

Selective atomic photoionization and its use in isotope separation and spectroscopy

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The development of selective photoionization of atoms is reviewed. This is a very general method for laser isotope separation, and it has extremely interesting spectroscopic applications. Processes tending to restrict the applicability of the method are discussed. Examples cited include the use of selective photoionization to study the superior structure in atomic spectra, the resonance transfer of excitation energy, and the spectroscopy of atomic Rydberg states. Questions involved in laser isotope separation by selective photoionization are discussed.

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1. INTRODUCTION

The resonance interactions of intense laser beams with matter are attracting increasing interest. Research and development and the industrial applications of continuously tunable lasers have made selective photoprocesses, the study of these processes, and their practical applications one of the most important applied fields of quantum electronics. The most convincing results of the feasibility of selective processes through a resonance interaction of an intense laser beam with matter have been obtained in laser isotope separation, which is the subject of three recent reviews.¹⁻³ There are three methods for laser isotope separation: selective photoionization of atoms, multistep selective dissociation of molecules by an intense IR laser beam, and selective heterogeneous processes. The first two of these methods are being actively pursued and are finding an increasing number of applications. The selective heterogeneous processes, i.e., processes which occur selectively under the influence of resonance laser radiation in decidedly heterophase systems, are extremely interesting and hold much promise, but their actual applicability for laser isotope separation is not clear at this point, and there is uncertainty regarding the mechanisms for many of the observed effects (see the review by Karlov and Prokhorov⁴).

Selective photoionization of atoms is the most obvious selective interaction of resonance laser beams with matter. This photoionization leads to the most general method for laser isotope separation, which is applicable to all isotopes of all the elements in the periodic table, and it has extremely interesting spectroscopic applications. Unfortunately, this method runs into both fundamental and technical difficulties, which are serious obstacles to achieving its full potential. Under these circumstances it is worthwhile to examine in de-

tail the selective photoionization of atoms and its applications, including spectroscopic. This is our purpose in the present review.

In relatively recent reviews^{3,5} on the problem of laser separation at the atomic level, the emphasis was on laser isotope enrichment of uranium through selective photoionization of atoms. Comparatively little attention was paid there to the spectroscopic applications of this selective method.

A general concept of realizability of selective photoprocesses reduces to a separation of the overall process into two steps. The first step is essentially a resonance step and therefore, under certain conditions, this step can take the form of the selective excitation of a substantial number of microscopic particles in the system being treated. The second step is distinguished from the first in that it must lead to an irreversible change in the physical properties of the particles which have been selectively excited. This change in properties can be arranged, for example, by altering the structure or state of the system being treated. The first step of the resonance effect must obviously be a radiative step in all cases. The second step, the "power" step, does not, in general, have to be a resonance step, and it can even be radiationless. Possible examples of radiationless second steps are chemical reactions of the selectively excited atoms or molecules and their deflection, ionization, or dissociation in static electric or magnetic fields. Nevertheless, it is the radiative photoionization and photodissociation processes which have been adopted most widely, primarily because of their versatility.

This idea of breaking up the radiation process into two steps in order to arrange selectivity was actually advanced some time ago.⁵ The first experimental re-

sults, however, on the two-step ionization of rubidium atoms and the dissociation of diatomic HCl molecules,⁶ were published much later, along with a theory for the selective dissociation of polyatomic molecules.⁷ This two-step selective photoionization of atoms was soon adapted successfully for isotope separation of uranium,^{8,9} a crucial element from the standpoint of energy resources. The successful use of this method in the case of the relatively light elements lithium¹⁰ and calcium,¹⁰ as well as for essentially all such heavy elements as the rare earths,¹¹⁻¹⁶ convincingly demonstrated the general applicability of this method. Here we should emphasize that the selective photoionization of atoms can be an economical method for isotope separation, especially if relatively small amounts of isotopes of some element are required with a high degree of enrichment.

