{-15}–10^{-16} cm^2. Hence, the problems mentioned above are to a certain degree tempered. Search for appropriate autoionization levels is one of the most important problems in spectroscopy. By tuning the frequency of a tunable laser one can find from the electron yield due to ionization or luminescence processes the efficiency of exciting autoionization levels. The radiation lifetime of autoionization levels is usually a few orders longer than the time of atom autoionization decay into electrons and ions. Hence, we can neglect the losses related to spontaneous emission from such levels.

Conventionally, the isotopic structure with hyperfine line splitting is rather dense and overlapped with Doppler broadening. In this case, the Zeeman effect can be used by applying a magnetic field in order to separate the lines by a frequency shift sufficient for selective excitation of atoms. In particular, this method is recommended for palladium isotopes [68].

One more method of photoionization is to excite long-living Rydberg states lying close to the ionization threshold. A relatively high ionization cross-section and proximity to the ionization threshold make employment of powerful infrared lasers (CO_2, CO, etc.) probable.

Under an electrostatic field applied, Rydberg levels shift. If then the electric field is switched off, some high levels may become higher than the ionization threshold and the atom may decay into electrons and ions. A drawback of such ionization via Rydberg states is a high sensitivity of the state positions to weak induced external electric fields, which smears the levels and hinders their excitation.

1.4
Theoretical Description of the AVLIS Process

We have considered above some basic methods of photoionization. Two physically different cases are observed in actual investigations of laser isotope separation. In the first case, incoherent interaction between radiation and atoms occurs, whereas in the second case this interaction is principally of coherent character. In the incoherent interaction model, radiation is considered as a flux of photons, which excite or de-excite atomic levels. The radiation itself is described by transport equations for a flux of particles. This approximation is often used in laser kinetic calculations. Equations for incoherent approximation are considered in more details in many papers, see, for example, review [19].

Coherent interaction of radiation with atoms is considered by means of a density matrix and the radiation itself is described by the equation for the electric field intensity that follows from the Maxwell equations.

Incoherent interaction between radiation and atoms occurs if the radiation coherence time or time of level transversal relaxation is much shorter than the characteristic time of variations of the atomic level population (actually it is comparable to the radiation pulse duration). In the opposite case, the interaction is of coherent character.

If the isotopic frequency shifts lie in the gigahertz range, then the selectivity of atom excitation is provided by the radiation with a considerably broad spectral width of line (0.5–1 GHz). This value is in accordance with the estimate $\Delta\nu\tau_{\mathrm{coh}} \simeq 1$ (here $\Delta\nu$ is the effective line width and τ_{coh} is the characteristic coherence time) corresponding to the coherence time $\tau_{\mathrm{coh}} \simeq$ 1–2 ns. An actual pulse duration of the frequency-tunable visible or UV radiation lies in the range 5–50 ns. Hence, the coherence time is much shorter than the duration of the radiation pulse and the process of isotope separation can be described in the approximation of incoherent interaction. If the isotopic shifts are less than 1 GHz, then the incoherent approximation is rarely applicable.

1.4.1
Theoretical Description of the Method for Incoherent Interaction Between Radiation and Atoms

We have considered some basic photoionization methods. However, physics of level excitation may differ for radiation pulses with different durations and line widths. At early investigation stages, mainly a broadband radiation was used. The spectral width of radiation exceeded the inverse pulse duration time or inverse radiation lifetime. Under these conditions, the analysis may be performed in the incoherent approximation of the interaction between radiation and atoms.

The method of isotope separation considered in the case of incoherent interaction can be described in the framework of the kinetic model, which is widely used for the analysis in gas laser physics. We will assume Doppler distribution of atoms over velocities. Let us first consider the point model without taking into account spatial variations of parameters. For better perception we also assume that the spectral width of the atomic absorption line is far less than that of the radiation line and of Doppler profile. Later, we will make corrections for the case where such assumptions are not applicable.

Under the conditions mentioned, we may assume that binary impacts between atoms and photons corresponding to frequency ν occur during the radiation pulse. For such cases, we will employ the density of atoms and photons per unit frequency interval and for other cases the total particle concentration will be assumed. As is shown in Appendix A, the kinetic equations can be obtained automatically. It suffice to indicate all the processes in the form of chemical reactions with the corresponding rate constants. Reactions given below are the same for all isotopes.

