

# Laser detection of single atoms

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This review deals with the problem of selective detection of single atoms by laser radiation. It begins with a classification of the detection methods (fluorescence, photoionization, deflection), discusses detection conditions (atomic vapor, atomic beam, buffer gas), and gives estimates of the parameters of laser radiation ensuring effective detection. Next, a detailed comparison is made of each of the detection methods. It is shown that in the fluorescence method the maximum efficiency of the detection process is achieved for cyclic interaction of atoms with laser radiation. In the photoionization method the most suitable technique is multistage photoionization of atoms by laser radiation. The highest ionization selectivity and a high efficiency are obtained by multistage excitation of an atom either to a Rydberg state followed by ionization with an electric field pulse or to a narrow autoionizing state with a large excitation cross section. Both these techniques are considered from the point of view of the sources of background and ways of discriminating against it, detection selectivity, and absolute sensitivity; the experimental results are analyzed. In discussing the deflection method consideration is given to deflection of an atom in a magnetic field after excitation with laser radiation and to deflection of atoms by resonant optical pressure. The review concludes with a brief discussion of the prospective applications of these detection methods in nuclear physics, atomic physics, and chemistry.

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## 1. INTRODUCTION

The problem of detection of single particles has been solved in experimental physics to various degrees depending on whether the particles in question are charged or neutral, and if they are neutral, then the detection

efficiency depends strongly on their energy.

Detection of charged single particles is a well-developed branch of experimental nuclear physics.<sup>1,2</sup> It is based on the fact that a charged particle can acquire a considerable energy in an electric field and on passing

through matter it can cause ionization and excitation of a large number of atoms and molecules which can then be easily detected, sometimes even without any additional instruments. This has been the operating principle of the earliest fluorescence counters in which the fluorescence was observed visually. A great variety of counters utilizing the ionization effect is now available (for example, the Geiger-Müller counter, ionization chamber, crystal counter, etc.).

Neutral particles such as neutrons or  $\gamma$  quanta, do not cause ionization or excitation directly but their passage through matter creates secondary charged particles (recoil nuclei, electrons, ions, electron-positron pairs, etc.) which can be detected. In the case of the most widely encountered neutral particles—atoms and molecules—the situation is much less favorable. Some atoms can be detected when they hit a surface because of the surface ionization effect,<sup>3</sup> but this detection method is not universal and it suffers from low selectivity. This large difference between the efficiencies of detection of charged or high-energy neutral particles and of low-energy neutral atoms or molecules is self-evident. Detection of a particle requires that a significant effect be produced in a detector and a neutral atom or molecule is usually incapable of producing such an effect. Therefore, the problem of detection of single atoms and molecules has remained unsolved in physics and only very recently new laser methods have been suggested and implemented. The present review deals with these methods. We shall discuss only the detection of atoms. Some of the methods considered below, particularly the photoionization method, have been applied with great success to molecules. However, on the whole the problem of detection of single molecules even by means of laser radiation is far from completely solved and we shall postpone discussion of this problem to some future date. Readers interested in all the problems of laser spectroscopy, including detection of molecules present in a very low concentration, are directed to the existing reviews and monographs.<sup>4-6</sup>

### a) Classification of methods

The three main laser methods for selective detection of single atoms are shown schematically in Fig. 1. They utilize all the effects resulting from a resonant interaction of an atom with light. Firstly, in a resonant field an atom emits spontaneously the absorbed radiation and the resultant fluorescence photons can be detected (Fig. 1a). Detection of a single atom is possible

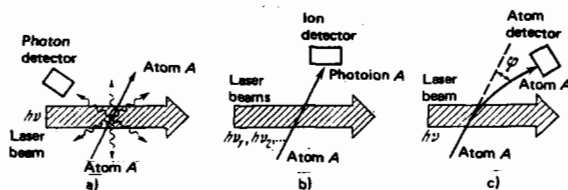


FIG. 1. Mechanisms of interaction between laser radiation and atoms, which can be used to detect atoms: a) spontaneous emission from an excited atom and detection of the emitted photons; b) photoionization of an atom and detection of the resultant ion and electron; c) deflection of an atom because of a resonant optical pressure and detection of the deflected atom.

if during the time of interaction with the laser field an atom emits a number of photons sufficiently large for the light-collecting system and photodetector to produce a clear useful signal. Secondly, multifrequency laser radiation can produce a resonant selective ionization of an atom (Fig. 1b) with a quantum efficiency close to unity. The resultant photoion can then be detected reliably by the available methods. Finally, interaction of an atom with an optical field can alter the trajectory of its motion (Fig. 1c). This is possible either because of the transfer of momentum from a laser beam to an atom in the case of repeated reemission of photons or because of a change in the nature of motion of an atom in an external electromagnetic field caused by a change in its polarizability or magnetic moment as a result of laser excitation.

The first two methods—fluorescence and photoionization—are fairly universal and efficient. Laser radiation ensures both high selectivity and high detection efficiency. The selectivity due to the resonant nature of the interaction of laser radiation with atoms and the detection efficiency is ensured by the ease of subsequent detection since either a large number of fluorescence photons or an easily detected photoion is produced. Both methods are suitable for atoms in a vapor, buffer gas, or atomic beam. The third (deflection) method is much less universal and efficient. In this case, laser radiation ensures only detection selectivity because of the resonant nature either of the recoil or of the change in the quantum state of an atom. It leaves unresolved the problem of detection of a neutral low-energy atom. Therefore, this method is suitable only for atoms of, for example, alkali metals which can easily be detected by the surface ionization technique. It is possible to combine the deflection and fluorescence or photoionization methods. Moreover, the deflection method is suitable only for atoms in a beam.

### b) Formulation of the problem

The problem of detection of single atoms can be considered in several variants which depend on the conditions of the experiment in which a small number of atoms of some element is produced (Fig. 2). Atoms in a vapor at a very low pressure cross randomly the zone of interaction with laser radiation (Fig. 2a). In this case the absorption line is broadened by the Doppler effect and it is necessary to illuminate the whole of its Doppler-broadened profile. In an experiment of this kind the resolution is limited by the Doppler effect

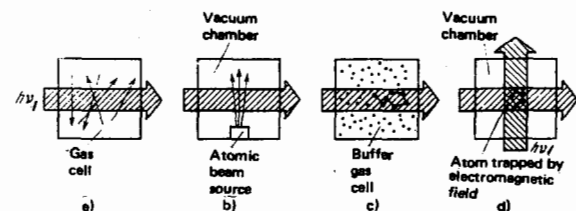


FIG. 2. Different cases of motion of an atom in the irradiated region: a) free random crossing of a laser beam by vapor atoms; b) free flight of atoms in a collimated atomic beam; c) diffusion of atoms in a buffer gas; d) prolonged residence of a trapped ultracold atom in the irradiated region.

because the velocity of an atom is not known in advance. The exception to this rule is the case of two-photon excitation of an atom in the field of a standing wave when all the atoms interact with the field irrespective of their velocity.<sup>7</sup> The transit time of an atom  $\tau_{tr}$  traveling at an average thermal velocity across a laser beam is relatively short ( $\tau_{tr} = 10^{-4} - 10^{-6}$  sec). Therefore, it is necessary to use either continuous illumination or pulses with a repetition period  $T_{rep} < \tau_{tr}$ . Otherwise a considerable proportion of atoms crosses the detection zone without interaction with laser radiation. Continuous illumination is most convenient in the fluorescence method, whereas in the multistage ionization method it is possible only to use pulses because of the rapid decay of intermediate quantum states. The scheme of Fig. 2a has been used experimentally in the fluorescence method detection of Na atoms employing a cw dye laser.<sup>8</sup>

The situation is more favorable when atoms in a colimated atomic beam are detected (Fig. 2b). In this case we have the simultaneous advantages of higher resolution and lower minimum intensity of laser radiation, which are improved by a factor equal to the ratio of the width of absorption lines for a vapor and an atomic beam. All the comments made on the scheme in Fig. 2a apply also to the case of an atomic beam. However, it should be pointed out that in the case of Fig. 2b we can use not only the fluorescence and photoionization methods, but also the atom deflection method. Experiments of the type shown in Fig. 2b have been carried out by: 1) the fluorescence method using continuous illumination (uranium,<sup>9</sup> sodium,<sup>10</sup> and barium<sup>11</sup> atoms); 2) the photoionization method using pulses applied with a repetition period  $T_{rep} \gg \tau_{tr}$  (sodium<sup>12</sup> and ytterbium<sup>13</sup> atoms); 3) the deflection method using continuous illumination (sodium atoms<sup>14</sup>).

It is worth noting that, in experiments of the type shown in Figs. 2a and 2b, atoms are lost rapidly to the walls and this requires a relatively large number of atoms to investigate the whole absorption spectrum.

Detection of atoms becomes much easier if an atom can spend a long time in the interaction zone. This lowers the laser radiation power required for detection and reduces the total number of atoms which are needed to measure its absorption spectrum. If the investigated atom is in an inert buffer gas of sufficiently high pressure (hundreds of torr), its residence time in the irradiation zone is governed by the diffusion time  $\tau_{diff}$  and can be relatively long ( $10^{-3} - 1$  sec). Diffusion confinement of an atom to the irradiation zone (Fig. 2c) is achieved at the expense of a considerable loss in the resolution because of the pressure broadening of the spectral lines. Experiments in accordance with the scheme in Fig. 2c have been made by the fluorescence method involving continuous irradiation of <sup>20</sup>Na atoms formed as a result of a nuclear reaction<sup>15</sup> and by the photoionization method in the case of pulsed irradiation of Cs atoms.<sup>16</sup> It should be noted that the pulsed operation becomes easier in the case of diffusion confinement of atoms because one can then increase the repetition period of laser pulses  $T_{rep}$  to  $\tau_{diff}$ . This is particularly

important in the implementation of the photoionization method of detection of single atoms, achieved first by Hurst *et al.*<sup>16</sup>

The ideal case is that of trapping and subsequent retention of free atoms with a low kinetic energy in an inhomogeneous electromagnetic field by gradient forces.<sup>17</sup> In this case (Fig. 2d) the time spent by an atom in the irradiated region may amount to hours.<sup>18</sup> We can then, in principle, determine the whole absorption spectrum employing just one atom. The recent first successful experiments on laser cooling of Na atoms<sup>19</sup> show that such near-ideal method is quite realistic. It should be noted that in studies of the spectra of ions which have lines in the accessible part of the optical spectrum the situation is much easier, because we can use the method of confinement of ions in an electromagnetic trap. This method has already been used in experiments involving visual observation of the fluorescence of single ions in a resonant laser field.<sup>20</sup>

### c) Tunable lasers for use in detection

Clearly, all these methods for the detection of single atoms have become practical only after the appearance of tunable lasers. Only such lasers can ensure resonant saturation of quantum transitions accompanied by repeated emission of photons or fast ionization, i.e., can ensure a sufficiently high detection efficiency. The usual monochromatic radiation sources are unsuitable for this purpose because of the extremely low rate of stimulated transitions in atoms in the field of laser radiation.

Tunable pulsed or cw dye lasers are employed in all the laser methods for the detection of single atoms (dye lasers are reviewed in Ref. 21). In the fluorescence method the most suitable are the cw lasers, which now operate over a wide range of wavelengths. For example, the commercially available Spectra-Physics M-375 dye laser model, pumped by a cw argon laser, can operate throughout the visible range of wavelengths with the aid of a number of different dyes (Fig. 3). The cw power needed in the fluorescence method is governed by the intensity of saturation of the absorption of the resonant transition employed:

$$I_{sat} = \frac{h\nu}{2\sigma_{01}\tau_{sp}}, \quad (1.1)$$

where  $\sigma_{01}$  is the cross section of the resonant transition and  $\tau_{sp}$  is the spontaneous decay time of an excited state. Usually, the saturation intensity  $I_{sat}$  lies in the range 0.01–10 W/cm<sup>2</sup>. Difficulties are encountered in

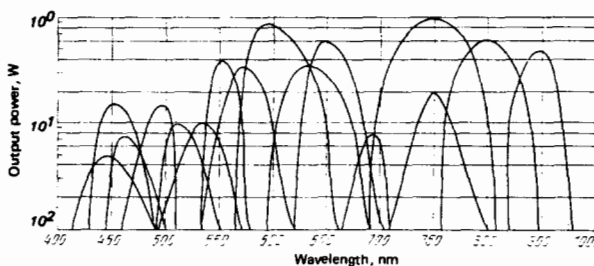


FIG. 3. Wavelength tuning ranges of a Spectra-Physics cw dye laser pumped by an argon laser.<sup>22</sup>

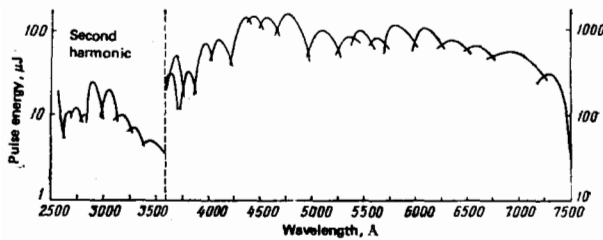


FIG. 4. Tuning ranges of a Molectron pulsed dye laser pumped by a pulsed ultraviolet nitrogen laser.<sup>23</sup>

supplying this cw power in the ultraviolet and vacuum ultraviolet range, since the harmonic generation methods are not very efficient when the power of the converted radiation is low. This restricts seriously the capabilities of the fluorescence method and it is at present suitable only for atoms with resonant lines in the visible part of the spectrum.

Pulsed tunable lasers with a high repetition frequency are the preferred sources for the photoionization method. One of the most widely used pump sources is a molecular  $N_2$  laser ( $\lambda = 3371 \text{ \AA}$ ), which ensures lasing in dyes throughout the visible range, and (with the aid of the second harmonic) can also be employed in the ultraviolet range. This is true, for example, of a commercial dye laser made by Molectron, whose tuning range is shown in Fig. 4. The power level needed for the photoionization method is again governed by the need to saturate each quantum transition by a multistage excitation scheme. The maximum quantum efficiency of the photoionization is reached when the duration of a pulse at each excitation stage is less than the decay time of the initial and final levels of the transition. Under these circumstances, saturation of a  $k \rightarrow n$  transition requires energy of density

$$\mathcal{E}_{\text{sat}}^{\text{hn}} = \frac{\hbar \omega_{\text{hn}}}{2\sigma_{\text{hn}}}, \quad (1.2)$$

where  $\omega_{\text{hn}}$  and  $\sigma_{\text{hn}}$  are the frequency and cross section of the quantum transition being saturated. The value of  $\mathcal{E}_{\text{sat}}$  lies in the range  $10^{-8} - 10^{-5} \text{ J/cm}^2$  for allowed quantum transitions and  $10^{-5} - 10^{-3} \text{ J/cm}^2$  for weak quantum transitions. The average power is governed by the pulse repetition frequency needed in the detection system.

The peak output power of a dye laser can be increased, which is extremely desirable in efficient conversion of the laser frequency to the ultraviolet and particularly vacuum ultraviolet range, employing a KrF excimer laser ( $2470 \text{ \AA}$ ) as the pump source.<sup>24</sup> A high pulse repetition frequency, needed in detection of single atoms when they cross the interaction zone rapidly, can be achieved by employing a copper vapor laser ( $5105$  and  $5782 \text{ \AA}$ ) with a repetition frequency up to  $10^4 \text{ Hz}$  as the pump source.<sup>25</sup>

## 2. FLUORESCENCE ATOM DETECTION METHOD

### a) Repeated emission of photons by atoms

In detection of single atoms by the fluorescence method the basic point is the experimental realization of repeated cyclic interaction of atoms with laser radiation,

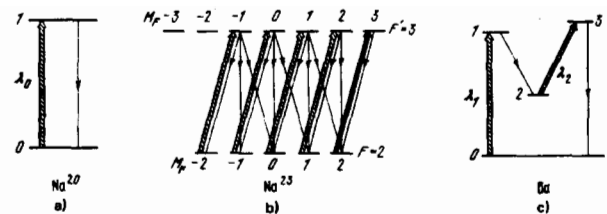


FIG. 5. Quantum transition schemes for cyclic interaction of laser radiation with atoms: a) ideal two-level scheme for an atom of  $^{20}\text{Na}$  without hyperfine structure; b) oriented  $^{23}\text{Na}$  atoms; c) universal scheme for the interaction between a two-frequency field and atoms with a metastable state.

as a result of which the atoms spontaneously emit the absorbed radiation. There are several ways of realization of such cyclic interaction of atoms with laser radiation (Fig. 5). These ways depend on the energy structure of the excited levels and on the spectrum of laser radiation used to excite the atoms.

The simplest is the case of interaction of laser radiation with a resonant transition in an atom unsplit by any hyperfine interaction, i.e., an atom with an ideal two-level quantum scheme (Fig. 5a). In this case we can ensure cyclic interaction simply if the laser radiation frequency is stable during the interaction time so that it remains within the homogeneous width of the atomic absorption line. Examples of suitable atoms are light isotopes of alkali and alkaline-earth elements, in which there are no metastable levels between the ground and first excited states (Mg, Sr, Ca).

When an atom has a hyperfine structure (Fig. 5b), there are several ways of implementing repeated cyclic interaction with laser radiation.

1) An atom may be transferred to a specific hyperfine-structure state in which it may interact repeatedly with radiation. For example, in the case shown in Fig. 5b the interaction of circularly polarized laser radiation with the  $3^2S_{1/2}, F=2 - 3^2P_{3/2}, F'=3$  transition in an Na atom results in optical pumping to the state with  $F=2, m_F=2$  and then a stimulated transition is possible only to the higher state  $F'=3, m_{F'}=3$  and spontaneous decay back to the initial state  $F=2, m_F=2$ . This method of repeated emission of photons by an atom has been used<sup>26</sup> to study the behavior of a two-level system in a strong field and to detect single Na atoms.<sup>27</sup>

2) An atom may be excited from both sublevels of a hyperfine structure by a multimode laser emitting modes separated by an energy interval equal to or a multiple of the separation between the hyperfine structure components.<sup>10, 28</sup>

3) An atom may be subjected to laser radiation of a fixed frequency but directed at various angles relative to the motion of an excited atom.<sup>29, 30</sup> For certain angles between laser beams we can expect the Doppler shift to result in simultaneous excitation of atoms from both sublevels of the ground state.