2. TWO-STEP SELECTIVE PHOTOIONIZATION

The selective two-step photoionization of atoms is based on the fact that resonance absorption of an intense laser beam can be used to change substantially the population ratio of energy levels coupled by a resonance transition. In other words, this process is based on the saturation of a resonance transition, which is a very familiar effect in rf spectroscopy and which is crucial to quantum electronics. The excited atoms can revert to their initial state by many pathways, among which the most important are spontaneous radiative transitions and the collisional transfer of excitation energy to atoms which were not excited by the radiation. If the ionizing beam is sufficiently intense, the photoionization of excited atoms can occur faster than the atoms can revert to their initial state. If the photon energy, below the ionization potential of the unexcited atom, is sufficient to ionize the excited atoms, then the photoionization can be selective. The obvious necessary condition for selectivity of two-step photoionization is

$$U_{\text{ion}} > h\nu_{\text{ion}} > U_{\text{ion}} - h\nu_{\text{exc}}, \quad (1)$$

where U_{ion} is the atomic ionization potential, $h\nu_{\text{exc}}$ is the energy of the resonance-excitation photon (the first step), and $h\nu_{\text{ion}}$ is the photon energy of the ionizing radiation (the second step).

On the basis of these simple considerations we can also find a rough estimate of the laser intensities required in the first and second steps for effective ionization:

$$I_{\text{exc}} > \frac{h\nu_{\text{exc}}}{\sigma_{\text{exc}} \tau}, \quad I_{\text{ion}} > \frac{h\nu_{\text{ion}}}{\sigma_{\text{ion}} \tau}; \quad (2)$$

where τ is the lifetime of the excited level, and σ_{exc} and σ_{ion} are the cross sections for the corresponding processes. Conditions (2) correspond to a high rate of radiative excitation and ionization in comparison with the decay rate of the excited level, $1/\tau$. In the radiative mechanism for decay of the excited level, the cross section for resonance excitation is inversely proportional to the spontaneous lifetime τ . In this case I_{exc} is thus independent of τ , while I_{ion} decreases with increasing τ , showing that a metastable level should be chosen as the intermediate level in the two-step selec-

tive photoionization.

The marked difference in the cross sections for resonance excitation ($\sigma_{\text{exc}} = 10^{-12} - 10^{-13} \text{ cm}^2$) and nonresonance ionization ($\sigma_{\text{ion}} = 10^{-17} - 10^{-18} \text{ cm}^2$) means that very different intensities are required for the exciting and ionizing radiation for effective ionization.

An analysis¹⁷ based on the rate equations for an optically thin slab or, equivalently, in the approximation of given exciting and ionizing fields, shows that the two-step laser effect on a beam of atoms which do not interact with each other can, in principle, perform a selective photoionization of atoms at a 100% efficiency. This point has been demonstrated experimentally for laser isotope separation by this method.⁸⁻¹⁶

The most important processes tending to degrade the selectivity as the density of atoms is increased are resonance charge exchange and resonance transfer of excitation energy.¹⁸ The effective cross sections for these processes are much larger than the ordinary gas-kinetic cross sections, reaching values of¹⁹ $10^{-13} - 10^{-14} \text{ cm}^2$.

The analysis method of Ref. 18 reduces to the solution of the rate equations for the system of energy levels shown in Fig. 1. A mixture of isotopes of species A and B, in the gas phase, is irradiated. The radiation is at resonance with a spectral line of atoms A, and it has a spectral width sufficient to excite all the atoms of species A within the Doppler contour. At the same time, the atoms are subjected to radiation with a photon energy such that the absorption of these photons leads to the ionization of excited atoms A and B in accordance with inequalities (1). The excited atoms A and B have the same radiative lifetime τ_1 . In addition, these atoms can transfer excitation energy to unexcited atoms A and B in a resonance process with a rate constant K_1 . Analogously, the ionized atoms of either species can exchange electrons with neutral atoms of the other species in a resonance charge exchange with a rate constant K_2 . The average time for the loss of ions from the volume in which the atoms interact with the radiation is τ_2 .

The equations given in Ref. 18 lead to simple solutions in the steady state, and these solutions are easily interpreted. In the simplest case, in which the excitation of atoms B at the wing of their resonance-absorption line is ignored, we easily find the following equation for the separation factor α , which is a measure of the selectivity of the process:

$$\alpha = \frac{1}{N^A} \frac{1 + (I_{\text{ion}} \sigma_{\text{ion}} / h\nu_{\text{ion}}) \tau_1}{K_2 \tau_2 [1 + (I_{\text{ion}} \sigma_{\text{ion}} / h\nu_{\text{ion}}) \tau_1] + K_1 \tau_1 (1 + K_2 \tau_2 N^B)}. \quad (3)$$

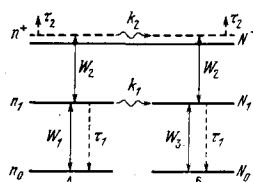


FIG. 1. Simplified level scheme of atoms of species A and B, showing processes which degrade the selectivity of the laser effect¹⁸ (k_1 and k_2).