Excitation and depopulation of atomic levels by radiation is described by the following reactions:

$$N_i + h\nu_i \Rightarrow N_{i+1}; \qquad \alpha = ck_i(g_{i+1}/g_i)$$
$$N_{i+1} + h\nu_i \Rightarrow N_i + h\nu_i + h\nu_i; \qquad \alpha = ck_i$$

Here N_i is the atom at the ith level; $h\nu_i$ refers to the radiation in a transfer from the $(i+1)$st to the ith level. To the right of the reactions, the corresponding rate constants are given, where c is the speed of light; g_i is the statistical weight of the ith level; and $k_i = A_{i+1}\lambda_i^2/(8\pi)$ (λ_i is the wavelength and A_{i+1} is the Einstein factor for the transition considered).

The photoionization reaction looks like

$$N_{\text{up}} + h\nu_{\text{ion}} \Rightarrow N^+ + e \tag{1.1}$$

where N_{up} is the upper level in the stepwise scheme of photoionization; $h\nu_{\text{ion}}$ refers to the ionizing radiation; and N^+ and e denote ions and electrons, respectively. The rate constant depends on the details of atom excitation to the autoionization state. It is worth noting that the corresponding experimental data seem to be more reliable than the theoretical formulae available.

If a spontaneous decay of level occurs at the preceding level in the scheme of stepwise ionization, then we can write

$$N_{i+1} \Rightarrow N_i; \qquad \alpha = A_{i+1} \tag{1.2}$$

and if the decay occurs at the levels that are not taken into account in the model, then we can write

$$N_{i+1} \Rightarrow \quad ; \qquad \alpha = 1/\tau_{i+1} - A_{i+1} \tag{1.3}$$

Here, τ_{i+1} is the total radiation lifetime of the level.

In certain cases, one should also take into account the reaction of energy transfer in impacts from the atom of one isotope to the atom of another isotope:

$$N_i^* + N_j \Rightarrow N_j^* + N_i \tag{1.4}$$

where the indices refer to different isotopes.

The concentration of atoms can be limited above due to the charge exchange reaction for ions:

$$N_i^+ + N_j \Rightarrow N_j^+ + N_i \tag{1.5}$$

The rate constants for the reactions depend on the distribution function of particles over velocities. Calculation of rate constants for a particle flux is a complicated problem and beyond the scope of this book.

The impact of heavy particles will be considered in more details in Chapter 3.

The reactions considered describe mainly a conventional point model of the process of pulse radiation. Nevertheless, this model neglects the possibility of superluminescence from one of the considered levels to the levels that are not directly excited by radiation in the process of stepwise photoionization. The latter factor is important if the upper state comprises Rydberg states. The cross-sections of induced transitions between them are so high that a superluminescence occurs at the density much lower than a typical operating concentration of atoms. A mathematical model of cascade superluminescence is presented in Section 5.4.3.

In lifting restrictions on the widths of the atomic absorption line and radiation line, one should make certain corrections. The excitation and de-excitation rate constants are multiplied by the parameters depending on the line profiles.

Let the profile of the atom absorption line be given by the normalized function $L(\nu)$. Then, these parameters are

$$\alpha_N(\nu) = \int_0^\infty \frac{n_{\mathrm{ph}}(\nu' - \nu)}{n_{\mathrm{ph}}(\nu)} L(\nu') d\nu', \qquad \alpha_s(\nu) = \int_0^\infty \frac{N_i(\nu' - \nu)}{N_i(\nu)} L(\nu') d\nu'$$

where n_{ph} is the photon density at the corresponding transition.

In the equations for level populations, the rate constants of excitation and de-excitation by radiation are multiplied by α_N. In the equations for photon density, the rate constants are multiplied by α_s.

In a one-dimensional model, variables depend on the coordinate along the laser beam. The only change to be made in writing the equations is to substitute the ordinary derivative by a substantial one in the photon density equation:

$$d/dt = (1/c)\partial/\partial z + \partial/\partial t \tag{1.6}$$

where z is the coordinate along the laser beam.