The most common method of cyclic interaction of atoms with radiation involves the use of several transitions in an atom excited by a multifrequency laser (Fig.

5c). Radiation of wavelength  $\lambda_1$  transfers an atom from its ground state 0 to an excited state 1, from which it drops to the ground state or to an intermediate metastable state 2. After transition to the ground state the atom is again excited by the same radiation and the excitation continues cyclically. If the atom drops to the metastable state 2, it can be returned to the initial state 0 via a level 3 by excitation with radiation of different wavelength  $\lambda_2$ . A similar repeated emission scheme has been used<sup>31</sup> in experiments on deflection of an atomic Ba beam by the optical pressure force and also<sup>20</sup> in cooling Ba<sup>+</sup> ions.

Let us assume that an atom crosses a laser beam whose frequency is tuned to a resonant absorption line. Then, under cyclic excitation by laser radiation the atom absorbs and emits (during the transit across the laser beam) photons whose number is given by

$$n = \frac{\tau_{tr} A_{21}}{1 + (I/\rho)} = \frac{\tau_{tr}}{\tau_{21} [1 + (I/\rho)]}, \quad (2.1)$$

where  $A_{21}$  and  $\tau_{21}$  are, respectively, the Einstein coefficient of the transition in question and the lifetime of the upper level;  $\rho$  is the ratio of the average populations of the upper and lower levels;  $\tau_{tr}$  is the transit time across the laser beam. If the intensity of laser radiation is higher than the saturation intensity of this transition, the number of emitted photons becomes

$$n_{max} = \frac{\tau_{tr}}{2\tau_{21}}. \quad (2.2)$$

It follows from Eq. (2.2) that the maximum photon emission rate  $n_{max}/\tau_{tr} = 1/2\tau_{21}$  is governed by the excited-state lifetime. For example, for a resonant transition in an Na atom characterized by  $\tau_{21} = 1.6 \times 10^{-8}$  sec, we have  $n_{max}/\tau_{tr} = 3.1 \times 10^7$  photons/sec.

## b) Sources of background and ways of suppressing it

In the fluorescence atom-detection method the sensitivity is limited by the optical background resulting from the scattering of laser radiation by parts of the cell in which the fluorescence signal is recorded. If the atoms being investigated are in a buffer gas, we are faced with an additional background signal due to the Rayleigh scattering. The methods for extracting a useful signal depend strongly on the quantum transition scheme (Fig. 5). When the schemes of Figs. 5a and 5b are used, the fluorescence frequency  $\nu_{f1}$  is identical with the frequency of the exciting laser radiation  $\nu_l$ , and, therefore, it is necessary to suppress very thoroughly the background because it is indistinguishable in respect of the frequency from the useful signal. When the scheme of Fig. 5c is used, extraction of the signal from the background becomes much easier since the excitation  $\nu_l$  and fluorescence  $\nu_{f1}$  frequencies are now different.

1) *Case with  $\nu_{f1} = \nu_l$ .* In this case the signal cannot be distinguished from the background by frequency selectors (monochromators, interference filters, etc.). The main method for the suppression of the background involves the use of a cell with a very low degree of scattering and careful collimation of a laser beam, which must have a high spectral brightness. This makes it

possible to irradiate atoms with an intensity sufficient to saturate the relevant quantum transition and still ensure a low level of nonresonantly scattered radiation.

The background reaching the photocathode of a detector during the interaction time  $\tau_{tr}$  between an atom and radiation is

$$n_{back} = \xi \frac{p_l \tau_{tr}}{h\nu}, \quad (2.3)$$

where  $p_l$  is the laser radiation power at the entry to the cell and  $\xi$  is a parameter representing the degree of suppression of the scattered stray radiation, equal to the ratio of the power of the scattered laser radiation reaching the photocathode to the power of the laser radiation at the entry to the cell.

A necessary condition for the detection of a signal (atom) is  $n_{back} \ll n_{det}$ , i.e.,

$$\xi \ll \frac{n_{det} h\nu}{p_l \tau_{tr}}, \quad (2.4)$$

where  $n_{det}$  is the number of photons emitted by an atom and reaching the photodetector cathode, determined to within an error set by the efficiency of the light-collecting system described by Eq. (2.1). For example, a low-concentration saturated Na vapor was studied in Ref. 8 using a cell with the parameter  $\xi = 3 \times 10^{-10}$ . This corresponded to a fluorescence signal due to  $3 \times 10^3$  atoms. In the detection of uranium atoms in an atomic beam in Ref. 9 use was made of a chamber with  $\xi = 2 \times 10^{-12}$  and single atoms were detected in Ref. 10 in a cell characterized by  $\xi = 10^{-14}$ .

Apart from the purely technical measures, such as the use of a high-quality cell, one could employ finer discrimination methods based on the difference between the dependences of the useful and background signals on the frequency and intensity of laser radiation, and also on the difference between the statistical properties of these two signals. In particular, additional discrimination against the background could be achieved by frequency modulation of the incident laser radiation;<sup>8</sup> in this case the fluorescence signal should be modulated in intensity and the background signal should be constant. The method of synchronous detection could additionally suppress the background. In Ref. 10, the background was discriminated against by recording the fluorescence simultaneously using two photomultipliers. Since the background radiation was completely random in time and the signal scattered by the investigated atoms gave rise, during a time interval  $\tau_{tr}$ , to a photon "flash" simultaneously at both photodetectors, one could use a coincidence circuit to discriminate the useful signal from the background.

In the case of repeated interactions of an atom with radiation and under absorption saturation conditions, i.e., when an atom emits a large number of photons during transit across a laser beam, the photons from an atom should reach a detector mainly in groups, whereas the photons of the nonresonantly scattered light should reach the detector at random times. An analysis of the number of photons arriving at the detector during the transit time  $\tau_{tr}$  of an atom across a laser beam can distinguish the photon bunches from the atoms giving rise to a useful multiphotoelectron signal from the ran-

dom photons of the scattered light producing single photoelectron pulses at the detector.<sup>11, 27, 32</sup>

It has also been suggested that the useful signal can be distinguished from the background by recording the statistics of photoelectrons during the transit time  $\tau_{tr}$  of an atom crossing a laser beam.<sup>33</sup> In principle, we can then distinguish a multiphotoelectron signal due to the successive emission of photons by the same atom from a multiphotoelectron signal due to the simultaneous emission of several background photons.

2) *Case with  $\nu_{11} \neq \nu_1$ .* It is proposed in Refs. 34 and 35 that frequency discrimination of the useful signal from atoms be performed by a detection scheme in which repeated cyclic interaction of atoms with laser radiation of one frequency and saturation of the relevant transition (ensuring a large number of photons emitted by an atom) is combined and the fluorescence signal is recorded at the shifted frequency. The idea is explained in Fig. 6. Laser radiation saturates and excited a 0-1 resonant transition at a frequency  $\nu_0$ . Collisions of excited atoms with a buffer gas transfer the excitation to a nearby level 2 and result in a further transition of the atoms to the ground state accompanied by the emission of photons at the shifted frequency  $\nu_{11}$ , at which the fluorescence signal is recorded. This method is called SONRES (saturated optical nonresonant emission spectroscopy). The method is suitable only for those elements in which the separation between the levels 1 and 2 is of the order of  $kT$ . Only then is the transfer of excitation from one level to another sufficiently effective.

Suppression of the background signal in the  $\nu_{11} \neq \nu_1$  case is ensured by the use of a monochromator or an interference filter, with a pass band whose center is tuned to the fluorescence frequency. The degree of suppression  $\xi$  of the background is governed by the Rayleigh  $K_R$  and Mie  $K_{Mie}$  scattering coefficients, the instrumental transfer function of the spectroscopic system employed  $f(\nu_1 - \nu_0)$ , and the degree of suppression of the scattered light in the cell  $\xi_0$ :

$$\xi = (\xi_0 + K_R l \Omega + K_{Mie} l \Omega) f(\nu_1 - \nu_0), \quad (2.5)$$

where  $l$  is the length of the interaction zone imaged by the optical system on the detector;  $\Omega$  is the solid angle in which the fluorescence signal is recorded. If the frequency difference  $\Delta\nu = \nu_1 - \nu_{11}$  is sufficiently large ( $\Delta\nu > 50 \text{ \AA}$ ), then the suppression of the background is influenced also by the light scattered in the spectroscopic

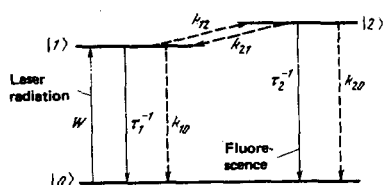


FIG. 6. Excitation of atoms by the SONRES method.<sup>35</sup> Laser radiation excites the 0-1 transition. Collisions with a buffer gas transfer the excitation to a state 2. The fluorescence signal is recorded at the 2-0 frequency. The dashed lines show the transitions due to collisions with the buffer gas.

system and it is this light that governs the maximum suppression of the background. In modern triple monochromators the degree of suppression of the background in the  $\Delta\nu > 50 \text{ \AA}$  range is  $f(\Delta\nu) = 10^{-10} - 10^{-12}$  (Ref. 36). If we bear in mind the contribution of just the Rayleigh scattering to the background, then for  $K_R = 5 \times 10^{-9} \text{ cm}^{-1}$  (Ref. 37),  $l = 1 \text{ cm}$ , and  $\Omega = 1 \text{ sr}$ , the minimum value of  $\xi$  is  $\xi_{min} = 4 \times 10^{-20}$ .

When atoms are detected by the two-frequency excitation system (Fig. 5c), the problem of suppression of the background signal is much easier to solve. In this case, cyclic excitation of atoms can be achieved in vacuum when there is no radiation scattered by the buffer gas. The fluorescence signal can again be detected at the shifted frequency  $\nu_3$  (Fig. 5c) and since usually the frequencies of the exciting radiation  $\nu_1$  and  $\nu_2$  differ greatly from  $\nu_3$ , it would not be difficult to discriminate the background from the signal. The parameter representing the suppression of the background signal then becomes

$$\xi = \xi_0 f(\Delta\nu), \quad (2.6)$$

where  $\Delta\nu$  is the minimum frequency detuning from the exciting frequencies  $\nu_1$  and  $\nu_2$  and the fluorescence frequency  $\nu_3$ .

Naturally, additional discrimination against the background can be performed by the methods mentioned above in discussing background suppression in the  $\nu_1 = \nu_{11}$  case.

### c) Detection selectivity

We shall consider a mixture of  $A$  and  $B$  atoms in which we have to detect rare  $B$  atoms against the predominant background of the  $A$  atoms. Let  $N_A$  and  $N_B$  be the concentrations of the  $A$  and  $B$  atoms in the mixture. We shall define the selectivity  $S$  of the process of detection of the  $B$  atoms against the background of the  $A$  atoms as the reciprocal of the ratio of the minimum concentration  $N_B$  detectable against the background of the  $N_A$  concentration:

$$S = \frac{N_A}{N_B}. \quad (2.7)$$

The existing optical spectroscopy methods suffer from limited detection selectivity because of the unavoidable overlap of the spectral line wings. The maximum selectivity in optical detection of the  $B$  atoms against the background of the  $A$  atoms of the same element is

$$S_0 \approx \left( \frac{\Delta\omega_{AB}}{\Gamma} \right)^2, \quad \Delta\omega_{AB} = 2\pi\Delta\nu_{AB}, \quad (2.8)$$

which is governed by the absorption of the wing of the line of a  $A$  atom at the center of the absorption of a  $B$  atom, where  $\Gamma$  is the homogeneous half-width of the absorption lines (Fig. 7a). For example, in the case of detection of rare isotopes we have  $S_0 \approx 10^4 - 10^6$ .

When laser radiation interacts repeatedly with an atom and the fluorescence signal is due to generation of  $k \gg 1$  photoelectrons by each atom, we can construct a detection system which ensures a considerable increase in the sensitivity of detection of the  $B$  atoms against the background of the  $A$  atoms.



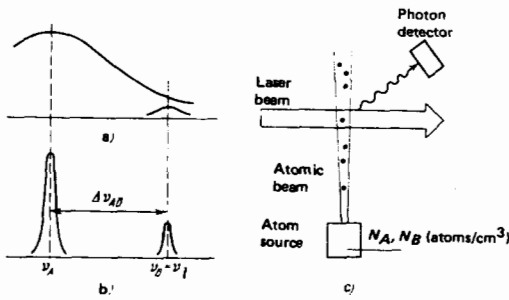


FIG. 7. Suppression of the wing of a spectral line and increase of the detection selectivity by multiphotoelectron recording of the fluorescence signal of atoms. Profiles of the fluorescence lines of the background isotope (central frequency  $\nu_A$ ) and the investigated isotope (central frequency  $\nu_B$ ) are shown on the left for combined recording of the fluorescence signal (a) and for multiphotoelectron recording (b). The arrangement for observing the spectral line from an atomic beam is shown on the right (c).

The idea for this increase in the selectivity is as follows.<sup>27,33</sup> Let us consider an atomic beam of a very low density consisting of a mixture of  $A$  and  $B$  atoms (Fig. 7c) intersecting a cw laser beam of frequency  $\nu_l$ , and let us assume that not more than one  $A$  atom is present at a given time in the interaction zone ( $N_A \gg N_B$ ); estimates of the maximum permissible atomic concentrations in this method will be given later. Let us assume that the laser radiation frequency  $\nu_l$  is tuned exactly to the frequency  $\nu_B$  of a resonant transition in a  $B$  atom and, consequently, this frequency is in the wing of the absorption line of an  $A$  atom (Fig. 7a). The intensity of laser radiation is sufficient to saturate the resonant transition in the  $B$  atoms and the structure of the quantum equations ensures that the atom returns, after fast fluorescence decay in a time  $\tau_{sp}$ , to the initial quantum state. Then, an atom of  $B$  which is in exact resonance with the laser radiation field emits on the average  $n_B = \tau_{tr}/2\tau_{sp}$  photons in the transit time  $\tau_{tr}$  across the laser beam. Since the  $A$  atoms are not in exact resonance with the field, the cross section for the quantum transition in these atoms far in the wing of a Lorentzian profile is  $(\Delta\omega_{AB}/\Gamma)^2$  times less and, therefore, an atom of  $B$  emits during transit time an average of  $\bar{n}_A = \bar{n}_B(\Gamma/\Delta\omega_{AB})^2$  photons. We shall assume that the total efficiency of the photon counting process is  $\eta$  (it represents the photon collection frequency and the quantum efficiency of the photocathode). Then, a  $B$  atom crossing the laser beam creates on the average  $\bar{k}_B = \eta\bar{n}_B$  photoelectrons and the number of photoelectrons emitted by the  $A$  atoms due to off-resonance transitions is

$$\bar{k}_A = \eta\bar{n}_A = \eta\bar{n}_B \left( \frac{\Gamma}{\Delta\omega_{AB}} \right)^2 \ll \eta\bar{n}_B. \quad (2.9)$$

If  $\eta\bar{n}_B \gg 1$  and also  $\eta\bar{n}_A \ll 1$ , the transit of the  $B$  atoms can be distinguished from the background of the  $A$  atoms by recording only the multiphotoelectron events and ignoring the signal due to single photoelectrons. The excitation spectrum of the fluorescence of the investigated atoms, obtained by recording the multiphotoelectron events, should exhibit strong narrowing of the lines and suppression of their wings, as reported in Ref. 11. This effect can be used to increase the selectivity of the fluorescence detection method.

We shall now estimate the potential detection selectivity. Let  $p_B$  be the probability of recording a  $B$  atom, i.e., the probability that a transit of a  $B$  atom across a laser beam produces photoelectrons in a number sufficient to exceed the threshold value needed for detection. Then, the detection selectivity is equal to the ratio of the probabilities of detection of a  $B$  atom against the background of the  $A$  atoms when  $\nu_l = \nu_B$ , i.e.,

$$S = \frac{P_B(\nu_B)}{P_A(\nu_B)}. \quad (2.10)$$

The probability of detecting an atom depends both on the average number of photoelectrons received from the investigated atom  $k = \eta\bar{n}$  and on the discrimination threshold  $k_{th}$  of the number of arriving photoelectrons:

$$P(\bar{k}, k_{th}) = \sum_{m=k_{th}}^{\infty} \frac{e^{-\bar{k}} \bar{k}^m}{m!}. \quad (2.11)$$

Then, the expression for the detection selectivity becomes

$$S(\bar{k}_A, \bar{k}_B, k_{th}) = \frac{P(\bar{k}_B, k_{th})}{P(\bar{k}_A, k_{th})}. \quad (2.12)$$

The increase in the selectivity due to such multiphotoelectron discrimination can be studied by determining the dependence of the detection probability  $P(\bar{k}, k_{th})$  on the detuning of the laser radiation frequency from the center of the absorption line. This was done in Ref. 33. A cw dye laser was used to determine the absorption line profile of Na in an atomic beam in the case of the transition

$$3^2S_{1/2}, F=2 \rightarrow 3^2P_{3/2}, F'=3 \quad (\lambda = 589.0 \text{ nm}). \quad (2.13)$$

The interaction time was increased (i.e., the number of emitted photons was made larger) by ensuring that the atomic beam intersected the laser beam at a small angle ( $7^\circ$ ), so that the interaction zone was 4 mm long. The average number of photoelectrons emitted per atom was  $\bar{k} = 1.8$ . The frequency dependences of the amplitude of the signal due to the Na atoms in the atomic beam were determined (Fig. 8) under conditions of discrimination based on the number of the received photoelectrons. The discrimination threshold was varied from 1 to 4. The dependences showed clearly the suppression of the wings of the spectral lines when the discrimination threshold was increased.