We see from this equation that the selectivity falls off with increasing density of the atoms involved, in proportion to $1/N^A$, in the case of binary collisions, as might be expected. Far from ionization saturation we have $I_{\text{ion}} \sigma_{\text{ion}} / h\nu_{\text{ion}} \ll 1/\tau_1$, and the decrease in selectivity is due to charge exchange (K_2) and excitation transfer (K_1) in equal measure. The atoms of species B increase in importance; an increase in their density N^B further degrades the selectivity. With a pronounced ionization saturation ($I_{\text{ion}} \sigma_{\text{ion}} / h\nu_{\text{ion}} \gg 1/\tau_1$), the effective resonance excitation transfer can be eliminated, as mentioned earlier in the discussion of this process. Then

$$\alpha = \frac{1}{K_2 \tau_2 N^A} \quad (4)$$

The selectivity is high at a low density N^A and may be ultimately governed by the frequency spread of the laser beam and the overlap of spectral lines. Obviously, the productivity of the process, which is proportional to N^A , is low in this case. In isotope separation by selective two-step photoionization we have a clear example of the well-known contradiction²⁰ between the requirements of high productivity and high selectivity.

For given rate constants for charge exchange and energy transfer, K_2 and K_1 , we find the obvious requirement from Eqs. (3) and (4) that we must reduce the ion removal time τ_2 and the effective lifetime of the atoms in the excited state. This lifetime can be reduced by increasing the intensity of the ionizing radiation. The separation factor α which is required determines the permissible density of the atomic gas. With $\alpha = 10$, $K_2 = 5 \cdot 10^{-10} - 10^{-9}$ cm³/sec, and $\tau_2 = 10^{-5}$ sec, this permissible value is $N^A \approx 10^{13}$ cm⁻³. If $N^A \leq 0.1N^B$, then the total density can exceed 10^{14} cm⁻³.

These arguments show the importance of knowing the rate constants of the parasitic processes which degrade the selectivity of the ionization and of finding ways to increase the ionization cross section effectively. Increasing this cross section is important both for simplifying the use of this method and making full use of the output of existing lasers and for increasing the selectivity of the method.

We wish to emphasize again that selective two-step ionization is the most general method for laser isotope separation, being applicable in principle to any element in the periodic table, but only if a suitable vapor density of this element can be achieved.

The difficulties encountered in evaporating many elements, especially the heavy metals, are technical in nature, but they restrict the use of the method in many ways or at least they cause serious complications.

The first experiment on two-step ionization of atoms was carried out with rubidium.⁶ The selectivity of the process was not studied, and the ions were not extracted from the gas-filled cell. This experiment⁶ was important as the first demonstration of the principle of two-step photoionization, and it used approaches which have since become quite common: the use of a tunable dye laser for resonance excitation and the use of a laser beam (the second harmonic of a ruby laser)

TABLE I. Isotope separation by selective photoionization of atoms.

Element	Excited transition, Å	Photoionization source	Separation factor	Reference
Lithium	² S - ² P, 6707.8 Å	Nitrogen laser, 3371 Å	—	65
Calcium	³ P ₂ - ³ S, 6162 Å	Argon laser, 4880 Å	—	10
Neodymium	² I ₈ - undetermined 5887 Å	Mercury lamp, 2500 Å	50-100	38
Samarium	⁷ F ₁ - undetermined 5916 Å	Nitrogen laser, 3371 Å	50-90	11, 18
Europium	⁸ S _{7/2} - ⁶ P _{7/2} , 5765 Å	Nitrogen laser, 3371 Å	100	12, 32
Gadolinium	² D _{5/2} - ² F _{5/2} , 5856 Å	Nitrogen laser, 2500 Å	10-43	32
Dysprosium	² F ₈ - ³ P ₁ , 5988 Å	Mercury lamp, 2500 Å	20-800	35
Erbium	² H ₆ - ³ P ₁ , 5828 Å	Mercury lamp, 2500 Å	50-100	33
Ytterbium	¹ S ₀ - ² P ₁ , 5556 Å	Xe-Cl excimer laser, 3080 Å	—	16
Uranium	⁵ L ₆ - ⁷ M ₇ , 5916 Å	Mercury lamp 2500 Å	—	32
Uranium*	⁶ K ₈ - undetermined 3781 Å	Krypton laser, 3564 Å 3507 Å	4	33