1.4.2
Features of Coherent Two-Photon Excitation

Development of the laser technique resulted in an extremely small width of the radiation line limited only by the pulse duration. A typical pulse duration of most powerful sources of tunable radiation is in the range 5–50 ns, which is close to the characteristic time of level radiation decay. In this case, the coherent model of the interaction between radiation and atoms should be used. The model is based on the Liouville equation for the density matrix of a multilevel system:

$$i\hbar(\partial/\partial t + \hat{\Gamma})\hat{\rho} = [\hat{H}_0 + \hat{V}, \hat{\rho}] \tag{1.7}$$

where $\hat{\Gamma}$ is the operator describing system relaxation; $\hat{H}_0$ is the Hamiltonian of the undisturbed system; and $\hat{V}$ is the operator responsible for the interaction with the electric field of radiation.

A detailed writing of Equation (1.7) will be given in Chapter 5.

In the coherent approximation, excitation of the third upper level is not considered as subsequent excitation via an intermediate level. Interaction of a multilevel system with radiation occurs as a single process. Under optimal conditions, it is possible to obtain almost 100 % excitation of the upper level at an extremely narrow exciting line. This is the advantage of the coherent excitation as compared to a conventional scheme, where the absorption lines can undergo field broadening by the radiation and by decay radiation of levels. In the coherent case, the frequency tuning may help reduce an influence of an intermediate level on the excitation efficiency and on the width of the absorption line. Coherent two-photon excitation will be considered in particular examples in Chapter 5.

1.4.3
Evaporation of Separated Material, Collimation of an Atomic Beam, and Ion Extraction

In addition to the consideration of photoionization problems, the AVLIS method requires solving some other important problems. Generally, isotope separation includes the following stages: evaporation of material; producing a collimated atomic beam; ion extraction and acquisition of certain isotopes at collectors; photoionization of atoms; and gathering and extracting atoms not subjected to photoionization (excavation system and gas evacuation from the working chamber), see Fig. 1.3.

Volatile elements can be obtained with a crucible-type vapor source, where material is evaporated in a closed volume and gets out through slits. At high pressure, a gas-dynamic jet can be formed in the evaporation chamber. In the latter case,

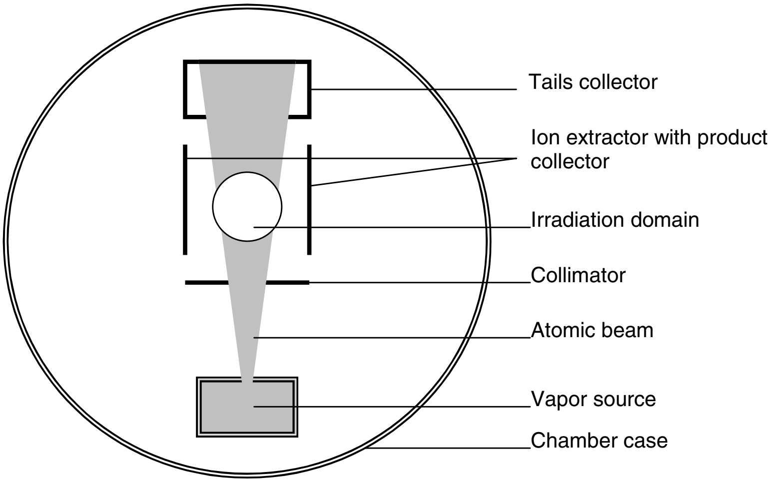

Fig. 1.3 Schematic diagram of installation in a cross-sectional view.

clusters capable of scattering and absorbing radiation may probably be formed. At low pressure, collision-free gas flow is used. The advantage of the crucible evaporation method is simple construction and low voltages applied across heating elements.

Electron-beam evaporator may be an alternative vapor source. Its principle of operation is as follows. An electron beam hits the surface of the material to be evaporated and heats it to a high temperature, so that gas-dynamic vapor flow is produced. While expanding, the vapor is cooled, which results in low temperatures in the irradiation zone ($\simeq$ 200 K). Such a temperature favors the reduced Doppler broadening and lower concentration of low metastable atomic states. High voltage, high coefficient of reflecting electrons from a surface, and undesirable vapor ionization are drawbacks of the method.

In view of hyperfine splitting, the isotope line structure is partially or completely overlapped by the Doppler profile in most of the atoms. Collimation of an atomic beam is used to reduce the Doppler width. Across the vapor path, the construction is placed made of tubes or plates with slits. By this way, a rather narrow atomic beam is separated from the flux with comparatively small velocity deviation along the radiation beam. Atoms not passed through the slits are removed by the gas-evacuation system. It is a great drawback of the collimation system that only negligible part of the atomic beam passing from the evaporator is used in the isotope separation process. The remaining atoms produce an undesirable background, which reduces the selectivity of isotope separation because atoms may fall to the collectors intended for specific isotopes. High vacuum needed in this case ($10^{-6} - 10^{-7}$ Torr) requires employment of a cumbersome pumping system.