The degree of suppression of the spectral line wings

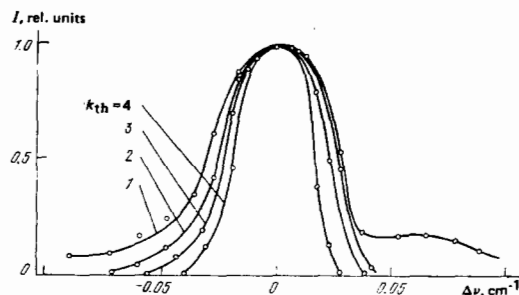


FIG. 8. Changes in the fluorescence profile of Na atoms in a beam due to the  $3^2S_{1/2}, F=2 \rightarrow 3^2P_{3/2}, F'=3$  transition in multiphotoelectron recording of the fluorescence signal.<sup>27</sup> Here,  $k_{th}$  is the discrimination threshold of the number of detected photoelectrons.

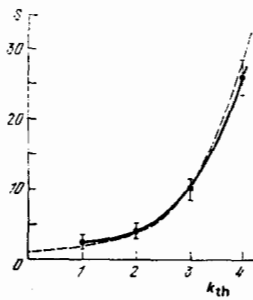


FIG. 9. Potential detection selectivity of Na atoms plotted as a function of the discrimination threshold of the number of detected photoelectrons in the case when the detuning from the center of the absorption line is  $\Delta\nu = 0.036 \text{ cm}^{-1}$  (Ref. 27).

could be used to determine the maximum attainable detection selectivity. The dependence of this selectivity for the Na atoms on the discrimination threshold (Fig. 9) was based on the results of Fig. 8 for the case when the frequency detuning from the center of the absorption line was  $\Delta\nu = 0.036 \text{ cm}^{-1}$ . We included in Fig. 9 the dependence of the detection selectivity calculated using Eq. (2.12) and assuming that  $\bar{k} = 1.8$ ; the data were taken from the same experiments in which measurements were made of the profile of the fluorescence excitation line under multiphotoelectron recording conditions. The two curves were found to coincide within the limits of experimental error. In these experiments the detuning from the center of the absorption line was of the same order as the half-width of the measured absorption line profile, so that the increase in the detection selectivity was relatively small (by a factor of 25).

The suppression of the line wings and increase in the detection selectivity under multiphotoelectron recording conditions increased strongly on increase in the detuning from the center of the absorption line compared with the line half-width because of the strong-reduction in the number of recorded photoelectrons. Figure 10 shows the dependences of the detection selectivity on the detuning for various values of the discrimination threshold in the case of a Lorentzian absorption line. The dependences were plotted on the basis of Eq. (2.12)

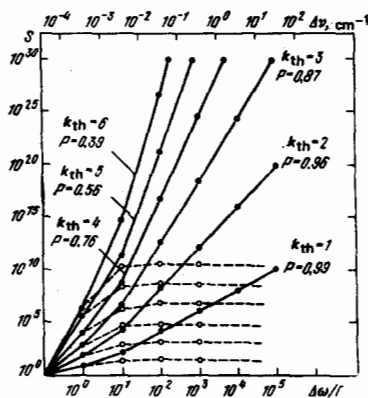


FIG. 10. Calculated detection selectivity of atoms plotted as a function of the detuning from the center of the absorption line for different values of the discrimination threshold  $k_{th}$  of the number of detected photoelectrons. Here,  $P$  is the probability of detection of an atom.<sup>27</sup>

assuming that the average number of the received photoelectrons at the center of the absorption line is  $\bar{k} = 5$ . It is clear from Fig. 10 that on slight reduction in the recording probability the detection selectivity may, in principle, reach  $10^{30}$ .

In real experiments the maximum selectivity is limited by stray noise and by the finite measurement time. For example, the main noise in the experiments reported in Ref. 33 was the background due to the laser radiation. For the minimum background signal of  $3 \times 10^3$  photoelectrons/sec, the average number of the background photoelectrons during the recording time ( $T = \tau_{tr} = 12 \text{ } \mu\text{sec}$ ) was  $\bar{k}_{\text{back}} = 4.5 \times 10^{-2}$ . The dashed curves in Fig. 10 show how the dependences  $S(k_{th}, \nu)$  change when allowance is made for the background signal. It is clear from this figure that in the presence of background photoelectrons we cannot increase the selectivity no matter how large is the detuning of the absorption frequency of the investigated atoms from the absorption frequency of the unwanted atoms.

Another factor which seriously limits the realistic detection selectivity is the low permissible intensity of an atomic beam. When this intensity is high, more than one A atom will be present in the laser beam at a given time. Clearly, in this case it will be more difficult to satisfy the condition (2.9) because of the appearance of multiphotoelectron events due to the A atoms. Let  $m_A$  be the number of the A atoms which are present simultaneously in the laser beam, and  $\bar{k}_A$  and  $\bar{k}_B$  be the average numbers of photoelectrons due to one A atom and due to one B atom in the  $\nu_A = \nu_B$  case ( $\nu_B$  is still the central frequency of the absorption line of the B atoms present in a low concentration). Then, if  $\bar{k}_B \gg 1$ , but  $\bar{k}_A, \bar{k}_A m_A \ll 1$ , the detection selectivity is given by<sup>33</sup>

$$\bar{S}(k_{th}) = S(k_{th}) \frac{1}{m_A^{k_{th}} P(\nu_B)} \approx \frac{S(k_{th})}{m_A^{k_{th}}}, \quad (2.14)$$

where  $S(k_{th})$  is the detection selectivity in the case when not more than one atom is present in the laser beam [compare with Eq. (2.12)].

The above expression can be used to estimate the time necessary to achieve a high selectivity and to find the reduction in the selectivity when denser (more intense) atomic beams are used. For example, it follows from Fig. 10 that if  $\Delta\omega = 10\Gamma$  and  $k_{th} = 5$ , the detection selectivity in the presence of a background is  $10^{10}$ . The maximum intensity of a beam of atoms crossing a laser beam at which not more than one atom is present in the laser beam is  $F = \nu/d = 3.5 \times 10^5$  atoms/sec when the average velocity of the atoms is  $\nu = 4 \times 10^4$  cm/sec and the diameter of the laser beam is  $d = 0.2$  cm. This selectivity can be achieved if the detection time is  $T = S(k_{th})/F = 2.85 \times 10^4$  sec. An increase in the intensity of the atomic beam by a factor of 10 reduces this time to  $2.85 \times 10^3$  sec, but then the selectivity falls to  $\bar{S}(k_{th}) = 10^5$ . Thus, as usual, extraction of the useful signal from the background can be achieved only if the observation time is increased.

#### d) Discussion of experiments

1) *Atoms in a vapor.* The use of the fluorescence emitted by atoms in the absolute and relative determin-



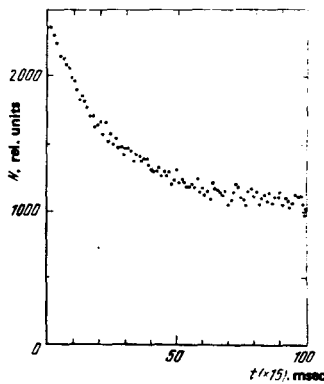


FIG. 11. Time dependence of the concentration of  $^{20}\text{Na}$  atoms in an Ne buffer gas determined by the fluorescence method.<sup>15</sup> Atoms of  $^{20}\text{Na}$  were formed as a result of the  $^{20}\text{Ne}(p, n)^{20}\text{Na}$  nuclear reaction on passage of a 20 MeV proton beam through a chamber filled with neon of concentration  $3.5 \times 10^{18}$  atoms/cm<sup>3</sup>.

ation of the concentration of elements dates back to the period before the appearance of lasers. Even conventional light sources can be used to obtain good results. The best results in the excitation of atoms by nonlaser light sources were reported in Ref. 38 and the minimum detected Na vapor concentration was  $10^7$  atoms/cm<sup>3</sup>.

The use of dye lasers tunable over a wide spectral range made it possible not only to increase greatly the sensitivity of the fluorescence method, but also to approach anew the problem of detection of single atoms. A tunable dye laser was used in Ref. 5 to detect a very low concentration of atoms of the radioactive isotope  $^{20}\text{Na}$  ( $N < 3 \times 10^3$  atoms/cm<sup>3</sup>). The  $^{20}\text{Na}$  isotope was produced by the  $^{20}\text{Ne}(p, n)^{20}\text{Na}$  nuclear reaction when a proton beam of 20 MeV energy crossed a chamber in which the concentration of neon was  $3.5 \times 10^{18}$  atoms/cm<sup>3</sup>. Measurements were made of the time dependence of the density of the  $^{20}\text{Na}$  atoms (Fig. 11) after irradiation of Ne with a proton beam; moreover, the radioactive decay time of the  $^{20}\text{Na}$  atoms and the time of diffusion of these atoms in neon were measured. The minimum detected concentration in this experiment was limited by the laser radiation scattered in the chamber and by the Rayleigh scattering in neon.

The next step in the detection of single atoms was made in Ref. 8 by absolute measurements of very low concentrations of Na atoms. The aim was to determine the saturated vapor pressure in a sealed cell. The necessary precision of the measurements of the temperature dependence of the pressure in the cell was ensured by making the laser radiation intensity much less than the saturation intensity. The concentration of the atomic vapor ranged from  $10^{11}$  atoms/cm<sup>3</sup> ( $t = 144^\circ\text{C}$ ) to  $10^2$  atoms/cm<sup>3</sup> ( $t = -28^\circ\text{C}$ ), as shown in Fig. 12. The Na atoms were excited by a single-mode dye laser whose emission frequency was tuned in resonance with the  $D_2$  line of sodium. The fluorescence signal was recorded at the same frequency. The cell containing sodium vapor was constructed carefully to minimize the scattering of laser radiation. The ratio of the intensity of the scattered light reaching the photomultiplier cathode to the intensity of the incident laser radiation was  $\xi = 3 \times 10^{-10}$ . This corresponded to a fluorescence signal

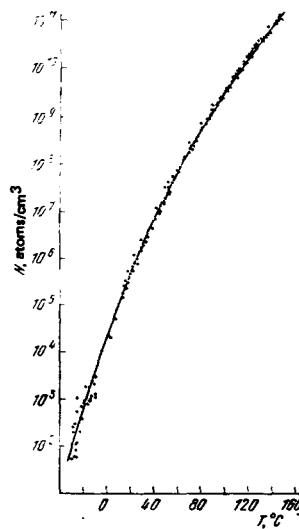


FIG. 12. Temperature dependence of the saturated vapor pressure of Na measured by the fluorescence method.<sup>8</sup>

from 3000 atoms/cm<sup>3</sup>. Lower concentrations were detected by frequency modulation of laser radiation, which made it possible to improve the signal/noise ratio by another factor of 30. The minimum concentration of the vapor which could be detected in this way was governed by the background fluctuations and the imperfections of the system for modulation of the laser radiation. The minimum recorded concentration ( $100$  atoms/cm<sup>3</sup>) corresponded to one or two atoms in the interaction zone. One should point out that in this experiment a signal was produced by many atoms during long measurement times and single atoms were not truly detected, but nevertheless the very high sensitivity of the fluorescence method was clearly demonstrated.

2) *Atoms in a buffer gas.* Low concentrations of Na atoms in a buffer gas were detected in Refs. 34 and 35 using the SONRES method described in Sec. 2b. Laser radiation excited and saturated the  $3^2S_{1/2} \rightarrow 3^2P_{1/2}$  ( $\lambda = 589.6$  nm) resonant transition. Collisions of the excited atoms with the buffer gas transferred the excitation to the nearest energy level  $3^2P_{3/2}$  and resulted in a further transition of the investigated atoms to the ground state, accompanied by the emission of a photon at the shifted frequency at which the fluorescence signal was recorded ( $\lambda = 589.0$  nm).

One should point out the existence of several potential channels of the absorption of energy from the laser beam. Firstly, one should mention here the nonradiative transitions from the  $3^2P_{1/2}$  and  $3^2P_{3/2}$  states to the ground state. Secondly, not more than half the excited atoms underwent the transition to the  $3^2P_{3/2}$  state. Therefore, the maximum number of the scattered photons in this method under  $I \gg I_{\text{sat}}$  conditions was

$$n_{\text{SONRES}} = \frac{1}{\tau_2} \left( 1 + \frac{2k_2}{k_{11}} \right)^{-1}, \quad (2.15)$$

where  $\tau_2$  is the decay time of the state 2;  $k_2 = k_{21} + k_{20} + (1/\tau_2)$ ;  $k_{12}$ ,  $k_{21}$ , and  $k_{20}$  are the rates of nonradiative transitions of atoms between the relevant levels.

The potentialities of the SONRES method were demon-

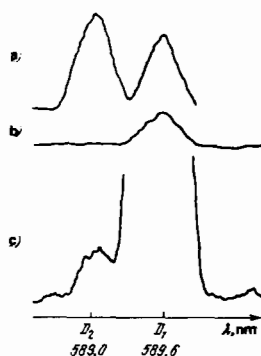


FIG. 13. Example of application of the SONRES method in detection of low concentrations of Na atoms in the flame of an acetylene burner.<sup>34,35</sup> Spectral scanning of the  $D_1$  and  $D_2$  emission lines of the Na atoms is shown for the case when these atoms are excited by laser radiation at the  $D_1$  wavelength: a) high concentration of NaCl in a solution entering the flame; b) no supply of NaCl to the flame (the signal at the frequency  $D_1$  is due to the Rayleigh scattering); c) same as b) but for a sensitivity increased by a factor of 30 (the signal at the frequency  $D_2$  is due to Na impurities in air).

strated by detecting Na atoms in a flame and in a buffer gas. Radiation from a commercial pulsed dye laser (CMX-4) was tuned to the  $D_1$  absorption line of the Na atom (589.6 nm) in the flame of an air-acetylene burner. Fluorescence due to the Na atoms was passed through a monochromator and recorded with a photomultiplier. The signal could be obtained for the  $D_1$  or the  $D_2$  line and the background was discriminated against by the monochromator.

The high sensitivity of the method is illustrated in Fig. 13. Each scan excited the  $D_1$  line. Figure 13a shows the spectral profile of the emission of the  $D_1$  and  $D_2$  lines when the concentration of NaCl introduced into the burner was high. The sodium fluorescence signal was stronger than the Rayleigh and Mie scattering intensities. The results of scanning in the same frequency interval but in the absence of an NaCl solution in the burner flame gave the results shown in Fig. 13b. When the sensitivity of the apparatus was increased by a factor of 30, the result was that shown in Fig. 13c. The signal at the frequency corresponding to the fluorescence of the  $D_1$  lines consisted mainly of the Rayleigh and Mie scattering. At the shifted (relative to the exciting radiation) frequency of the  $D_2$  line the signal was due to the fluorescence of Na present in air. The minimum detectable signal in the burner flame corresponded to  $10^4$  atoms/cm<sup>3</sup>. When the flame was replaced with a sealed cell containing metallic Na in an argon atmosphere, the maximum sensitivity of the detection of the Na vapor improved to 10 atoms/cm<sup>3</sup> (0.2 atoms on the average in the detection zone). The sensitivity increased because of the increase in the rate of transfer of excitation between the sublevels by the  $3^2P_{1/2} \rightarrow 3^2P_{3/2}$  transition and because of weakening of the quenching of the excited states by argon, compared with air. The estimates obtained by the authors indicated that it should be possible to attain the maximum sensitivity of  $10^{-4}$  atoms in the detection zone and to detect single atoms by the SONRES method at atmospheric

pressure of the buffer gas.

3) *Atoms in a beam.* In the above experiments on the detection of atoms in vapors and in a buffer gas there were on the average several atoms in the interaction or irradiation zone. The actual signal was produced by a much larger number of atoms because the residence time of atoms in the interaction zone was considerably less than the measurement time and, therefore, new atoms appeared in place of those which left the interaction zone. Therefore, the final target of detection of single atoms was not achieved in these experiments. From this point of view it would be more convenient to use atomic beams because this would provide means for controlling the arrival of atoms in the zone of interaction with a laser field. Such experiments were carried out by the fluorescence method first in 1977 at the Institute of Spectroscopy of the USSR Academy of Sciences<sup>10,28</sup> and at the Minnesota University in the USA.<sup>11,32</sup>

The possibility of detection of single Na and Ba atoms by the resonance fluorescence method was investigated by Balykin *et al.*<sup>10</sup> and by Greenlees *et al.*<sup>11</sup> It was assumed that in the case of repeated interaction of atoms with laser radiation under absorption saturation conditions, when an atom should emit a large number of photons on crossing a laser beam, the photons from such an atom should arrive mainly in groups or bunches, whereas photons representing the scattered light should arrive randomly and (on the average) uniformly in time.

An analysis of the number of photons reaching a detector in a time equal to the transit time of an atom across the laser beam should make it possible to distinguish the atomic photons from the scattered light background.

In the detection of the Ba atoms<sup>11</sup> the number of photons emitted by one atom was 24 photons/atom and it was governed by the transition of an atom from an excited to a metastable state (Fig. 14a). The average number of the detected photons was governed by the efficiency of collection of the scattered photons and by the quantum efficiency of the photomultiplier cathode. The scattered photons were collected by an ellipsoidal mirror (Fig. 14b) with two foci: at one focus ( $F_1$ ) the radiation interacted with the investigated atoms and the photomultiplier cathode was placed at the other focus

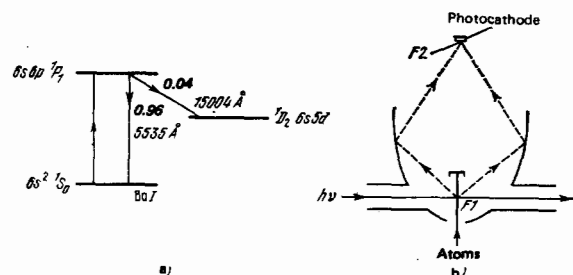


FIG. 14. Fluorescence detection of Ba atoms in an atomic beam<sup>11</sup>: a) energy level diagram of the Ba atom; b) use of ellipsoidal mirrors for the collection of photons scattered by atoms ( $F_1$  and  $F_2$  are the mirror foci).