*Separation in weighable amounts.

to ionize the excited atoms. This method was subsequently used to separate isotopes of calcium,¹⁰ magnesium,²¹ rare earths,¹¹⁻¹⁶ uranium,²²⁻²⁶ and lithium.⁶² Table I summarizes the results. Figure 2 shows an experimental arrangement for separation of uranium isotopes.²³

The pioneering papers in this field²²⁻²⁴ were soon followed by reports^{25,26} of work which had been in progress for some time on the separation of uranium isotopes in accordance with the patent in Ref. 27. The work described in Ref. 25 had actually been carried out in 1971. Here, in contrast with Refs. 22-24, pulsed lasers were used, and the uranium vapor was produced by electron-beam evaporation. This work is interesting because of its spectroscopic results, and we will return to it in the discussion below. In Ref. 26 Jones *et al.* summarized their research at relatively high uranium vapor densities ($10^{13} - 10^{14}$ cm⁻³). Much work on extracting ions of the desired mass from the plasma produced in the ionization was reported in Ref. 26. It was shown there that a pulsed process with a high repetition frequency (10 kHz) is preferable; here pulsed electric and magnetic fields are used to extract the ions. With a high uranium vapor density, a single-stage enrichment of the uranium to 6% was achieved; this is suitable for producing nuclear fuel for light-water reactors, either from natural uranium or from the tailings depleted in standard uranium enrichment processes. The successful results of Ref. 26 inspired plans

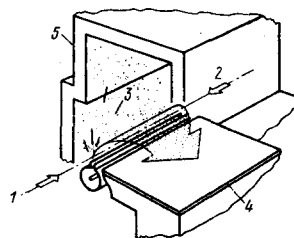


FIG. 2. Experimental arrangement for laser separation of metallic uranium.²³ 1, 2) Laser beams; 3) atomic vapor; 4) collector plate; 5) chamber wall.

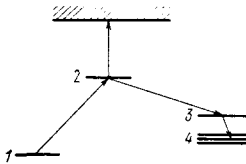


FIG. 3. Level scheme showing a possible pathway for laser emptying (transitions 2-3, 3-4) of a selectively excited level²⁹ (the transition 1-2).

for constructing a pilot plant to test the method.

Jones *et al.*²⁶ concluded that selective photoionization of atoms was not suitable for producing uranium with a high degree of enrichment in a single stage, since the increase in the ²³⁵U concentration in the evaporated metal causes difficulties associated with spontaneous lasing during laser excitation of this atom with its many energy levels.^{26, 28, 29} Specifically, during the intense selective excitation of some selected atomic state, a population inversion of this state arises with respect to some lower level which is not part of the level scheme chosen for the laser isotope separation. This population inversion leads to amplification and emission at the corresponding wavelength (Fig. 3). This emission empties the selectively excited level and thereby prevents selective photoionization. Accurate calculations require knowledge of the characteristics of all the states involved in the overall process and of the possible transitions. A rough estimate leads to the conclusion that the density of ²³⁵U atoms along a possible emission direction should not exceed 10^{15} cm⁻². Cantrell *et al.*²⁹ gave equations for the amplification which occurs during laser isotope separation in an atomic vapor with selective photoionization; the anisotropy of the excitation and the stimulated Raman scattering were taken into account.

Among the published papers on laser isotope separation by selective photoionization of atoms, an important place is occupied by a series of studies on elements of the rare earth group.^{11-16, 30-32}

The rare earths were selected for study because they constitute a large group of rather heavy atoms which, although different, have similar properties. Their physical and chemical properties are the same in many ways, but there are large variations in the melting point, the isotopic composition, and the relative abundances of the isotopes in the natural mixtures. The optical spectra, isotopic shifts, and ionization potentials of the rare earths have been studied thoroughly, and the results have been of much assistance.³⁴⁻³⁶ On the whole, these elements can be used for a representative series of experiments on laser isotope separation. Experiments have been carried out for neodymium, samarium, europium, gadolinium, dysprosium, erbium, and ytterbium, i.e., for all the rare earth elements whose natural mixtures contain more than a single stable isotope.