An extractor is used to draw out ions from the atomic flux. There are various methods for extracting ions. The most known one is electrostatic extraction. A voltage is applied across the electrodes of the extractor, which provides ion extraction at the cathode.

The photoionization results in producing quasi-neutral plasma. The time of electric field penetration into the plasma depends on the density of the latter. Under a voltage pulse, the plasma polarizes due to shift of electrons toward the anode. A thin (relative to the electrode separation) layer of ions outcrops at the cathode: $d = (U/2\pi en)^{1/2}$, where U is the potential difference and n is the plasma density. Under standard conditions ($n = 10^9$ cm^{-3} and $U = 100$ V) the estimate yields $d \simeq 0.3$ cm. All the potential difference is applied across this layer. Then it is depleted of ions due to their passing to the cathode. Hence, the cathode layer width increases and the boundary of the quasi-neutral plasma shifts to the anode. Efficient ion extraction occurs when the cathode layer width becomes close to the separation between the electrodes. It is also required that the transit time in the plasma was longer than the extraction time. As is shown in [69], in the plasma with density 10^{10} cm^{-3} the extraction time is $\simeq$ 100 μs at the separation of 2 cm between the electrodes, which is much longer than the time of the plasma passage through the electrode zone.

The situation becomes better if the voltage between the electrodes is constant and the plasma enters this domain permanently. Such a regime can be realized by means of photoionization in the domain behind the extraction zone along gas flow and at high repetition frequency of pulses, where the transit time is not longer than the time interval between pulses. The latter condition can be realized at conventional repetition frequencies ($\geq$ 10 kHz). In this case, the stationary layer of the cathode drop is established that expands up the flux. Estimates show that at acceptable distances between the electrodes the ion extraction can be efficient.

At a higher plasma density, the role of electron gas pressure becomes noticeable, which is higher than the pressure of ions because of the higher electron temperature [69]. Electron gas tends to expand and involve ions producing ambipolar flux to peripheral of the extraction zone. Plasma expansion occurs at the speed of the ion sound. The extraction time for the interelectrode separation of 2–3 cm is estimated as 20–60 μs, which also exceeds the characteristic transit time for the plasma. The plasma also expands in the longitudinal direction, which reduces the number of ions hitting the electrodes. In addition, ions motion toward flux increases the probability of undesirable charge exchange in impacts with neutral atoms.

The limiting plasma density is estimated to be 10^{10} cm^{-3} in the extraction processes described above.

An alternative extraction method is crossed electric and magnetic fields. It is known that the electric field in plasma accelerators penetrates quite dense quasi-neutral plasma. This is possible due to drastic fall in the mobility of magnetized electrons along the electric field direction (see Fig. 1.4). For electrons to be magnetized, their Larmor radius should be much shorter than the separation between the electrodes. In contrast, the Larmor radius for ions is much longer than this separation. Strongly magnetized electrons drift at the velocity cE/H along equipotential surfaces (see Fig. 1.4), thus forming the Hall current, whereas ions accelerate in an electric field not affected by magnetic forces. Since there is no electron drift in the direction of the electric field, the latter almost completely penetrates the plasma.

The principle of ion acceleration is quite clear; however, in practice, there are certain difficult problems: to shunt the Hall current; provide emission of electrons, compensating ions departure to the cathode; match extractor geometry with the construction of a separation chamber, etc.

According to calculations [69], in the Hall extractor the ion density may be as high as 10^{12} cm^{-3}.

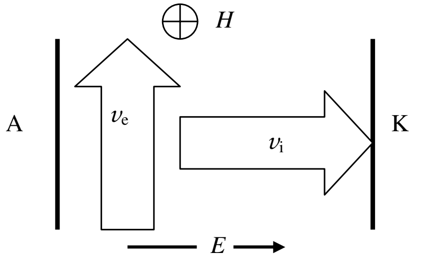

Fig. 1.4 Ion acceleration in crossed electric and magnetic fields (v is the drift velocity).