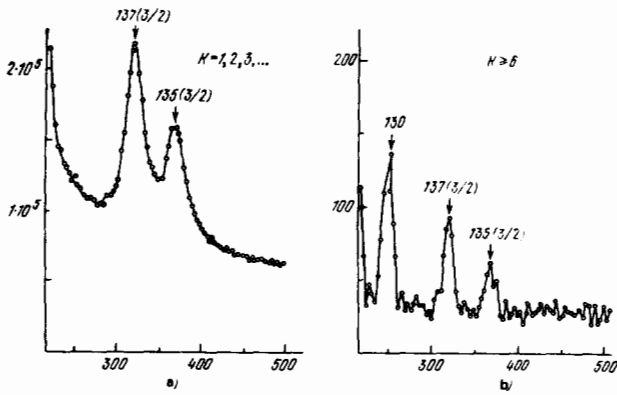


FIG. 15. Excitation spectra of the fluorescence of a natural mixture of Ba isotopes recorded by the multiphotoelectron pulse method<sup>11</sup>: a) overall spectrum; b) spectrum obtained by recording pulses due to six or more photoelectrons showing more clearly the appearance of the <sup>130</sup>Ba isotope line.

( $F_2$ ). In this experiment, 46% of the photons emitted by the investigated atoms reached the photodetector and the quantum efficiency of this detector was 12% at the recorded wavelength ( $\lambda = 5535 \text{ \AA}$ ). The overall detection efficiency was 5.5%. Thus, each atom interacting with the laser radiation was expected to produce about one photoelectron. Nevertheless, due to the statistical nature of the reemission and detection processes, some fraction of the atoms could produce two, three, etc. photoelectrons.

The average number of photons from one Ba atom found in this experiment was 1.3. The excitation spectrum of the fluorescence of a natural mixture of Ba isotopes, obtained in recording one-, three-electron etc. pulses, was obtained during recording of a flux of Ba atoms (Fig. 15). Narrowing of the spectral profile of the excitation line was observed when only the multiphotoelectron pulses were recorded. This made it possible to distinguish clearly the <sup>130</sup>Ba isotope from the Ba mixture although usually this isotope did not appear in the combined line absorption spectrum. Thus, in spite of the fact that not every atom crossing the laser beam was detected, single atoms were recorded. In other words, the fluorescence signal due to single atoms exceeded the background and its intensity was sufficient for detection.

Balykin *et al.*<sup>10,28</sup> used a different principle in recording the signal due to single atoms and suppressing the background. They employed a two-channel system with a coincidence circuit. The fluorescence signal was recorded with two photomultipliers during the transit time of an atom across a laser beam, i.e., the signal was accumulated in a time interval  $\tau_{tr} = 20 \text{ \mu sec}$ , and was then applied to the coincidence circuit. When the excitation conditions were such that the fluorescence signal due to an atom was more than one photoelectron for each photocathode, i.e., when it was definitely possible to detect a signal from each atom, the number of recorded pulses in a single channel should be equal to the number of pulses in the coincidence circuit. Measurements of the ratio of the number of recorded pulses in one channel and in the coincidence circuit should give the probability of detection of an atom crossing the la-

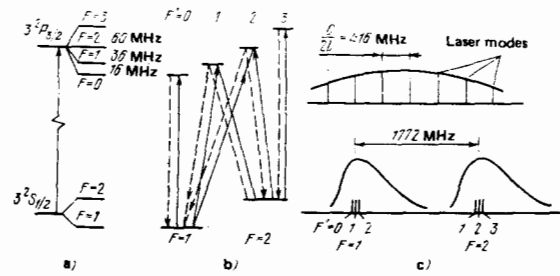


FIG. 16. Cyclic interaction of a Na atom with multimode laser radiation<sup>10,28</sup>: a) energy diagram of the ground and excited Na states; b) spontaneous and stimulated transitions; c) laser emission spectrum and profile of the absorption line of a Na atomic beam.

ser beam. This was subject to a natural restriction on the background signal: the background signal reaching the photomultiplier cathode in the time  $\tau_{tr}$  should be less than the signal due to the investigated atoms. In the experiments described in Ref. 10 the background amounted to  $10^{-2}$  photons in the time  $\tau_{tr}$ .

Cyclic interaction of atoms with radiation was ensured<sup>10,28</sup> by using multimode dye laser radiation (intermode interval  $\Delta\nu_m = c/2l = 415 \text{ MHz}$ ) of high power ( $0.18 \text{ W/cm}^2$  in each axial mode). When the frequency of one of the axial modes was tuned to the  $F=2 \rightarrow F=3$  transition (Fig. 16), the high power resulted in broadening of the absorption line due to this transition and this made it possible to excite atoms to the upper sublevels with  $F'=2$  or  $1$ . From the sublevels  $F'=2$  or  $1$  an atom would drop to the ground state with  $F=1$ , where it could interact with the nearest axial mode in the wing of the absorption line. This ensured continuous cyclic interaction of the atoms with the laser radiation. In these experiments use was made of the apparatus shown in Fig. 17 as a block diagram. Dye laser radiation of line width  $\Delta\nu_l = 0.16 \text{ cm}^{-1}$  excited atoms in a cell. The resultant fluorescence signal was recorded with photomultipliers, which were connected to an amplifier, discriminator, pulse shaper, and coincidence circuit. The fluorescence signal could be recorded in each channel and in the coincidence circuit. The time constant of the recording system was selected to be equal to the transit time  $\tau_{tr}$  of an atom crossing a laser beam. The coinci-

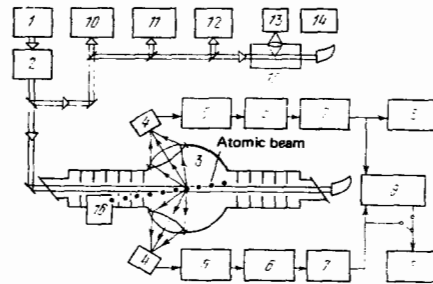


FIG. 17. Schematic diagram of the apparatus for the fluorescence detection of single Na atoms<sup>10,28</sup>: 1) Ar<sup>+</sup> laser; 2) cw dye laser; 3) cell; 4), 13) photomultipliers; 5) amplifier; 6) discriminator; 7) pulse shaper; 8) frequency meter; 9) coincidence circuit; 10) spectrometer; 11) Fabry-Perot interferometer; 12) power meter; 14) oscilloscope; 15) control cell with Na vapor; 16) atomic beam source.

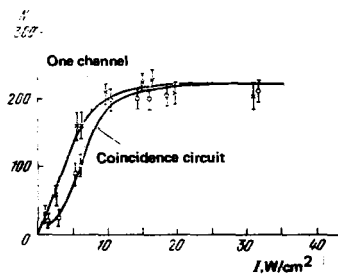


FIG. 18. Dependence of the number of pulses recorded in one channel and in the coincidence circuit on the intensity of laser radiation in fluorescence detection of atoms in a two-channel system.<sup>10,28</sup>

dence circuit operated when the interval between the pulses of the two channels did not exceed  $\tau_{tr} = 20 \mu\text{sec}$ .

The cell was constructed so as to minimize the scattered light. The ratio of the power of the scattered light reaching a photomultiplier cathode to the power of the incident laser radiation was  $\xi = 10^{-14}$ .

Figure 18 shows the dependence of the number of pulses recorded in a single channel and in the coincidence circuit on the laser radiation power. We can see that far from saturation, when a single atom did not emit sufficient number of photons for reliable detection in each of the channels, the number of pulses in a single channel was greater than the number of pulses in the coincidence circuit. At high laser radiation powers the number of pulses in a single channel was equal to the number of pulses in the coincidence circuit, indicating that practically each atom crossing the laser beam was detected. In the case shown in Fig. 18 the atomic flux was 210 atoms/sec. The dependence of the atomic flux on the temperature of the oven in which the experiments were performed was also recorded (Fig. 19). The minimum flux of atoms crossing the interaction zone was 10 atoms/sec and it was limited by the background due to the laser radiation.

In a different experiment, Balykin *et al.*<sup>27</sup> detected Na atoms employing a system which combined those described in Refs. 10 and 11. The background signal in each of the channels was suppressed by an analysis of the number of photoelectrons which were recorded followed by discrimination based on this number; more-

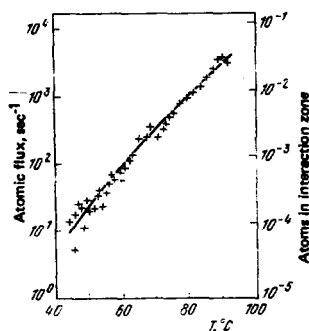


FIG. 19. Results of fluorescence detection of a flux of sodium atoms interacting with laser radiation plotted as a function of the source temperature.<sup>10,28</sup> The scale on the right represents the number of atoms in the interaction zone.

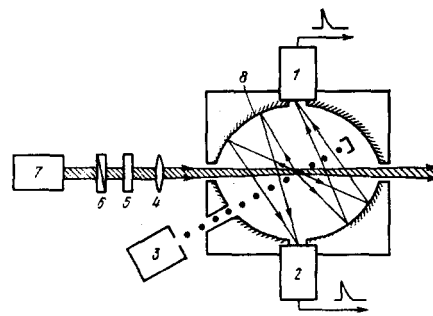


FIG. 20. Apparatus used for the fluorescence detection of Na atoms<sup>27</sup>: 1), 2) photomultipliers; 3) atomic beam source; 4) lens; 5)  $\lambda/4$  plate; 6) Glan prism; 7) dye laser; 8) ellipsoidal mirrors.

over, a coincidence circuit was employed for additional discrimination against the background and for determination of the probability of detecting an atom. The arrangement used is shown schematically in Fig. 20. Cyclic interaction of atoms with the laser radiation was ensured by preliminary orientation of Na atoms, as a result of which the atoms were in the state with  $F=2$  and  $m_F=2$ , and further interaction occurred as a result of the transition  $F=2, m_F=2 \rightarrow F'=3, m'_F=3$ . Collection of the scattered photons was improved by employing ellipsoidal mirrors arranged in such a way that at one of the foci (common to both ellipsoids) the atoms interacted with the radiation and the photomultiplier cathodes were located at the upper foci.

The number of photons emitted by each atom crossing the laser beam was a random quantity and was described by the Poisson distribution. The statistics of photoelectron emission was also described by the Poisson distribution. This distribution could be determined by repeating the experiment involving the reception of the signal from the Na atoms crossing a laser beam.<sup>27</sup> Knowing the distribution of the number of photoelectrons, we could find the average numbers of photoelectrons emitted by one atom. This gave the number of recorded (due to a flux of sodium atoms) photoelectron pulses as a function of the discrimination threshold (Fig. 21) and this information was used to find the average number of photoelectrons emitted by a single atom, which amounted to  $\bar{k} = 1.3$ .

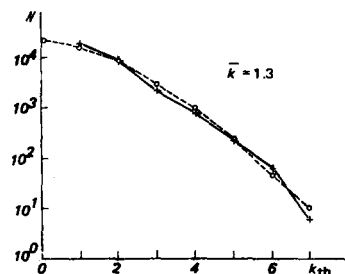


FIG. 21. Determination of the average number of photoelectrons emitted by an atom. The figure shows the dependence of the number of photoelectron pulses emitted by a flux of sodium atoms on the discrimination threshold. The dashed curve is the Poisson distribution function for  $\bar{k} = 1.3$ , which approximates best the experimental points.<sup>27</sup>

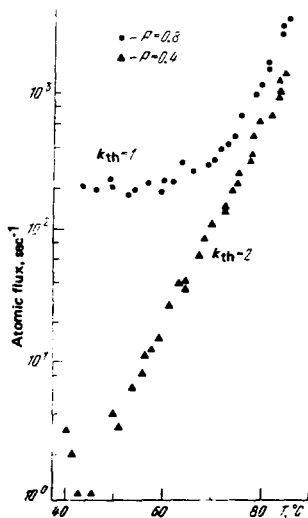


FIG. 22. Dependence of the flux of atoms recorded by the fluorescence method on the source temperature in the case of different discrimination thresholds of the number of photoelectrons.<sup>27</sup> The upper dependence (●) corresponds to the discrimination threshold  $k_{th} = 1$  and the lower dependence (▲) to  $k_{th} = 2$ .

Figure 22 shows the dependences of the atomic flux on the oven temperature obtained for different discrimination thresholds in this experiment. The upper dependence was obtained for  $k_{th} = 1$ , when all the events creating one or more photoelectrons were recorded; the lower dependence was obtained for  $k_{th} = 2$ , when only the atoms creating at least two photoelectrons were recorded. Clearly, for  $k_{th} = 1$  the minimum recorded flux was 200 atoms/sec. The probability of recording each atom was then 0.8. For  $k_{th} = 2$  the background signal decreased and there was a corresponding increase in the sensitivity of the system. In this case the minimum detectable atomic flux was only a few atoms per second. However, in this case the detection probability decreased to 0.4.

### e) Absolute sensitivity

The fundamental question is the minimum number of atoms needed to record their spectrum. A clear signal within one allowed spectral interval  $\delta\omega$  can be recorded with an error not exceeding  $\Delta = 10\%$  if the signal due to the atoms is  $1/\Delta^2 = 100$  photoelectrons. This value is dictated by the observation statistics. A hyperfine structure in a spectrum can be determined when this number is increased by the factor  $\Delta\omega_{hfs}/\delta\omega$ . Thus, details of the structure of a single spectral line can be recorded, in principle, when the signal is  $10^4 - 10^5$  photoelectrons. Depending on the experimental conditions (Fig. 2), this can be done using either different atoms (Figs. 2a and 2b) or a small number of atoms subjected to repeated observations (Fig. 2c) or ideally one atom subjected to a cyclic process (Fig. 2d). This is the ultimate aim of the laser methods of atomic spectroscopy, which has not yet been achieved. We shall now give some estimates of the absolute sensitivity from the point of view of signal reception.

Two main methods are in use in detection of optical

signals: heterodyne (coherent detection) and direct (noncoherent) detection.<sup>39,40</sup> In the fluorescence atom-detection technique use is made of the second (noncoherent) signal detection method, because photons scattered by an atom, which represent the signal being detected, are not coherent with the exciting laser radiation which might, in the principle, be used as the heterodyne signal.

It is known from information theory that in the noncoherent photodetection method the maximum information which can be obtained from a signal of intensity  $P$  (photons/sec) is<sup>41,42</sup>

$$H = \frac{R}{2} T \log_2 \left[ 1 + \frac{P}{N + (h\nu B/\epsilon)} \right] \text{ (bit)}, \quad (2.16)$$

where  $B$  is the band width of the system (Hz);  $N$  is the background noise;  $\nu = \omega/2\pi$  is the frequency (Hz);  $h$  is the Planck constant;  $\epsilon$  is the quantum efficiency of the detector;  $T$  is the observation time. The quantity  $h\nu B/\epsilon$  is the noise resulting from quantum fluctuations of the signal itself. We can easily find from Eq. (2.16) the minimum scattered power necessary for the reception of a signal from an atom when the minimum information is recorded for this atom (a transit of an atom across a laser beam corresponds to  $H = 1$  bit):

$$P_{\min} = \left( N + \frac{h\nu B}{\epsilon} \right) (2^{2/BT} - 1). \quad (2.17)$$

For the observation time  $T$  equal to the transit time  $\tau_{tr} = 10^{-5}$  sec, the reception time constant  $\tau = 1/B = 10^{-7}$  sec, the quantum efficiency of the detector  $\epsilon = 0.1$ , and zero background ( $N = 0$ ), the minimum number of photons needed for reception is  $n_{\min} = P_{\min} \tau_{tr} = 14$ . Fuller information can be obtained when the power scattered by an atom is greater.

It follows from Eqs. (2.16) and (2.17) that there are several ways of increasing the maximum information that can be obtained from an atom. First of all, we can increase the radiation power  $P$  scattered by an atom; secondly, we can increase the band width  $B$  and, thirdly, we can increase the observation (reception) time  $T$ .

The high spectral brightness of laser radiation makes it possible to saturate resonant transitions in atoms and achieve the maximum scattered power. An increase in the band width  $B$  also increases the noise resulting from quantum fluctuations of the signal itself and this increases  $P_{\min}$ . The only parameter which can at present be used to achieve a significant increase in the amount of information received from an atom (and, therefore, increase the absolute sensitivity) is the duration of interaction  $T$  between an atom and the radiation. There are several methods for increasing the interaction time. We shall ignore the trivial method involving an increase in the path traveled by an atom within a laser beam and concentrate on a method which seems to be the most promising. It involves cooling of atoms by optical pressure forces and capturing of the cooled atoms in various traps, i.e., it involves realization of the general scheme shown in Fig. 2d.

The possibility of cooling and trapping of atoms has been considered in several theoretical investigations<sup>18,43-45</sup> (see also the review in Ref. 46) and there

have been several experimental studies demonstrating cooling of ions<sup>20,47</sup> and of atoms<sup>19</sup> by laser radiation. In principle, the methods of cooling and trapping should localize an atom within a trap for a time governed by collisions with the residual gas in a cell. For example, in vacuum with a residual pressure  $p \approx 10^{-10}$  Torr ( $N_{\text{at}} = 3.6 \times 10^6$  atoms/cm<sup>3</sup>) when the average thermal velocity of the residual particles is  $v \approx 10^4$  cm/sec, we find that for a typical total scattering cross section  $\sigma_{\text{scatt}} \approx 10^{-14}$  cm<sup>2</sup>, the confinement time of an atom and, consequently, the interaction time  $\tau_{\text{int}}$  should be

$$\tau_{\text{int}} = (\sigma_{\text{scatt}} N_{\text{res}} v)^{-1} \approx 1 \text{ h.} \quad (2.18)$$

Under these conditions we can achieve a prolonged interaction of an atom with laser radiation and record fully its spectrum.