Figures 4-6 show some mass spectra of the results of the separation. Here we see some sharply different situations: Figure 4 shows two europium isotopes of approximately the same abundance; Fig. 5 shows the



FIG. 4. Mass spectrogram showing the emergence of either the isotope ¹⁵³Eu (at the left) or ¹⁵¹Eu (at the right) as the wavelength of the exciting laser is tuned.¹⁶

systematic emergence of each of five gadolinium isotopes; and Fig. 6 shows the enrichment of erbium in the isotope ¹⁶²Er, whose abundance in the natural mixture is only 0.1%.

In summary, laser isotope separation has been used successfully for a large group of elements with similar but distinct properties. Despite the differences in the isotopic and hyperfine structures, melting points, chemical activities of the molten metals, and ionization potentials, the present-day capabilities of quantum electronics are such that it is possible to separate the isotopes of heavy metals reliably by selective two-step photoionization of atoms. We again emphasize the importance of using a laser beam in the ionizing step. Table I summarizes the published results on laser isotope separation by this method.

Estimates of the cross section for the photoionization from the excited state, σ_{ion} , lead to values of the order of 10^{-17} cm² for essentially all the cases studied. Direct measurements for ytterbium¹⁶ yield a cross section for photoionization from the ³P₁ excited state of 1.3×10^{-17} cm² \pm 10% at 0.05 eV above the ionization potential.

Obviously, the cross section for photoionization from the excited state and a search for methods for increasing this cross section, or circumventing the problem if the cross section is extremely small, are of fundamental importance to selective ionization.

One possible method is resonance photoionization through autoionization states.¹⁹ In this approach the ionization cross section can be increased to a level 1

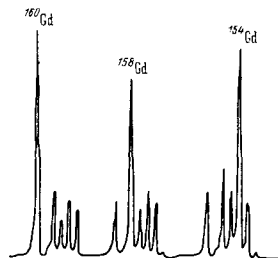


FIG. 5. Examples illustrating the ability to emphasize a desired isotope of gadolinium.¹⁶

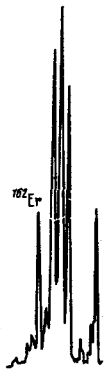


FIG. 6. Enrichment of the photoionization current in the low-abundance isotope ^{162}Er in a laser effect on erbium vapor with the natural isotopic abundances.¹⁶

to 1.5 orders of magnitude above the typical value in the nonresonance case, $\sim 10^{-17} \text{ cm}^2$. For uranium, for example, there are autoionization levels 500 cm^{-1} above the ionization threshold of the atom³⁷ (the ionization potential is $\approx 6.2 \text{ eV}$). These autoionization levels stem from an interaction of the metastable f^3dp^2 , f^3dsp , f^3s^2p , and f^4s^2 configurations of the neutral atom with the f^3ds configuration of the ion, according to a theoretical analysis. A theoretical estimate of the cross section for the best of the autoionization transitions yields $\sigma_{\text{ion}} = 5 \cdot 10^{-16} \text{ cm}^2$. It is highly likely that the autoionization resonances of the heavy atoms will prove quite narrow. Narrow-band tunable lasers will be required to detect and study them and for use in the ionizing step. In the two-step method, these lasers must have an extremely short wavelength, and this condition may be difficult to meet.

A direct generalization of the method of two-step photoionization is the multistep (N -step) method, in which there is a sequential resonance excitation of the desired atom by several lasers, to an energy level near the continuum. Here there are several possibilities. First, if the resonance-excitation level lies near the continuum the ionization can be performed with an IR laser, whose photons are "cheap" in comparison with those of a UV laser. A candidate IR laser is the CO_2 laser ($\nu \approx 1000 \text{ cm}^{-1}$, efficiency of $\approx 30\%$). Furthermore, multistep selective excitation below the ionization potential allows us to search for and use narrow autoionization resonances with the most reliable and readily acceptable dye lasers e.g., rhodamine 6G lasers. Another possibility is that the intense multistep resonance excitation may remain selective up to energy levels near the ionization potential as the atomic vapor density is increased. The collisions of such highly excited atoms with the remaining low-density electrons or with neutral excited atoms or unexcited atoms will lead to an effective ionization which remains selective. The cross section for this collisional ionization is large for the atomic electrons excited into high orbitals.