1.5
Photochemical Laser Isotope Separation in Atomic Vapors

Long-term intensive investigations of the laser photoionization method for isotope separation revealed the following drawbacks in industrial employment:

- large volumes of separation chambers needed because the density of the separated isotope is low;
- maintaining high vacuum in order to avoid a background density of atoms;
- complicated cumbersome optical systems needed for aligning and focusing beams with the optical length of dozens or hundreds of meters;
- a complicated system for ion collimation and extraction;
- the necessity of using gas fluxes at near-sound velocities, which results in that atoms are irradiated only once during the transit time.

These drawbacks are absent in the laser photochemical method of isotope separation, though it has its own negative features. However, historically the photoionization laser method for isotope separation was preferred. The photochemical method did not actually develop. Only in the last few years the interest to this method has tend to increase and the prospects were being determined.

Rapid evolution of photochemistry reveals a large number of photoinduced reactions. It seems that for most of the chemical elements, specific reagent can be found capable of binding excited atoms, thus forming a molecule. However, in a fundamental state an atom has no energy sufficient for breaking chemical binds and it does not chemically react with reagent. The molecules formed in this way may be separated from a gas mixture by known physicochemical methods.

The development of a laser technique made it possible to selectively excite any atomic level of a particular isotope. For laser isotope separation, long-living (metastable) states are preferred. This is explained by the following. It is obvious that the chemical interaction probability for an excited atom should exceed the probability of radiation decay of the level, that is, the condition

$$k^* N > 1/\tau \tag{1.8}$$

should hold, where k^* is the rate constant of the reaction; N is the concentration of reagent molecules; and τ is the radiation lifetime. The molecule concentration is limited to the approximate value 10^{17} cm^{-3}. At higher concentrations, the undesirable impact broadening of lines becomes noticeable (see Chapter 3) as well as the isotope exchange given by the reaction

$$A_1R + A_2 = A_2R + A_1 \tag{1.9}$$

where A_1 and A_2 are two different isotopes and R is a molecular group. Hence, even at sufficiently high rate constant ($k^* = 10^{-10}$ cm^{-3}) the condition $\tau \gg 100$ ns should be met. Consequently, the excited states in which an atom reacts chemically are interesting if their radiation lifetime is not shorter than 1 µs.

Possible schemes for exciting long-living levels are shown in Fig. 1.5. The simplest one is single-photon excitation of a long-living level (see Fig. 1.5a). If the isotope structure of levels is smoothed by the Doppler profile, then the isotopic selectivity is provided by frequency detuning from the central radiation frequency (see Chapter 4).

One more scheme is based on two-photon excitation of a high level followed by a decay into a long-living state (see Fig. 1.5b). The decay may occur due to spontaneous transitions as well as result from the development of superluminescence from the upper level. For the intermediate level, a long-living one is preferable, because it can be populated due to spontaneous emission from the upper level. Coherent two-photon excitation of the upper level is desirable because of its higher selectivity. With oncoming radiation beams, it is possible to noticeably reduce the width of the Doppler profile under two-photon excitation. The scheme considered has been used for separating zinc isotopes (see Chapter 5).

Metastable states are often disposed lower than the resonance level (Pb, Ba, Cu, Au, Mn, Eu, etc.). In this case one can employ the scheme shown in Fig. 1.5c. Two-photon coherent excitation is also preferable (in addition to the reasons mentioned above it helps in suppressing the superluminescence from the upper level

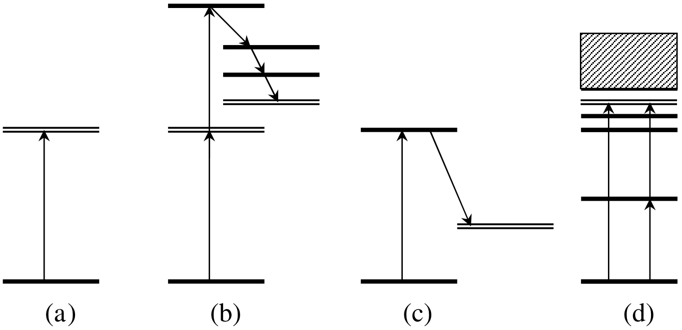
(a) (b) (c) (d)

Fig. 1.5 Photoexcitation of long-living states (marked with a double line).

to a metastable level, which prevents the broadening of the absorption line and hindering the isotope selectivity during excitation).