We shall conclude this subsection by stressing that we are dealing with the number of atoms needed for detection and for investigation of the spectrum by the fluorescence method in the zone of interaction with laser radiation. In many applications, such as those in nuclear physics, the important aspects are the absolute number of atoms in a source and the "transport" of these atoms to the zone of interaction with radiation. These aspects are considered in Refs. 49 and 50.

#### f) Additional potentialities of the fluorescence method

The fluorescence method for the detection of single atoms, based on the reception of a large number of photons scattered by an atom during its interaction with laser radiation, can give additional information on atoms, which is a feature of this method alone.

One of the possible experiments is the direct determination of the velocity of individual atoms.<sup>48</sup> The idea of such an experiment is as follows (Fig. 23). A cw dye laser beam is split into two parallel components of equal intensity separated by a distance  $d$ . The two beams are directed to a chamber containing moving atoms. The concentration of atoms in this chamber is such that the region from which the fluorescence signal is received contains no more than one atom at a time. When an atom crosses both laser beams and the laser frequency is tuned in resonance with the absorption frequency of an atom, two consecutive fluorescence signals reach the detection system. Each of these signals is the result of interaction of an atom with one of the laser beams. When the time between two pulses  $t_p$  is measured on the screen of an oscilloscope, we can find the velocity of an individual atom:  $v = d/t_p$ . This

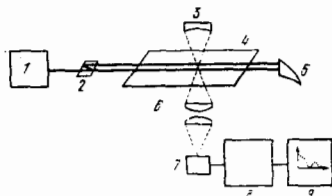


FIG. 23. Experimental arrangement used to measure the velocity of individual atoms<sup>48</sup>: 1) cw dye laser; 2) beam splitter; 3) mirror; 4) cell; 5) light trap; 6) lens; 7) radiation detector; 8) signal analyzer; 9) oscilloscope.

technique opens up the possibility of various experiments with atoms which have a definite velocity in the direction of motion, and such information can be used in subsequent experiments on atoms.

### 3. PHOTOIONIZATION ATOM-DETECTION METHOD

The currently available methods for recording charged particles allow us to detect ions and electrons with an efficiency practically equal to unity. Consequently, ionization is one of the possible methods for detecting atoms and molecules on the basis of their ionization products (involving recording of an ion or an electron, or both simultaneously). The efficiency and selectivity of detection of a neutral particle is then governed mainly by the efficiency and selectivity of the ionization process. We shall begin by discussing the methods of highly efficient selective ionization of atoms by laser radiation.

#### a) Multistage photoionization of atoms

The most suitable method for the selective ionization of atoms is the multistage ionization by laser radiation first used by Ambartsumyan *et al.*<sup>51</sup> In this method, atoms are excited by laser radiation to an intermediate state in one or more stages, and this is followed by photoionization of the excited atoms. Since the process of excitation of atoms to intermediate levels is resonant, saturation of the relevant transitions, i.e., efficient excitation of the atoms, requires only moderate laser radiation intensity. It has been shown<sup>52,53</sup> that in the presence of sufficiently strong ionizing radiation the quantum efficiency of the photoionization process is close to unity. Under these conditions the multistage ionization method can be used effectively to detect atoms.<sup>4,54</sup>

Detection of a single atom clearly requires that it be photoionized during the transit time  $\tau_{tr}$  across the laser beam. This time depends strongly on the experimental arrangement (Fig. 2) and varies from  $10^{-6}$  sec (free flight of an atom across the laser beam) to seconds (diffusion of an atom out of the irradiation zone). This time is considerably longer than the lifetime of intermediate atomic states, with the exception of rare cases of metastable states. Therefore, guaranteed photoionization of each atom by the multistage excitation method (Fig. 24a) can be achieved by ensuring that the rate of induced transitions at each excitation stage  $W_{kn}$  is considerably greater than the rate of relaxation of the population of each of the intermediate states  $1/\tau_k$  and  $1/\tau_n$ .

Optimal conditions are provided by simultaneous irradiation of a multilevel system with a train of laser pulses of the same intensity  $\tau_p \ll \tau_k$  ( $k=i, \dots, f$ ) at the resonance frequencies  $\omega_{kn}$  of the consecutive quantum transitions (Fig. 24a). If the energy flux  $\mathcal{E}(\omega_{kn})$  of each of these pulses satisfies the saturation condition

$$\mathcal{E}(\omega_{kn}) \gg \mathcal{E}_{\text{sat}}^{kn} \quad (3.1)$$

where  $\mathcal{E}_{\text{sat}}^{kn}$  is the saturation energy density for the resonant transition  $k-n$ , given by Eq. (1.2), it follows that multistage laser irradiation establishes on the average a uniform distribution of the quantum system between



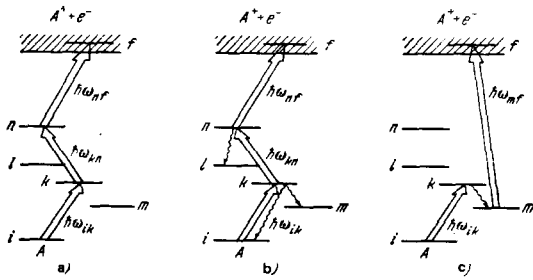


FIG. 24. Multistage excitation and ionization of atoms: a) general scheme for the excitation with short pulses free of capture by inactive intermediate levels; b) irradiation with long pulses ( $\tau_p \gg \tau_k$ ) with capture by intermediate levels ( $l, m$ ); c) possible excitation and ionization by long pulses in the case of relaxation of excited atoms to one metastable level.

the initial, all the intermediate, and final levels<sup>1)</sup>:

$$\frac{n_i}{g_i} \approx \frac{n_k}{g_k} \approx \dots \approx \frac{n_f}{g_f}, \quad (3.2)$$

where  $g_k$  is the statistical weight of the  $k$ -th state. If the statistical weight increases on increase in the quantum state number, a considerable proportion of atoms becomes concentrated in a highly excited state.

If the conditions for the saturation of the intermediate quantum transitions (3.1) are satisfied by a large margin, the distribution of the quantum systems between the intermediate levels (3.2) is established in a short time, shorter than the duration of irradiation:

$$\tau_{exc} \approx \sum_k \frac{1}{W_{kn}} \ll \tau_p, \quad (3.3)$$

where  $W_{kn} = \sigma(\omega_{kn}) \cdot I(\omega_{kn})$ .

A strongly excited atom may go over to the continuum, i.e., may become ionized, spontaneously or under the influence of radiation or external perturbation. If the rate of such transitions to the continuum  $W_{fc}$  is low compared with the photoexcitation rate  $1/\tau_{exc}$  and the decay occurs mainly after irradiation, the absolute efficiency is limited by the relative population of the final excited level:

$$\beta \ll \frac{g_f}{\sum_k g_k}. \quad (3.4)$$

However, if during the photoexcitation time the channel of decay of the quantum system is open and the rate of such decay  $W_{fc}$  is sufficiently high,

$$W_{fc} \gg \frac{1}{\tau_{exc}}, \quad (3.5)$$

then such single irradiation may empty the initial, all intermediate, and final levels, ensuring the maximum photoionization efficiency  $\beta \approx 1$ .

The conditions (3.1) and (3.3) may be too stringent. However, as a rule, an atom is in the irradiation zone much longer than the lifetime of excited states. Therefore, prolonged irradiation can guarantee photoionization even far from saturation of each excitation stage. In principle, this is true of ideal three- or four-level atoms. In reality, an atom usually has many other

<sup>1)</sup>We shall ignore here the coherent interaction effects.

intermediate states which it can reach as a result of slow excitation and from which it cannot be photoionized by radiation at some exactly defined radiation frequencies (Fig. 24b). This is why we can ensure that the quantum photoionization efficiency is unity by arranging optimal pulse excitation conditions with the pulse duration:

$$\tau_p \ll \tau_k. \quad (3.6)$$

This is precisely the case that will be considered later. One possible exception to this general rule is the case of rapid decay of intermediate states to one long-lived intermediate level  $m$  (Fig. 24c). We can then implement, for example, a two-stage photoionization scheme shown in Fig. 24c when the condition imposed on the rate of induced transitions is less stringent:

$$\tau_{exc} \ll \tau_p \ll \tau_m. \quad (3.7)$$

The condition for detection of each atom during the time it spends in the interaction zone determines the necessary laser pulse repetition period,

$$T_{rep} \ll \tau_{tr}. \quad (3.8)$$

Hence we obtain the requirement of the necessary average radiation power at each stage:

$$P_{av}^{kn} = \frac{g_k^{kn} s a I_s}{T_{rep}}, \quad (3.9)$$

where  $s$  is the cross-sectional area of the laser beam.

To satisfy the conditions (3.1) and (3.3) we have to use quantum transitions with the largest cross section. This is particularly critical in the case of the last quantum transition from the intermediate state to the ionization continuum. The mechanism of ionization of atoms from the intermediate state in the multistage method makes it possible to distinguish formally three submethods (for reviews see Refs. 55 and 56) illustrated in Fig. 25:

- 1) nonresonant photoionization of an excited atom;
- 2) electric field ionization of an atom from a Rydberg state;
- 3) resonant photoionization of an excited atom by excitation of an autoionizing state.

We shall now consider in detail each of these submethods.

1) *Nonresonant photoionization of atoms.* In this case an excited atom is ionized by additional laser radiation

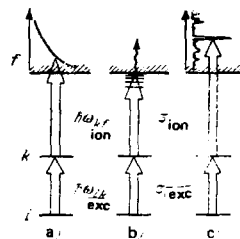


FIG. 25. Methods for selective multistage ionization of atoms: a) nonresonant photoionization; b) ionization of an atom by an electric field from a Rydberg state; c) ionization of an atom via an autoionizing state.

or by radiation used in one of the resonant excitation stages. This approach is characterized by relatively small cross sections  $\sigma_{ion} = 10^{-17} - 10^{-19} \text{ cm}^2$  compared with the resonant excitation cross sections of the intermediate levels  $\sigma_{exc} = 10^{-11} - 10^{-14} \text{ cm}^2$ . For effective excitation and subsequent photoionization of excited atoms the energy density of the pulses should satisfy the following conditions<sup>51</sup> representing a special case of the conditions (3.1):

$$\mathcal{E}_{exc} \geq \mathcal{E}_{exc}^{sat} = \frac{\hbar\omega_{exc}}{2\sigma_{exc}}, \quad \mathcal{E}_{ion} \geq \mathcal{E}_{ion}^{sat} = \frac{\hbar\omega_{ion}}{\sigma_{ion}}. \quad (3.10)$$

The saturation energy density of an ionizing pulse  $\mathcal{E}_{ion}^{sat}$  lies within the range  $0.01 - 1 \text{ J/cm}^2$  (for an exciting pulse the corresponding values  $\mathcal{E}_{exc}^{sat}$  are  $2\sigma_{exc}/\sigma_{ion}$  times smaller). Such energy densities of laser radiation are attainable with the aid of currently available pulsed lasers if the required repetition frequency is within the range of a few tens of hertz. However, according to the requirement (3.8), ionization of each atom which has entered a laser beam can be ensured if the time interval between the pulses is less than the transit time of such an atom across the beam  $\tau_{tr}$ . For an atom moving at a thermal velocity, this transit time is  $\tau_{tr} \approx 2 \times 10^{-5} \text{ sec}$ . Thus, the repetition frequency has to be  $f_{rep} \geq 1/\tau_{tr} = 50 \text{ kHz}$ . Under these conditions the average intensity of laser radiation necessary for efficient ionization should amount to a few kilowatts:

$$I_{av} = (10^4 - 10^5 \text{ Hz}) \times (0.01 - 1 \text{ J/cm}^2) = 10^2 - 10^5 \text{ W/cm}^2.$$

However, if atoms are detected in a dense vapor or in a buffer gas, the transit time of atoms across the laser beam is governed by their diffusion in the gas and then the values of  $\tau_{diff}$  range from tens of milliseconds to several seconds. In spite of the high energy density of the ionizing pulses, efficient ionization can then be achieved employing laser radiation of moderate average intensity:

$$I_{av} = f_{rep} \mathcal{E}_{ion}^{sat} = (10^2 - 1 \text{ Hz}) (0.01 - 1 \text{ J/cm}^2) = 0.01 - 100 \text{ W/cm}^2.$$

However, in an experiment of this kind we cannot achieve a high spectral resolution because the presence of a buffer gas results in considerable collisional broadening of the absorption lines. In those cases when the maximum spectral resolution has to be achieved, detection should take place in a rarefied gas or in vacuum and an atomic beam should be employed. Atoms then move at a thermal velocity practically without collisions, and as shown above, the use of the nonresonant ionization method is possible only when the energy of the ionizing laser radiation is very high. These difficulties can be overcome successfully by employing the method of ionization of Rydberg atoms by an electric field.

2) *Resonant excitation of a high Rydberg state and its ionization by an electric field.* In this method, proposed in Ref. 57, an atom from an intermediate state is excited to a Rydberg (high) state below the ionization threshold and is then ionized by an electric field pulse. Investigations of the ionization of Rydberg atoms by an electric field were reported in Refs. 58-60. Subsequent studies<sup>61-64</sup> demonstrated that Rydberg atoms are unique in the relative ease of ionization in an electric field ir-

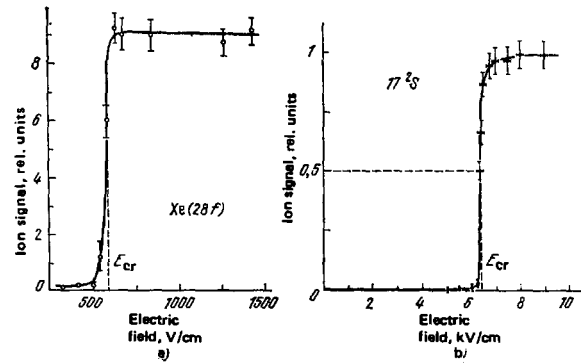


FIG. 26. Ionization of Rydberg atomic states by an electric field: a) dependence of the ionization signal on the electric field for the  $28f$  state of a xenon atom<sup>59</sup>; b) same for the  $17s$  state of a sodium atom.<sup>63</sup>

respective of the nature of the atom. Figure 26 shows the dependences of the ionization signal of a Rydberg state on the intensity of pulsed electric field for the  $28f$  state of the xenon atom<sup>59</sup> (Fig. 26a) and for the  $17s$  state of the sodium atom<sup>63</sup> (Fig. 26b). We can see that each state has its own critical electric field at which the ionization signal has a threshold behavior. The dependence of the critical electric field on the effective principal quantum number  $n^*$  of a state is described well (for the majority of elements) by the following classical formula:

$$E_{cr} = \frac{1}{16n^{*4}} \text{ a.u.} \quad (1 \text{ a.u.} \approx 5 \cdot 10^9 \text{ V/cm}). \quad (3.11)$$

When the electric field intensity exceeds the critical value for a given high state, the ionization efficiency of Rydberg atoms is close to unity. The ionization cross section of an atom excited to an intermediate state is then governed by the cross section of its resonant excitation to a Rydberg state. This cross section is several orders of magnitude greater than the cross section for nonresonant ionization to the continuum.

An atom can be excited to a high state in two or three stages using pulsed dye lasers synchronized with one another. The excitation method depends on the actual atom. In the case of alkali metal atoms it is convenient to use the two-stage excitation method. In the case of heavy elements with complex spectra of atomic states and ionization potentials in excess of 6 eV, it is preferable to use a three-stage method of excitation of an atom to higher states. Since the processes of multi-stage excitation of an atom to a Rydberg state are resonant, saturation of such transitions requires relatively low laser pulse energies which are attainable with the aid of the existing dye lasers. Typical values of the saturation energy density are in the range  $\mathcal{E}_{exc}^{sat} = 10^{-6} - 10^{-4} \text{ J/cm}^2$ . Therefore, even in the case of interception of each atom moving at the thermal velocity the average intensity of the exciting laser radiation is

$$I_{av} = (10^4 - 10^5 \text{ Hz}) (10^{-6} - 10^{-4} \text{ J/cm}^2) = 10^{-2} - 10 \text{ W/cm}^2.$$

It is most convenient to apply an electric field pulse to an atom after the end of a laser pulse. In this case the process of excitation of an atom is not complicated by the Stark shift and splitting of the last high level.

The absolute photoionization efficiency is then limited by the relative population of the last excited discrete state, given by Eq. (3.4). Therefore, in order to achieve the maximum ( $\beta = 1$ ) absolute efficiency of multistage ionization at moderate average powers of photoionizing radiation, it is best to use autoionizing states.

3) *Resonant ionization of an atom via an autoionizing state.* Another way of increasing the photoionization cross section of atoms is to excite them at the last stage to an autoionizing state. In the case of many-electron atoms such states may be sufficiently narrow and the cross section of an autoionizing transition may be several orders of magnitude larger than the nonresonant ionization cross section.<sup>65,66</sup> On the other hand, even in the case of a very small width of an autoionizing resonance, for example,  $\Delta\nu_{ai} \approx 0.01 \text{ cm}^{-1}$ , the lifetime for decay to the continuum is a few nanoseconds. Consequently, when such a state is excited by a laser pulse of typical  $10^{-8}$  sec duration, it becomes effectively emptied during a single laser pulse. This ensures attainment of the maximum absolute ionization efficiency  $\beta = 1$ .