Figure 7 shows some possible schemes for multistep ionization which have been studied experimentally for uranium.²⁶ We should emphasize again that the radiative transitions in Figs. 7d and 7e are resonance transi-

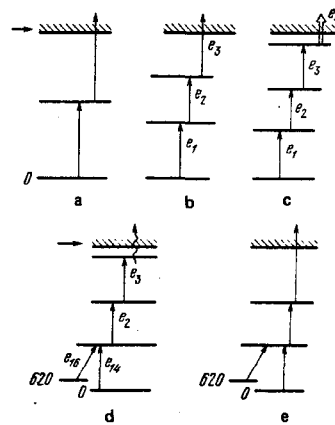


FIG. 7. Possible schemes for multistep selective photoionization of uranium atoms.²⁶

tions and thus have large cross sections.

Multistep excitation also raises another very interesting possibility³⁸: the ionization of selectively excited atoms in an electrostatic field strong enough to deform the electronic terms of the atom substantially. Here selective ionization is possible when the atoms are selectively excited to states near but below the ionization potential, with a subsequent ionization of the highly excited atoms by the electric field. The field adjusts the electronic terms in such a manner that some of the discrete levels near the ionization threshold move into the continuum, while others become autoionization levels through tunnel transitions. The probability for the autoionization decay of these levels increases rapidly with increasing principal quantum number n . In a multistep method with lasers, the selective population of states with large values of n can be achieved easily and quite efficiently. It thus becomes possible to arrange autoionization of selectively excited atoms controlled by an electric field; the field and the rate of its pulsed application can be matched to the level in question to achieve an autoionization rate higher than the rate of radiative decay of this level. Then the probability for the ionization of an atom which has reached a highly excited state approaches unity, and the ionization cross section becomes equal to the cross section for the excitation of this state—several orders of magnitude larger than the cross section for ordinary photoionization.

The first experimental demonstration of autoionization of high-lying atomic states in an electric field used sodium atoms.³⁹ Tunable lasers were used for the resonance excitation of high-lying S and D states of sodium with quantum numbers n from 13 to 18. A sharp increase in the photocurrent was observed when the electric field exceeded a certain threshold. It was established that the effect was resonance with respect to the exciting wavelength. For the $15^2D_{3/2}$ state the threshold field was 12 kV/cm . In this field the cross section for photoionization through the $15d$ autoionization state is $0.7 \cdot 10^{-14} \text{ cm}^2$, or five orders of magnitude larger than the cross section for nonresonance (in the second step) photoionization. Although a direct experiment on isotope separation could not be carried out with single-isotope sodium, the experiment of Ref. 39

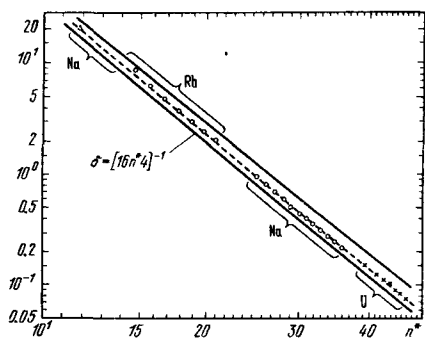


FIG. 8. Critical field for ionization of Rydberg states as a function of the effective principal quantum number.⁴⁴

demonstrated the possibility of substantially expanding the range of applicability of the method of selective photoionization. This experiment was carried out in a static electric field. There is also the possibility of using a pulsed method, in which the electric field would be turned on after the end of the laser pulses. The field should obviously be applied for a time shorter than the radiative decay time of the corresponding level. Ionization in a pulsed electric field has been achieved experimentally for sodium atoms⁴⁰ for $n = 26 - 37$, xenon atoms⁴¹ for $n = 24 - 28$, uranium atoms⁴² for $n = 40 - 50$, and rubidium atoms for⁴³ $n = 28 - 65$ and⁴⁴ $n = 15 - 22$. This series of experiments showed convincingly that the critical autoionization field can be described well by an $(n^*)^{-4}$ law in selective excitation to Rydberg states. In fields above the critical value the highly excited atoms are ionized with a unit yield. In this case the ionization cross section is equal to the cross section for excitation of the corresponding high-lying state.