Rydberg levels reveal high chemical activity due to a long distance between the valence electron and nucleus. Such levels are naturally long-living. Single- and two-photon schemes for exciting Rydberg states can be used (see Fig. 1.5d). A single-photon scheme was realized for separating rubidium isotopes (see Chapter 4).

In the photochemical method of isotope separation, the concentration of atoms is limited by the resonance transfer of excitation between atoms of different isotopes. This process certainly worsens the excitation selectivity. A cross-section of the excitation transfer in the dipole–dipole approximation is inversely proportional to the lifetime of the upper level [70]. The dipole momentum of a long-living state is not large and we may hope that the cross-section would be by a few orders lower as compared to typical conditions of the excitation transfer from a resonance level, in which case it is in the range 10^{-12}–10^{-13} cm^{-2} [70]. Estimating the cross-section of the excitation transfer by the value 10^{-13} cm^{-2} we obtain the above limit for the atomic concentration of the order of 10^{13} cm^{-3}. This value is three orders of magnitude higher than the limiting atom concentration acceptable in photoionization isotope separation.

The optical thickness in the photochemical method is much greater as compared to the photoionization method due to high concentration of atoms. The dimensions of the chamber are far smaller. A possibility arises to directly excite long-living levels, including metastable ones. Isotope-selective excitation of atoms becomes real at the frequency detuning from the central part of the absorption line equal to several Doppler widths (see Chapter 4). The velocity of gas flux reduces to 1–10 m s^{-1} and is provided by simple gas pumping through the chamber. Both the transversal and longitudinal gas flux are possible relative to the laser beam. These obvious advantages of the photochemical method for isotope separation stimulated intensive investigations of this approach. Investigations of isotope separation by the laser photochemical method on a large-scale installation in Russia were started only a few years ago; however, the results obtained show that this method can compete with the conventional photoionization method.

1.6
Other Methods of Isotope Separation

For separating small quantities of isotopes in atomic vapors some alternative methods were developed. Let us briefly discuss only two of them.

In [71], the method is described based on the effect of light pressure on atoms. The laser radiation crosses the atomic beam at a right angle. The radiation frequency is matched to excite certain isotopes. By absorbing light quantum, the atom acquires the momentum h/λ in the transversal direction with respect to the atomic beam. Spontaneous decay of a resonance level imparts a momentum of the same value, however, of an arbitrary direction to the atom. On average, the atom acquires a momentum Nh/λ, where N is the number of photon absorption events. Finally, such atoms escape atomic beam and isotopes are separated.

Another method is based on the known fact that particles with the magnetic momentum distinct from zero deviate from their trajectory in a nonuniform magnetic field. If an atom is excited to the state with the magnetic quantum number $m \neq 0$, then it acquires a magnetic momentum. It can be done by means of resonance radiation with circular polarization. It is important that if the level with $m \neq 0$ decays into metastable levels, then the latter acquire an average magnetic momentum distinct from zero. In a magnetic field, the upper level splits into sublevels with different m numbers. In this case, isotope-selective excitation simplifies, because the overlapping of the radiation lines of different isotopes can be avoided. In a nonuniform magnetic field, selectively excited atoms with nonzero magnetic momentum decline from a primary trajectory (see Fig. 1.6); the isotope composition in the atomic beam changes. In this way barium isotopes were separated [72].

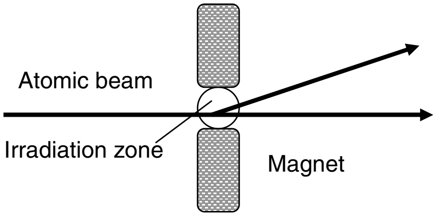

Fig. 1.6 Deviation of polarized atoms in a nonuniform magnetic field.

As far as LIS is concerned, the method of so-called photoinduced diffusion of atoms and molecules in the field of a monochromatic traveling wave [73–76] seems promising. The essence of the effect is that the velocity distribution for particles in excited or unexcited states becomes, due to the Doppler effect, asymmetric under the action of radiation with the frequency slightly different from that of atomic or molecular transition. In a mixture of buffer gas, such asymmetry results in an origin of the flux of absorbing particles directed along or opposite to the direction of radiation depending on the frequency detuning. By varying the experimental conditions, mainly the frequency detuning, one can spatially separate different isotopes. In [77], it is reported about approximately 70 % enrichment with respect to isotope ^{13}C in working with CH_3F molecule.