Systematic investigations of autoionizing states have become possible since the development of methods for multistage excitation of high atomic states by tunable laser radiation. Such states are of practical value in increasing the photoionization cross section of atoms by laser radiation and of intrinsic scientific interest because studies of these states help to understand, identify, and interpret atomic spectra of many-electron atoms. Since autoionizing states have been investigated only for a small proportion of the elements, further experiments involving search for and study of these states are highly desirable.

An investigation of autoionizing states of the gadolinium atom was made in Ref. 67 and a state with a lifetime of  $10^{-9}$  sec was discovered. Gadolinium atoms in a beam were excited to states lying  $300 \text{ cm}^{-1}$  below the ionization thresholds in three stages, employing radiation emitted by pulsed dye lasers (Fig. 27a). Figures 27b and 27c show the spectra of the Rydberg and auto-

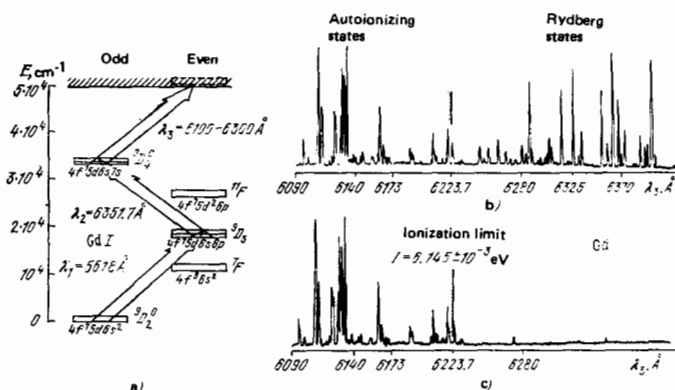


FIG. 27. Rydberg and autoionizing states of a gadolinium atom<sup>67</sup>: a) scheme for the excitation of a Gd atom to Rydberg and autoionizing states; b) spectrum of excited states obtained using electric field pulses of  $E = 13 \text{ kV/cm}$  intensity; c) spectrum obtained using a static electric-field  $E = 30 \text{ V/cm}$ .

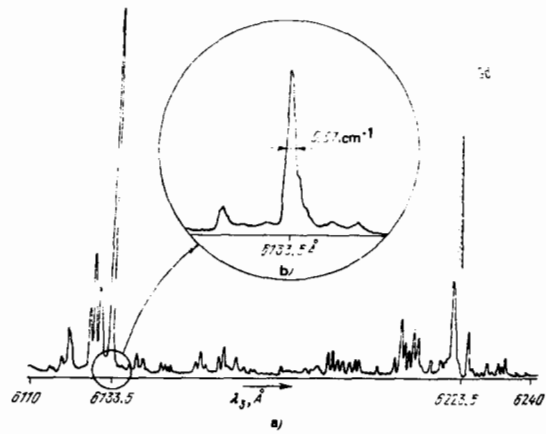


FIG. 28. Spectrum of autoionizing Gd states obtained with a resolution of  $\Delta\nu_i^{(3)} = 1 \text{ cm}^{-1}$  (a) and the strongest resonance recorded with a resolution  $\Delta\nu_i^{(3)} = 0.03 \text{ cm}^{-1}$  (b). Results taken from Ref. 67.

ionizing states of Gd, obtained in pulsed (b) and static (c) electric fields. It is clear from this figure that the amplitudes of the Rydberg and autoionizing resonances are similar. There is one outstanding autoionizing maximum at  $\lambda_3 = 6133 \text{ \AA}$ . Figure 28 shows the same part of the spectrum recorded at a higher resolution. In the experiment just described the third excitation stage involved the use of radiation from a pressure-tunable dye laser whose emission line width was  $\Delta\nu_i = 0.03 \text{ cm}^{-1}$ . The width of the autoionizing resonance at midamplitude, including the laser line width, was  $0.07 \text{ cm}^{-1}$ . Hence, the estimated lifetime of the autoionizing state was  $\tau_{ai} \approx 0.5 \text{ nsec}$ . The cross section of this autoionizing transition measured by the saturation method suggested in Ref. 52 was  $\sigma_{ai} = 0.8 \times 10^{-15} \text{ cm}^2$ .

This experiment demonstrated that narrow autoionizing states with a lifetime of the order of  $10^{-9}$  sec can exist in the spectra of many-electron atoms. The excitation cross sections of such states are comparable with the excitation cross sections of Rydberg states and these long-lived autoionizing states may be used effectively in the method of multistage ionization of atoms by laser radiation. There is no need to employ an ionizing electric field and the constant decay channel makes it possible to ionize during a laser pulse practically all the atoms in the ground state.

Each of these ionization methods has its own advantages and shortcomings. The nonresonant ionization method makes it possible to ionize in one laser pulse practically all the atoms interacting with laser radiation. However, this method is unacceptable if a high pulse repetition frequency is needed. The method of ionization of highly excited atoms by an electric field requires energies of ionizing laser radiation which are several orders of magnitude lower. This makes it possible to perform effective ionization of atoms in an atomic beam when a high pulse repetition frequency is required. The use of an atomic beam ensures maximum spectral resolution and the employment of a multistage excitation scheme gives an unusually high ionization selectivity. True, this method makes it possible to excite to Rydberg states only about half the atoms interacting

with laser radiation. As a result, only every second atom becomes ionized. However, this factor is not always important. The method of ionization of atoms via narrow autoionizing states is sufficiently promising because it represents a kind of synthesis of the other ionization methods, i.e., it retains the resonant nature of the ionization process and the presence of a constant decay channel of the states. However, its shortcoming is the absence of such states for a considerable number of elements. The most universal and accessible method for the ionization of atoms with the purpose of detecting them is selective excitation of Rydberg states by laser radiation and subsequent ionization by an electric field.

In discussing the kinetics of multistage excitation of atoms, particularly of the distributions of the populations of atoms between the excited states, we have adopted the simplest approximation for the rate equations when Eq. (3.2) is valid under steady-state conditions. A discussion of the transient behavior of atoms and of the role of coherent effects can be found in reviews.<sup>55</sup> Coherent effects of the  $\pi$  pulse type can be used to empty the lower state completely. True, one would then have to control rigorously not only the frequency but also the intensity of laser pulses. This can complicate greatly the use of such effects in practice. Therefore, the role of coherent effects in multistage excitation and photoionization of atoms has not yet been investigated experimentally.

#### b) Sources of background and ways of suppressing it

In high-sensitivity methods for the detection of atoms by photoionization one unavoidably faces the problem of the ion background. This background represents the ions which are not involved in the selective interaction of laser radiation with the atoms being detected. Such ions may form in the investigated region under the influence either of external agencies or experimental conditions. For example, the use of the method of non-resonant ionization of excited atoms requires application of high-intensity ionizing laser pulses. If detection takes place in a buffer gas, such an intense pulse may cause multiphoton ionization of atoms or molecules in the gas. Scattering of laser radiation by windows of the chamber employed and the incidence of this radiation on the walls may also give rise to unwanted electrons and ions. Their appearance is determined by the experimental conditions. Such stray ionization can be avoided by special treatment of the walls of the chamber and selection of a specific buffer gas characterized by a very small cross section of ionization by laser radiation.<sup>16</sup> A particularly promising approach is that involving methods for resonant ionization of excited atoms when only moderate intensities of laser radiation are required.

In the process of detection in an atomic beam in vacuum a considerable background is created by thermal ions and electrons. They originate from an oven heated to a high temperature in order to produce the atomic beam. A system of several apertures subjected to potentials of different sign and amplitude can reduce the background level to single ions and electrons. Further

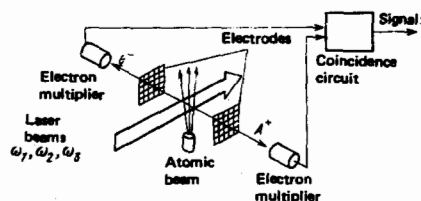


FIG. 29. Possible system for simultaneous recording of an ion and an electron formed as a result of an ionization event, designed to discriminate against unwanted ions and electrons.<sup>76</sup>

discrimination can be applied by the signal gating technique. This method makes it possible to record the useful signal effectively without background even of those ions which are formed in the chamber by cosmic radiation.

One of the ways of further reducing the ion background is to use a coincidence circuit in which electron multipliers are used to record simultaneously an ion and an electron formed in an ionization event (Fig. 29).

#### c) Detection selectivity

The multistage photoionization method for the detection of atoms ensures a very high selectivity (up to  $10^{10}$ ) when atoms of one kind are recorded against the background of a large number of atoms of another kind.<sup>68</sup> This is due to the fact that the frequencies of transitions are very different at all excitation stages. However, modifications of the same element (such as isotopes, nuclear isomers, etc.) for which the shift of the atomic energy levels is small and is due to a weak perturbation caused by the nuclear structure can be excited much less selectively. This is due to the unavoidable absorption in the line wings. However, a high selectivity can be achieved even in this case if a suitable scheme for multistage excitation of atoms to Rydberg states is employed.<sup>69</sup>

In the case of some atoms we can select such a sequence of quantum transitions that two or three intermediate levels are shifted (Fig. 30). Since the processes of excitation in each state are independent, the selectivity of the whole excitation and ionization procedure is equal to the products of the selectivities of excitation at each stage.

In the case of atoms of some elements, for example, alkali metals, the isotopic effect shifts significantly only the ground  $s$  state, whereas the  $p$  state is shifted

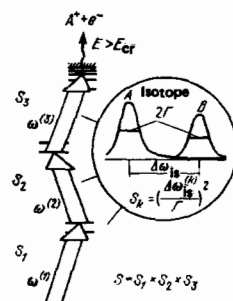


FIG. 30. Selective three-stage excitation of atoms in an atomic beam with the aid of isotopic shifts at each stage.<sup>69</sup>

an order of magnitude less. The isotopic shift of the remaining states is negligible. Therefore, only the first excitation stage is selective. However, for many elements the isotopic shift is observed at all three stages. Examples are elements of the lanthanum and actinium group: Yb, Gd, U.

When an atomic beam is excited by monochromatic laser radiation (Fig. 30), the absorption wing of a line is described by

$$\gamma(\omega) = \frac{\Gamma}{\pi [(\omega - \omega_0)^2 + \Gamma^2]}, \quad (3.12)$$

where  $\omega_0$  is the central frequency and  $\Gamma$  is the radiative half-width at half-maximum. Since usually  $\Gamma$  is much less than the isotopic shift  $\Delta\omega_{is}$ , excitation of one isotope occurs in the wing of the absorption line of another isotope. The maximum excitation selectivity of one of the isotopes whose line centers are separated by  $\Delta\omega_{is}$  is

$$S = \left( \frac{\Delta\omega_{is}}{\Gamma} \right)^2. \quad (3.13)$$

Where an atom is excited in three stages, the resultant selectivity increases to

$$S = S_1 \times S_2 \times S_3, \quad (3.14)$$

where  $S_i$  is the selectivity of excitation at the  $i$ -th stage.

If the width of the laser radiation spectrum  $\Delta\omega_1$  is greater than the radiative width of the absorption line, the real selectivity is less and it amounts to

$$S = \frac{2\Delta\omega_{is}^2}{\Gamma \cdot \Delta\omega_1}. \quad (3.15)$$

Multistage isotopically selective excitation makes it possible to achieve a sufficiently high selectivity even in the case of overlapping Doppler-broadened lines of the isotopes.<sup>69</sup> Let us assume that the excitation is due to a collimated laser beam with a spectral width  $\Delta\omega_1 \leq \Gamma$ . This represents a traveling wave of frequency  $\omega_1$  which excites only atoms in narrow intervals of the component of their velocity along the direction of the light wave  $\mathbf{k}$  (for details see Ref. 70)

$$|\mathbf{k}_1 \mathbf{v}_A - \omega_1 + \omega_{0A}| \ll \Gamma \text{ and } |\mathbf{k}_1 \mathbf{v}_B - \omega_1 + \omega_{0B}| \ll \Gamma, \quad (3.16)$$

where  $|\mathbf{k}_1| = \omega_1/c$  is the wave vector of the field during the first stage;  $\mathbf{v}_A$  and  $\mathbf{v}_B$  are the velocities of atoms of the A and B isotopes;  $\omega_{0A}$  and  $\omega_{0B}$  are the centers of the Doppler-broadened absorption lines of these isotopes.

Since  $\Delta\omega_D \geq \Delta\omega_{is}$ , there is no significant selectivity after the first excitation stage. However, the profile of an absorption line for a collinear monochromatic light wave changes greatly at the second and third stages. If the isotopic shift exceeds the homogeneous line width ( $\Delta\omega_{is} > 2\Gamma$ ), the profile of the absorption line in the second stage (Fig. 31) has two clear resonances due to the isotopes whose velocities obey

$$\mathbf{k}_1 \mathbf{v}_A \approx \omega_1 - \omega_{0A} \text{ and } \mathbf{k}_1 \mathbf{v}_B \approx \omega_1 - \omega_{0B}. \quad (3.17)$$

If the laser radiation frequency  $\omega_2$  is tuned to just one of the resonances, the excitation selectivity at the second stage is given by an expression of the (3.13) type. A similar situation arises when the radiation frequency  $\omega_3$  is tuned correctly to the peak of the resultant natural

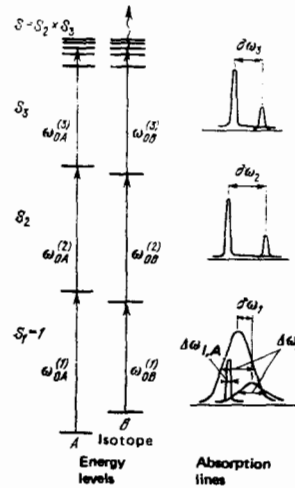


FIG. 31. Selective three-stage excitation under conditions of Doppler line broadening  $\Delta\omega_D$  with selectivity in the second and third stages.<sup>69</sup> Here,  $\Delta\omega_{1,A}$  is the width of the laser line or atomic transition.<sup>69</sup>

narrow resonance in the third stage.

We can see that the resultant selectivity of the method of three-stage excitation by three collinear traveling waves with correctly selected frequencies  $\omega_1$ ,  $\omega_2$ , and  $\omega_3$  can reach the value

$$S = S_2 \times S_3. \quad (3.18)$$

In spite of the absence of excitation selectivity in the first stage, a high selectivity can be achieved in the subsequent stages even when the atomic beam is not collimated.

Under favorable conditions when the isotopic shift is large and the line width  $2\Gamma$  is small, the excitation selectivity in one stage can reach  $10^6$  and in three stages it can be  $10^{18}$ . By way of example, we shall consider the three-stage excitation of the ytterbium isotopes 174 and 176. In the first stage ( $\lambda_1 = 555.6$  nm) the shift is  $\Delta\nu_{18}^{(1)}(174-176) = 0.032$  cm<sup>-1</sup> (Ref. 71) and  $\Gamma_1 = 0.6 \times 10^6$  sec<sup>-1</sup>. Since the second and third stages are linked by a common level with an isotopic shift, then the shift for these levels is the same and amounts to  $|\Delta\nu_{18}^{(2)}| = |\Delta\nu_{18}^{(3)}| = 0.013$  cm<sup>-1</sup> (Ref. 72) and  $\Gamma_2 = 0.5 \times 10^8$  sec<sup>-1</sup>. When the spectral width of the laser radiation is  $\Delta\omega_1 = 0.5 \times 10^8$  sec<sup>-1</sup>, the excitation selectivities are  $S_1 = 6 \times 10^5$  and  $S_{2,3} = 2.7 \times 10^5$ , respectively, and the total selectivity is  $S = 4.4 \times 10^{16}$ . This means that one of the isotopes can be recorded with the signal/noise ratio of unity when the relative concentration of this isotope is  $N_B/N_A \approx 2 \times 10^{-17}$ .

It should be pointed out that this high selectivity imposes serious limitations on the concentration of the main isotope because of the process of resonant transfer of the excitation from atoms at the first intermediate level to the second isotope. The probability of excitation transfer during the resonance time  $\tau_1$  at the intermediate level should be less than the reciprocal of the excitation selectivity in the first stage:

$$\sigma_{\text{res. tr}} N_A v_0 \tau_1 \ll \frac{1}{S_1}, \quad (3.19)$$

where  $\sigma_{\text{res. tr}}$  is the cross section for the resonant

transfer of excitation. A selectivity of  $S_1 \approx 10^6$  can be retained for  $\sigma_{res, tr} = 10^{-13} \text{ cm}^2$ ,  $\tau_1 = 10^{-8} \text{ sec}$ , and  $v_0 = 10^4 \text{ cm/sec}$  if the concentration of atoms is  $N_A \lesssim 10^{11} \text{ cm}^{-3}$ . We can easily see that the resonant charge exchange may induce the selectivity of isotope separation but not the total selectivity of detection of the rarer isotope.

We can see that the investigated methods increase the detection selectivity considerably and make it possible to record the presence of single atoms of a given isotope among  $10^{13} - 10^{18}$  atoms of other isotopes.

#### d) Discussion of experiments

Experimental studies of selective multistage photoionization of atoms, designed to achieve the maximum absolute photoionization efficiency and detection of single atoms, were carried out in all three cases of atoms in a vapor, atoms in a buffer gas, and atoms in a beam. We shall now consider them briefly.

1) *Atoms in a vapor.* Ambartsumyan *et al.*<sup>52</sup> reported an experimental investigation of two-stage ionization of rubidium atoms by selective excitation of components of the  $6p^2P$  doublet by radiation from a tunable dye laser ( $\nu_1 = 23\,799$  or  $23\,725 \text{ cm}^{-1}$ ) and simultaneous nonresonant ionization of the excited atoms by radiation from a ruby laser ( $\nu_2 = 14\,403 \text{ cm}^{-1}$ ) or its second harmonic ( $\nu_2' = 28\,806 \text{ cm}^{-1}$ ). The rubidium atoms were excited in a vapor whose concentration varied within wide limits right up to  $10^{14} \text{ cm}^{-3}$ . A study was made of the dependence of the number of detected ions on the intensity of the exciting and ionizing radiations, on the concentration of rubidium, and on the potential difference between the recording electrodes. Saturation in respect of the intensity of the ionizing radiation ( $\nu_2 = 14\,403 \text{ cm}^{-1}$ ) i.e., ionization of each excited atom, was achieved. This result demonstrated feasibility of using multistage photoionization by laser radiation in effective ionization of atoms.