Figure 8 shows the variation of the critical field with the effect, or principal quantum number n^* found experimentally for such different elements as sodium and uranium.⁴² Experiments with uranium vapor were carried out with three pulsed dye lasers emitting near 6000 \AA . The uranium atoms were excited in three steps to levels a few hundred reciprocal centimeters below the continuum. These levels can belong to both Rydberg and valence states. The Rydberg states belong to the $5f^3 7s^2 np$, nf , and $5f^3 6d^7 snp$ configurations. For Rydberg progressions with a limit at the ion ground state, it was found that the critical field corresponds well to the $(2n^*)^{-4}$ law below Eq. (5), see (Fig. 8). Interestingly, some of the highly excited valence states of uranium are also ionized in fields of about 1 kV/cm . The field dependence of the ionization rate, however, is much weaker than in the case of the Rydberg states.

In general, we can say that multistep excitation just below the ionization threshold is a very useful method for increasing the ionization efficiency. Furthermore, multistep excitation methods may prove useful in spectroscopy.

3. SPECTROSCOPIC APPLICATIONS OF SELECTIVE PHOTONIZATION OF ATOMS

The methods developed for selective two-step photoionization of atoms for laser isotope separation may

become very important for spectroscopic applications. High-resolution laser spectroscopy of course raises new possibilities, in particular, of studying the hyperfine structure or isotopic structure of atomic spectra.

The best-developed method for single-step laser spectroscopy is the resonance luminescence of well-collimated atomic beams in a laser cavity. This method has applications for precise measurements of isotopic shifts, for studying strongly forbidden intercombination lines, etc. For example, the method of resonance luminescence of atomic beams was recently used to study the doubly magic calcium nuclei ^{40}Ca and ^{48}Ca and also to study all other calcium isotopes.⁴⁵ This method has been used to observe the strongly forbidden transition at the wavelength 6573 \AA in the extremely rare isotope⁴⁶ ^{45}Ca (relative abundance of $3 \cdot 10^{-5}$). The changes in the resonance-luminescence spectrum during intense excitation of the atomic vapor and an increase in the vapor pressure can be taken as evidence of dimer formation, as recently shown in the case of lithium.⁴⁷

In many cases it is a difficult problem to interpret the luminescence spectra. Even with a well-collimated atomic beam and with excitation by a laser beam with a very narrow frequency spread, an unambiguous identification is not possible for heavy atoms with a rich structure in their luminescence spectra.

Experiments on isotope separation show, in particular, that the combination of the selectivity of the mass spectrometer (which measures the photoionization current produced by only those ions which have the desired mass) with the selectivity of the two-step laser effect expands the possibilities of high-resolution laser spectroscopy substantially. In the very first report on laser isotope separation for uranium,²² the separation results were tested by an experiment in which a mass filter was tuned to a mass of 235 and a laser was scanned over the uranium absorption spectrum. The frequency dependence of the photocurrent of the mass-235 ions was in excellent correspondence with the well-known hyperfine structure of the optical spectrum of ^{235}U .

The possibility of extracting spectroscopic information from experiments of this type was demonstrated in Ref. 49, where these new methods were used to study the hyperfine structure of atoms of the various isotopes of rare earth elements, dysprosium and erbium, with the natural isotopic abundances. This experiment was carried out with atomic beams produced by evaporating the corresponding metals in vacuum. The ions of the element under study, produced by selective two-step photoionization, were guided by a system of ion lenses to the external detector of a dynamic mass spectrometer. The spectrometer was tuned to a certain mass and thus served as a tunable selective mass filter. When the output frequency of the first-step laser (the exciting laser) was scanned, an ion current was detected which corresponded exclusively to the excitation spectrum of a preselected isotope among those in the atomic beam. The resolution required of the mass spectrometer here, 1 amu , is easily

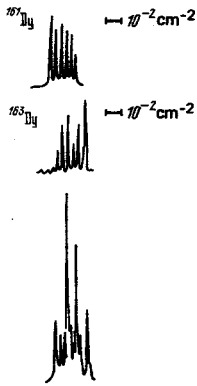


FIG. 9. Hyperfine structure of the odd isotopes of dysprosium. The curve at the bottom is the mass spectrum of dysprosium with the natural isotopic abundances.⁴⁹

arranged.

The spectral resolution of the method is governed by the width of the output line of the tunable laser; the recording capacity is governed by the sensitivity of the mass spectrometer and, far from ionization saturation, by the intensity of the ionizing radiation. With modern ion-counting techniques it is possible to study small amounts of the element to be analyzed.

Figure 9 shows the hyperfine spectra recorded for individual dysprosium isotopes. When the spectra of the various isotopes are combined, the result is an exact reproduction of the luminescence spectrum of a natural mixture of dysprosium isotopes.