2) *Atoms in a buffer gas.* The first successful detection of single atoms by multistage photoionization took place under similar conditions.<sup>16</sup> Cesium atoms in a buffer gas were excited to the  $7^2P_{3/2}$  state by radiation from a pulsed flashlamp-pumped dye laser. The same pulses were used to ionize the excited atoms. An estimate was obtained of the energy flux necessary for effective ionization of the atoms. The conditions for focusing laser radiation were selected on the basis of this estimate. The dependences of the ionization signal on the laser radiation intensity confirmed that saturation was reached during the ionization stage, exactly as in experiments of Ambartsumyan *et al.*<sup>52</sup>

A special feature of the experiments reported by Hurst *et al.*<sup>16</sup> was detection of the electrons created by ionization with the aid of a discharge in a gas. An ionization chamber was filled with a mixture of argon and methane at a pressure of 100-200 Torr and it acted as a gas-ionization proportional counter with a gain of the order of  $10^4$ . Cesium atoms diffused in the buffer gas to the region of interaction with the laser beam from a cesium source.

Figure 32 shows the distribution of the amplitude of

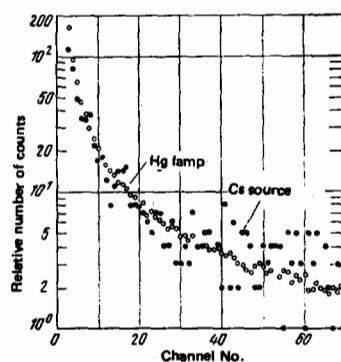


FIG. 32. Distribution of the amplitudes of pulses recorded by a proportional counter in the case of detection of a single cesium atom after 20 laser pulses.<sup>16</sup> For comparison, the figure includes the one-electron distribution obtained using a noncoherent light source.

the counter pulses for the case when one cesium atom was recorded per 20 laser pulses. For comparison, this figure also shows the one-electron distribution obtained with a mercury lamp. The fluctuations in the distributions are due to the statistics of the pulse counting. The similarity of the two distributions shows that the sensitivity of the system was sufficient for reliable recording of one cesium atom entering the laser beam. The volume of the interaction zone was  $0.05 \text{ cm}^3$ .

In subsequent experiments this method was used successfully to detect Cs atoms resulting from fission of Cf nuclei.<sup>73</sup>

Experiments of this type have the advantage of simplicity but they suffer from the use of a buffer gas, which results in collisional broadening of the absorption line and, consequently, in destruction of the isotopic shift and hyperfine splitting. Consequently, the detection selectivity is low for isotopes of the same element. Nevertheless, the method can be used successfully to detect atoms in a foreign gas in concentrations of  $10^{19}$  atoms/ $\text{cm}^3$  (Ref. 68).

3) *Atoms in a beam.* In the atomic beam experiments it is preferable to use the method of resonant ionization from excited states via Rydberg or autoionizing states. We can then use a high repetition frequency of laser pulses because only moderate energies are needed. This ionization method was used in Refs. 12, 13, 74, and 75 to detect single sodium and ytterbium atoms. Atoms of a given element in a beam (Fig. 33) were excited to Rydberg states by the multistage method using radiation emitted by pulsed tunable dye lasers (pulse duration 7 nsec, spectral width  $\Delta\nu_1 \approx 1 \text{ cm}^{-1}$ ). All the dye lasers were pumped simultaneously by one nitrogen laser at a repetition frequency of 12 Hz. The sodium atoms were excited in two stages, whereas ytterbium was excited in three stages. Laser beams intersected an atomic beam between two electrodes which were subjected to electric field pulses delayed by 20-50 nsec relative to the laser pulses. The ions produced in this way were extracted through a slit in one of the electrodes and were recorded with a secondary-electron multiplier. The geometry of the laser beams, atomic



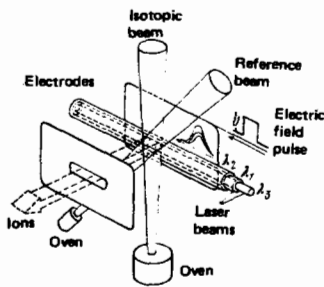


FIG. 33. Relative positions of atomic beams, laser beams, and electrodes in detection of atoms in a beam.<sup>76</sup>

beam, and slit made it possible to extract practically all the ions from the gap between the electrodes. Under experimental conditions the efficiency of detection of these ions by a secondary-electron multiplier was close to unity.

Effective excitation of atoms to higher states requires that all the quantum transitions employed be saturated. The intensity of electric field pulses should be sufficient for the ionization of Rydberg atoms with a near-unity probability. Only when these two conditions are satisfied, can one ensure the maximum yield of ions. Therefore, in an experiment of the kind described above the selection of the principal quantum number  $n$  of the Rydberg state is so important. The cross section for the excitation of atoms in the last stage decreases strongly on increase in the principal quantum number of the level ( $\sigma_{exc} \sim n^{-3}$ ). On the other hand, the critical field (i.e., the field in which the yield of ions is nearly 100%) rises strongly on reduction in  $n$ . The optimal conditions are obtained when the cross section for the excitation of a higher state is as large as possible and the intensity of the electric field needed for efficient ionization has a value easily attainable under laboratory conditions. This is true, for example, of the  $13^2D_{5/2}$  state of sodium ( $E_{cr} = 14.2$  kV/cm) and of the  $17^3P_2^0$  state of ytterbium ( $E_{cr} = 11.5$  kV/cm).

Figure 34 shows the dependences of the relative yield of ytterbium ions on the energy density of the laser pulses during the first, second, and third excitation stages (Figs. 34a–34c) and on the intensity of the electric field pulses (Fig. 34d) in the excitation of the  $17^3P_2^0$

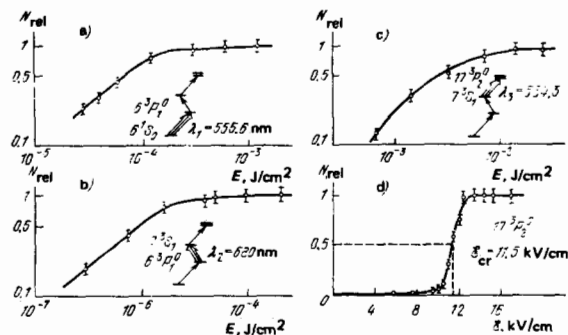


FIG. 34. Dependences of yields of ytterbium ions on the energy density of laser pulses used in the first, second, and third excitation stages (a–c, respectively) and on the intensity of electric field pulses (d).<sup>13</sup>

state (similar dependences are obtained for sodium). It follows from Eq. (3.2) that in the case of simultaneous saturation of all three transitions to the  $17^3P_2^0$  state the fraction of atoms observed is  $5/12$  of all the atoms in the zone of interaction with laser radiation. It follows that under optimal experimental conditions about half the atoms present in the interaction zone at the moment of arrival of laser pulses are excited to a higher state and each excited atom is then ionized.

These were the conditions in a study of the dependence of the ion signal on the temperature of the oven containing ytterbium (Fig. 35a). Cooling resulted in a gradual fall of the signal amplitude followed by its instability. This instability was due to fluctuations of the number of atoms in the interaction (excitation) zone. When the density of the atomic beam was low, such fluctuations became comparable with the average number of atoms in the zone.

The density of the atomic beam should be so low that in most cases there is no more than one atom in the interaction zone. This was the regime under which a study was made of the statistics of the appearance of atoms in the interaction zone (Figs. 35b and 35c). The similarity of the distributions obtained and the Poisson law led to the conclusion that the detection system recorded accurately the arrival of an atom in the excitation zone at the time of interaction with laser pulses.

We can thus see that this method of ionization of Rydberg atoms by an electric field is universal and makes it possible to use the existing tunable dye lasers with low values of the average power and employ practically any laboratory apparatus to detect atoms efficiently and with maximum sensitivity.

#### e) Absolute sensitivity

The whole problem of detection of single atoms can be divided nominally into three interrelated tasks:

- 1) accumulation, storage, and production of free

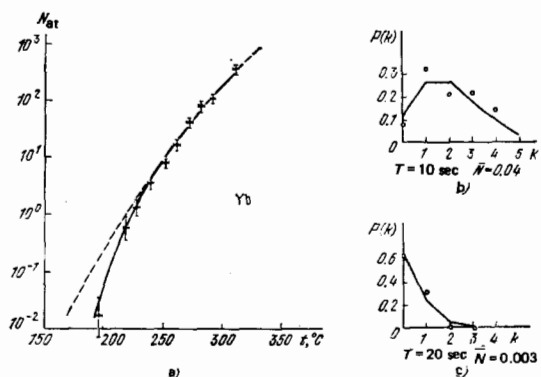


FIG. 35. Temperature dependence of the ytterbium ion signal: fluctuations of the number of atoms in the interaction zone<sup>13</sup>: a) dependence of the yield of ytterbium ions on the oven temperature under conditions of maximum ion yield (the dashed curve is calculated and the continuous curve is experimental); b) distribution of the number of ytterbium ions recorded in a time  $T = 10$  sec when the average number of ions is  $\bar{k} = 3$  and the average number of atoms in the interaction zone is  $\bar{N} = 0.04$ ; c) same as b) but for  $T = 20$  sec,  $\bar{k} = 0.35$ ,  $\bar{N} = 0.003$ .

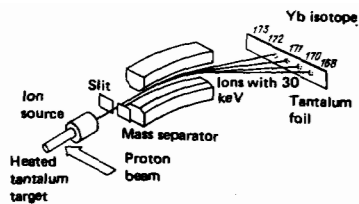


FIG. 36. System used to prepare samples with ytterbium isotopes by implantation of ions in a foil.<sup>76</sup>

atoms;

- 2) transport of atoms to the detection region;
- 3) detection of atoms by laser radiation.

The above examples clearly relate to the third task. A single atom interacting with laser radiation is subjected to various ionization and detection methods producing a selective ion signal and this signal exceeds the noise background to such an extent that the transit of an atom across the laser beam can be detected reliably. However, in all such experiments the sources of free atoms are samples containing macroscopic (by weight) amounts of the investigated chemical element. There are now many scientific and practical situations in which the absolute sensitivity is required at the level of  $10^3$ – $10^6$  or fewer atoms. Therefore, the first two tasks have become particularly important in the problem of detection of very small amounts of matter. An example of a successful search for such small amounts was reported by Bekov *et al.*<sup>76</sup> They made an investigation of the isotopic and hyperfine structure of the  $6^1S_0 - 6^3P_1$  transition of ytterbium using samples containing about  $10^{10}$  atoms of some ytterbium isotope.

Figure 36 shows the arrangement used to prepare such samples. This was done in an accelerator with a mass separator at the Leningrad Institute of Nuclear Physics, Academy of Sciences of the USSR<sup>2)</sup> by the method of implantation of ions in a metal. A tantalum target heated to 2000–3000°C was irradiated with an intense proton beam. Nuclear reactions of the target atoms with protons produced almost all the ytterbium isotopes, including those which were unstable. These reaction products were ionized in an ion source, collimated, and passed on to a mass separator. They were separated there spatially in accordance with their masses so that ions of different isotopes of about 30 keV energy reached different parts of the tantalum foil 50  $\mu$  thick. These ions penetrated the foil to a depth of 100 Å and became neutralized. The resultant atoms were thus isolated from the ambient medium and under normal conditions they could be retained for a long time in the foil. Thus, the method of implantation of ions in a foil provided a convenient technique for accumulating, storing, and transporting very small amounts of matter. As mentioned earlier, one could also implant an unstable isotope. The modern mass separators can create fluxes of  $10^7$ – $10^{11}$  ions/sec. This makes it possible to accumulate rapidly  $10^9$ – $10^{12}$  atoms

<sup>2)</sup>This experiment was carried out in cooperation with the group led by Prof. E. E. Berlovich of the Leningrad Institute of Nuclear Physics, Academy of Sciences of the USSR.

of an unstable isotope. Employing the above detection methods under on-line conditions, one can obtain spectral information on isotopes with a lifetime of a few seconds or less.

The method described above was used to implant about  $10^{10}$  ions of a stable ytterbium isotope in a tantalum foil. Heating of this foil above 1200°C resulted in considerable diffusion of ytterbium atoms out of tantalum. An atomic beam was formed from these ytterbium ions as follows. The foil irradiated in the accelerator was placed in a tantalum crucible with a narrow cylindrical channel (Fig. 37). This crucible was placed inside a tantalum tube heated by an electric current. The construction of the oven was such that the temperature in the small crucible could reach 1800°C. The free atoms were collimated by the narrow channel and formed a highly directional atomic beam.

The experimental method and the laser units were completely analogous to those described in the preceding section. A reference atomic beam (Fig. 33) was used to tune the laser radiation to the required transitions. This guaranteed a resonance with an absorption line of any of the isotopes because the width of the laser spectrum  $\Delta\nu_l = 1 \text{ cm}^{-1}$  was considerably greater than the widths of the isotopic and hyperfine structures of the transitions in ytterbium. Measurements of the energy density and saturation curve (Fig. 34) showed that practically every third atom reaching the excitation region at the moment of arrival of laser pulses became ionized. Under these experimental conditions the background signal was 2–3 pulses of the secondary-electron amplifier in 3 min. The crucible with the foil containing one of the ytterbium isotopes was then heated. Selective recording of the signal showed that the optimal temperature range was 1300–1400°C when the signal/noise ratio of at least 3 was maintained for 20 min. This period was sufficient for recording the structure of one of the transitions with a narrow-band laser. A dye laser continuously tunable by pressure and characterized by an emission line of width  $\Delta\nu_l \approx 0.04 \text{ cm}^{-1}$  was used for this purpose in the first stage.

Figure 38a shows the dependence of the ion current on

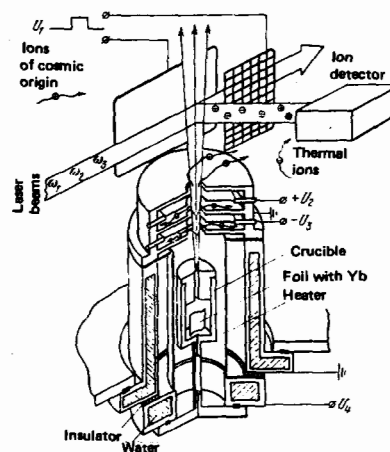


FIG. 37. Construction of a high-temperature oven for producing an atomic beam of an element implanted in a foil.<sup>76</sup>

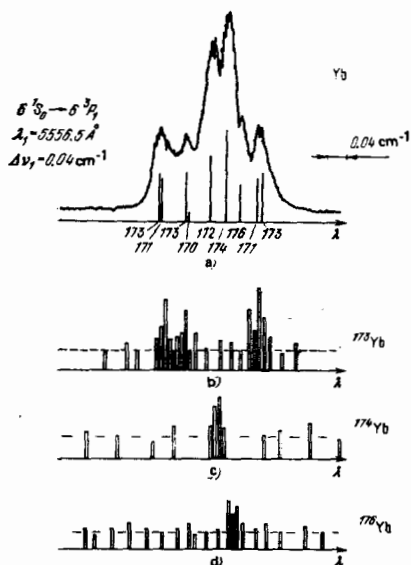


FIG. 38. Hyperfine and isotopic structure of the  $6^1S_0 - 6^3P_1$  transition in Yb (Ref. 36): a) obtained with  $0.04 \text{ cm}^{-1}$  resolution for a reference ytterbium beam with a natural isotopic composition; b)–d) same for the  $^{173}\text{Yb}$ ,  $^{174}\text{Yb}$ , and  $^{176}\text{Yb}$  isotopes evaporated from a foil containing about  $10^{10}$  atoms of the isotope.

the laser wavelength during the first stage, obtained for a reference beam formed by evaporation of ytterbium with natural isotopic abundances. The vertical lines give the positions of the absorption lines of the various ytterbium isotopes. Next, the reference beam was stopped, the crucible with the foil was heated, and the laser wavelength was adjusted again. Since the density of the investigated isotopic atomic beam was very low, the recording of the ion signal reduced to detection of single ions in the process of laser frequency scanning. Typical spectra in the form of single pulses obtained for different isotopes are shown in Figs. 38b, 38c, and 38d. The horizontal dashed lines represent the total background. The spectra make it possible to identify uniquely the ytterbium isotopes  $^{173}\text{Yb}$ ,  $^{174}\text{Yb}$ , and  $^{176}\text{Yb}$ .

The experimental results could be used to estimate the minimum number of atoms required to record the complete spectrum and also to find the yield of the atoms from the foil and crucible. Figure 39 shows how the absolute sensitivity of the method was estimated in this experiment. Stable recording of a single resolvable spectral interval could be obtained for just three

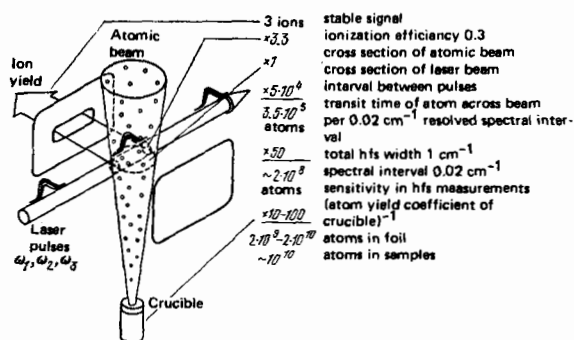


FIG. 39. Ways of estimating the absolute sensitivity of a system for detecting atoms in a beam.<sup>76</sup>

ions. Since the ionization probability was 0.3, 10 atoms were needed to obtain three ions. The recording zone represented only one seventh of the atomic beam cross section. When the velocity of atoms in this beam was  $5 \times 10^4 \text{ cm/sec}$  and the diameter of the laser beam was 1 mm, the off-duty factor of the laser pulses needed to ensure the interception of all the atoms was  $5 \times 10^4$  times less than the off-duty factor used in this experiment. Thus,  $3.5 \times 10^6$  atoms emitted from the crucible were needed to record one spectral interval. To record the full spectrum in an interval of  $1 \text{ cm}^{-1}$  with a resolution of  $0.02 \text{ cm}^{-1}$ , it was necessary to obtain 50 spectral intervals, i.e.,  $2 \times 10^8$  atoms were needed in the atomic beam. In the above experiment it was found that 3–4 spectra were recorded for each of the foil samples (with  $\sim 10^{10}$  ytterbium atoms), i.e.,  $\sim 3 \times 10^9$  atoms were used in each cycle. Therefore, the relative yield of these atoms from the foil and crucible was 0.07, which was a realistic value.

The above experiment shows that the method of detection in an atomic beam formed by atoms diffusing from a foil can be used successfully in combination with dye lasers characterized by low repetition frequencies. One can record the spectra of elements available in amounts of  $10^9 \text{--} 10^{10}$  atoms. The sensitivity of the method can be increased radically by pumping dye lasers with a proper vapor laser characterized by a repetition frequency of 10–20 kHz. This should make it possible to ionize practically every second atom crossing the interaction zone. An improvement in the geometry of the system should make it possible to record hyperfine spectra for  $10^5 \text{--} 10^6$  atoms in a foil.

#### f) Additional potentialities of the photoionization method

In the photoionization method an atom being detected is converted to an ion. This is both an advantage and a shortcoming of this method. In those cases when it is necessary to investigate further and accumulate the detected atoms, this conversion is an advantage because an electromagnetic field can be used to control easily the motion of ions, extract them from the interaction zone, accumulate them, etc. On the other hand, this observation method is destructive and, therefore, it is difficult to ensure repeated interaction between a given atom and the laser field, as can be done—for example—in the fluorescence method. If cyclic charging of an ion and return of an atom to the laser field is necessary, this essentially sole shortcoming of the photoionization method can be overcome in several ways. For example, an ion formed in an ionization event can be accelerated by an electric field and made to pass through a detector film. Secondary emission from the film is used to detect such an ion. The ion itself is returned by a system of electric and magnetic fields to the source, where it becomes neutralized. The resultant atom is subjected again to the laser field, becomes ionized, and the whole process is repeated. This makes it possible to introduce a new frequency into the detection system, which is the frequency of cyclic conversion of an atom into an ion and back to an atom, and thus reduce considerably the background due to unwanted ions.

#### 4. DEFLECTION ATOM-DETECTION METHOD

Atoms may also be detected by altering their trajectories as a result of interaction with a laser field (Fig. 1c). Here we have at least two possibilities. Firstly, a laser field may alter the quantum state of an atom and thus influence its trajectory in external fields. Secondly, repeated emission of photons by an excited atom may alter the initial direction of motion because of the recoil effect. One can also combine these two methods with the fluorescence and photoionization methods.

##### a) Deflection of atoms in a magnetic field

Selective excitation of an atom to a specific quantum state from the ground state alters its quantum numbers and this may be manifested by a change in the nature of its motion in external electric and magnetic fields. In other words, the trajectory of an atom may change as a result of laser excitation and this provides a very effective method for the detection of single atoms. One of the variants of this method has been implemented successfully: it is based on a redistribution of atoms between magnetic sublevels by laser excitation and subsequent "magnetic detection" of the optically oriented atoms.

The idea of magnetic detection of atoms dates back to the work of Stern and Gerlach. In a magnetic field of a certain configuration, for example, that produced by a six-pole magnet, atoms are deflected in accordance with their magnetic moment. If laser radiation can alter the magnetic moment of an atom, this effect can be used for selective optical detection of atoms. Such an approach to the problem of optical detection of atoms was discussed in Ref. 77. However, only the appearance of cw dye lasers has made it possible to implement this approach in the work described in Refs. 14, 78, and 79. A high-resolution laser spectroscopy method for Na atoms in beams was developed. It was applied successfully to determine the hyperfine structure and isotopic shifts of radioactive Na isotopes. This was done using the arrangement shown schematically in Fig. 40. Radioactive isotopes  $^{21}\text{Na}$ ,  $^{22}\text{Na}$ ,  $^{24}\text{Na}$ , and  $^{25}\text{Na}$  were produced by bombarding an aluminum target with 150 MeV protons, which gave rise to the nuclear reaction  $^{27}\text{Al}(p, 3p\text{n})\text{Na}$ . An atomic beam resulted from the evaporation of the target during continuous irradiation

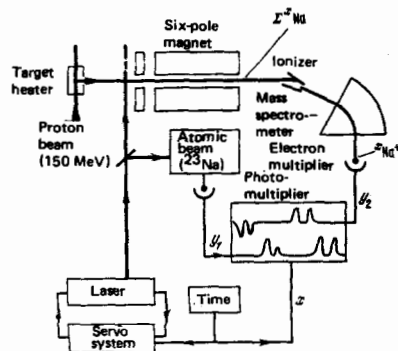


FIG. 40. Apparatus used in the optical detection of radioactive Na atoms, using one spectral line and an accelerator, by the method of magnetic deflection of optically oriented atoms.<sup>14, 79</sup>

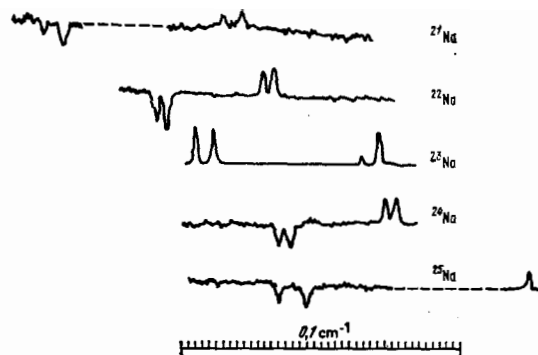


FIG. 41. Hyperfine structure and isotopic shifts of the  $D_1$  line of radioactive Na isotopes obtained using the apparatus shown in Fig. 40 (Refs. 14 and 79). The spectrum of each isotope was measured independently, relative to the spectrum of the stable  $^{23}\text{Na}$  isotope, and reduced to the common wavelength scale.

with protons. The total flux of radioactive Na atoms in the beam was  $10^8$  atoms/sec. The ground state of the Na atoms was split into two hyperfine sublevels, for example those with  $F=2$  and  $F=1$  in the case of the stable isotope. In a strong magnetic field these two sublevels were split again giving rise to two identically populated groups of sublevels characterized by  $m_j = \pm 1/2$ . A six-pole magnet could focus atoms at the magnetic sublevel  $m_j = +1/2$  in the ground state and, conversely, defocus atoms at the magnetic sublevel  $m_j = -1/2$ . Resonant laser irradiation altered the populations of these sublevels and this was manifested by a change in the number of focused atoms at the sublevels with  $m_j = +1/2$  which reached an ionization detector.

A reliable determination of the hyperfine structure of radioactive Na atoms in a beam of  $10^8$  atoms/sec intensity was reported in Ref. 14 (Fig. 41). The concentration of atoms in the zone of interaction with the laser beam was probably in the range  $1-10^2$  atoms/cm<sup>3</sup>. A reliable determination of the hyperfine structure of the individual Na isotopes was achieved by simultaneous separation of the isotopes in accordance with their masses, i.e., by combining the above method with mass spectroscopy.

Selective laser irradiation can also be used in other methods for deflection of atoms with the aim of selective detection. For example, selective multistage excitation of atoms to Rydberg states is possible and, in these states, in contrast to the lower states, they have a very high polarizability.<sup>66</sup> The polarizability  $\alpha$  of an atom is proportional to  $(n^*)^6$ , where  $n^*$  is the effective principal quantum number. Such highly excited atoms should be deflected very strongly in a spatially inhomogeneous electric field of moderate intensity.

##### b) Deflection of atoms by a resonant optical pressure

Repeated emission of photons from a resonant collimated laser beam (Sec. 2) results in an unavoidable deflection of the trajectory of an atom because of the recoil effect. Control of the motion of atoms by laser radiation is being investigated intensively since, in principle, it should be possible to cool atoms and to confine

them for a long time by an optical field, i.e., it should be possible to achieve the detection method shown in Fig. 2d. An interested reader is directed to special reviews of this subject.<sup>80,81</sup> Here, we shall consider briefly the simplest case of control of the motion by deflection, which—in principle—can also be used to detect atoms.

Let us assume that an atom absorbs resonantly radiation from a collimated optical beam and emits it isotropically. Then, the following optical force acts on an atom in the direction of the laser beam:

$$F_{\text{opt}} = \frac{I\sigma}{c} (|a_1|^2 - |a_2|^2), \quad (4.1)$$

where  $I$  is the laser radiation intensity,  $\sigma$  is the resonant absorption cross section, and  $|a_i|^2$  is the probability of finding an atom at an  $i$ -th level of a transition which is in resonance with the optical field. The first term in Eq. (4.1) clearly represents the absorption of a photon by an atom in a state 1, whereas the second term represents induced emission of a photon by an atom in a state 2 contributing to the same wave. When the quantum transition in question is strongly saturated so that on the average we have  $|a_i|^2 \approx 1/2$ , induced emission due to the opposite sign of the recoil momentum compensates almost exactly the optical force because of absorption. The difference of the probabilities in Eq. (4.1) tends to

$$(|a_1|^2 - |a_2|^2) \rightarrow (|a_1|_0^2 - |a_2|_0^2) \left(1 + \frac{I}{I_{\text{sat}}}\right)^{-1}, \quad (4.2)$$

where  $|a_i|_0^2$  is the initial relative population of the  $i$ -th state and  $I_{\text{sat}}$  is the saturation intensity of the quantum transition, which is essentially governed by the rate of excitation of excited atoms from the state 2 to the initial state 1. If  $I \gg I_{\text{sat}}$ , the force acting on an atom tends to the constant value

$$F_{\text{opt}}^{\text{max}} = \frac{h\omega\Gamma}{2c}. \quad (4.3)$$

The physical meaning of Eq. (4.3) is very simple. As a result of each photon emission an atom receives a momentum  $\hbar\omega/c$ . The number of such emissions is governed by the rate of relaxation  $\Gamma$  of an atom to the ground state and the factor  $1/2$  appears because, on the average, an atom spends only half the time in the ground state.

If an atom crosses a laser beam of diameter  $d$  at right angles and the transit time is  $\tau_{\text{tr}} = d/v_0$ , it acquires a velocity  $\Delta v$  in the direction of the optical wave and is deflected by an angle  $\Delta\varphi$ :

$$\Delta\varphi = \frac{\Delta v}{v_0} = \frac{\Gamma d}{2c} \cdot \frac{h\omega}{Mv_0} \approx \frac{\Gamma d}{2c} \frac{h\omega}{kT_0}, \quad (4.4)$$

where  $v_0$  is the average velocity of the atom governed by the temperature  $T_0$  of the atomic beam source. In the case of allowed transitions with  $\Gamma = 10^8 \text{ sec}^{-1}$ ,  $d = 1 \text{ cm}$ ,  $T_0 = 10^3 \text{ }^\circ\text{K}$ ,  $\hbar\omega = 2 \text{ eV}$ , an atom crossing an optical beam can emit  $10^3 - 10^4$  photons (Sec. 2) and be deflected by an angle  $\Delta\varphi \approx 0.04 \text{ rad}$ , which can be detected easily. Clearly, reliable observation requires that the angular divergence of the atomic beam should be less than the photodeflection angle.

The force of a spontaneous resonant optical pressure was studied experimentally<sup>82-84</sup> by photodeflection of

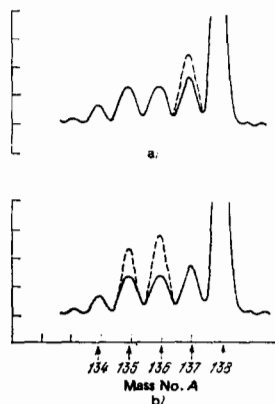


FIG. 42. Isotopically selective photodeflection of Ba atoms by resonant laser radiation of a natural mixture of isotopes.<sup>85</sup> The continuous curves show the mass spectrum in the absence of irradiation and the dashed lines give the mass spectrum after irradiation of the isotopes <sup>137</sup>Ba (a), <sup>136</sup>Ba and <sup>135</sup>Ba (b).

atoms in a Na beam illuminated with a collimated beam from an Na lamp<sup>82,84</sup> or with a beam from a tunable dye laser.<sup>83</sup> In these experiments a repeated cyclic interaction of atoms with laser radiation was not achieved and, therefore, atoms were deflected through a very small angle.

This experiment can now be improved significantly by the cyclic interaction described in Sec. 2. Much better results were obtained in the experiments reported in Refs. 85 and 86, where isotopically selective photodeflection of Ba atoms was achieved by interaction of a laser beam with the  $6s^2\ ^1S_0 - 6s6p\ ^1P_1$  transition at 553.5 nm. The lifetime of the <sup>1</sup>P<sub>1</sub> excited state was  $\tau_{\text{exc}} = 8.4 \text{ nsec}$  and, therefore, during the transit time of Ba atoms across the laser beam  $\tau_{\text{tr}} \approx 10^{-4} \text{ sec}$  an atom could emit  $10^4$  photons.

In reality, this did not occur because a Ba atom was quite likely to undergo a radiative transition from the <sup>1</sup>P<sub>1</sub> excited state to a lower metastable state <sup>1</sup>P<sub>2</sub>. The ratio of probabilities of returning to the ground and metastable states was 60 so that the maximum increase in the transverse velocity because of resonant optical pressure was  $60(\hbar\omega/Mc) = 45 \text{ cm/sec}$ . This selective photodeflection of the Ba atoms by selective excitation of a specific isotope was observed with the aid of mass analysis of the deflected atoms. Figure 42 shows the

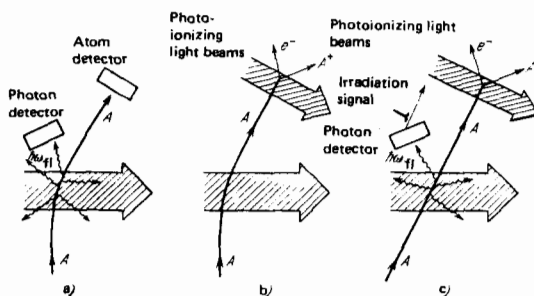


FIG. 43. Possible combinations of various laser methods for the detection of atoms: a) combination of the photodeflection and fluorescence methods; b) combination of the photodeflection and multistage ionization methods; c) combination of the fluorescence and multistage photoionization methods.

results of an experiment in which  $^{138}\text{Ba}$  was the main (71.66%) isotope in a natural mixture. Selective excitation of the  $^{137}\text{Ba}$  isotope resulted in an increase of the corresponding mass peak (Fig. 42a). Excitation of the hyperfine structure component corresponding to  $^{136}\text{Ba}$  resulted also in an increase in the  $^{135}\text{Ba}$  mass peak because of the overlap of two spectral components (Fig. 42b).

These experiments were not designed to detect single atoms but the effects observed could be used as the basis of methods for atom detection. A combination of the photodeflection with other methods described above (see Secs. 2 and 3) could be particularly successful.

### c) Possible combinations of methods

Figure 43 shows various possible combinations of methods for the laser detection of atoms. Multiple cyclic interaction of atoms with a laser beam can be used to observe both photodeflected atoms and isotropically reemitted photons (Fig. 43a). This combination of the fluorescence and photodeflection methods is useful also for increasing the deflection selectivity and for suppressing the background because photon and atom detectors can be arranged to work in a signal coincidence system. Photodeflected atoms can be detected by the method of multistage photoionization (Fig. 43b). This also ensures multiplication of the selectivities of each method and suppression of the background. Finally, we can combine the fluorescence and photoionization methods (Fig. 43c). Additionally, we can use the fluorescence signal to apply laser radiation with the aim of selective photoionization of the detected atoms and their extraction from the general atomic flux.

## 5. CONCLUSIONS. APPLICATIONS

The photoionization, fluorescence, photodeflection, and combined methods for the laser detection of single atoms developed in recent years can now be applied to almost all the elements in the periodic table. They promise to become an important branch of experimental physics with many applications in atomic physics, chemistry, photophysics, nuclear physics, astrophysics, and cosmological dating in many important and interesting problems which may be solved by laser methods for the detection of single atoms. Discussion of the new experimental opportunities that are now opening up is well outside the scope of the present paper and should best be the subject of a special review. Therefore, we shall confine ourselves to a simple listing of such applications.

One should mention particularly nuclear physics, where practically all the atoms with interesting and unusual nuclei are created in countable numbers: they are short-lived nuclei far from the stability band, atoms created in detectors of solar neutrinos, shape isomers, and nuclides of cosmic origin. Some experiments of this kind have already been carried out (measurements have been made of the deformation of nuclei of unstable isotopes of alkali<sup>14,15</sup> and some alkaline-earth elements<sup>11</sup>) and others are in the planning stage (similar measurements in the case of isotopes of rare-

earth elements<sup>76</sup>), while still others are in the development stage (detection of daughter atoms in the physico-chemical method of recording solar neutrinos<sup>87</sup>); there are also some methods which are still in the discussion stage (detection of superdense nuclei<sup>88</sup>), etc.

In the atomic physics and chemistry the technique of laser detection of single atoms can be used to study diffusion and chemical reactions of atoms, photodissociation of molecules and photoionization of atoms, broadening of absorption lines by collisions, detection of rare impurities in pure materials, ambient media, etc.

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