The experiment of Ref. 49 with dysprosium and erbium showed that the selectivity of two-step laser photoionization combined with ion-mass filtering is a simple, accurate, highly sensitive method with a good resolution for recording the hyperfine spectra of individual isotopes in their natural mixtures. This method is a very general method: It can be used for any isotope of any element in the periodic table. It becomes particularly effective in the case of rare or unstable isotopes or the isotopes of the transuranium elements, which are difficult to produce in large amounts.

Knowledge of the hyperfine structure of an atom in some electronic configuration or other is of course of considerable interest for atomic spectroscopy, since it can be used to calculate the characteristics of the magnetic interaction, A , and of the quadrupole interaction, B , which determine the hyperfine splitting; this information can also be used to find the resultant electric and magnetic moments of the electronic shell if the nuclear magnetic and quadrupole moments are known, and so forth.

Knowledge of the hyperfine structure of the particular isotope is also very important for laser isotope separation by the method of selective photoionization. Unfortunately, the isotopic and hyperfine structures frequently overlap in the excitation spectrum of a natural mixture of isotopes. Furthermore, the distribution of atoms with respect to hyperfine-structure components reduces the effectiveness of the laser effect if the laser output has a small frequency spread. We thus need an

accurate understanding of the hyperfine structure, and we need to search for transitions for which the hyperfine structure is minimized while the isotopic shift is maximized. This information is not available for many elements, of both large and intermediate mass. It can be obtained by the method described above.

The method developed in Ref. 49 for studying the hyperfine structure is of general applicability for the spectroscopy of high-lying atomic states, in particular, for studying the fine structure of autoionization states.

In recent years multistep laser spectroscopy has been finding increasing applications for studying highly excited atomic states. As an example we note that a thorough study^{51a} of the hyperfine structure of the highly excited P , S , and D states of alkali atoms was made possible only as the result of the development of a series of tunable cw dye lasers. Happer *et al.*^{51a} (see the bibliography given in Ref. 51a) used multistep excitation to measure the hyperfine-structure constants for many excited states of all the alkali atoms. They found that the magnetic-dipole coupling constant A increases in proportion to the three-halves power of the binding energy of the excited electron. They published extensive and useful data tables. The results of many years of careful study of the highly excited levels of alkali metals are also given in the reviews in Ref. 51b. We can say that the basic result of this series of experiments was to demonstrate that modern computational techniques can give very accurate information on the hyperfine constant, the Landé factors, the polarizability, etc., of the highly excited levels of alkali metals.

This list does not come close to being an exhaustive list of the possibilities of multistep laser spectroscopy. In addition to measurements of the Stark characteristics of the excited atoms, the characteristics of the quadrupole hyperfine structure, the lifetimes, etc., of any state of interest in the highly excited atom, there is particular interest in the spectroscopy of the so-called Rydberg states. A Rydberg atom, i.e., one whose electrons are energetically near the continuum, has interesting properties: Its dimensions are far larger than those of ordinary atoms, by four or five orders of magnitude; it interacts much more strongly with external fields; and its cross sections for ionizing collisions are much larger. The chemical and physical properties of atoms which have become Rydberg are intensified. These properties are now being studied widely, and the Rydberg atoms themselves are finding many practical applications, primarily for laser isotope separation, for stimulating chemical reactions, in plasma chemistry, and in the physics of plasmas, including the interstellar plasma.

The reason for the unique properties of Rydberg atoms is that the optically active electron in such an atom is moving at a distance from the ion core which is large in comparison with the first Bohr radius. At such distances the electric field of the core is nearly Coulombic and is only weakly perturbed by the electronic shells. The motion of an optically active electron in a Rydberg atom approximates the electron motion in the hydrogen atom. The energy of such a highly

excited atom is governed by the principal quantum number n and by the so-called quantum defect of the level, $\mu_l(E)$, which depends on both the orbital angular momentum l and the energy of the atom:

$$E = -\frac{13.6 \text{ (eV)}}{[n - \mu_l(E)]^2} = -\frac{13.6 \text{ (eV)}}{[n^*]^2}. \quad (5)$$

By definition here, n^* is the effective principal quantum number. In the way in which this equation is written, the quantum defect $\mu_l(E)$ incorporates the interaction of the optically active electron with the electronic shells of the ion core. At large values of n , the energy levels are closely spaced. With increasing excitation, these levels move even closer together, and they converge toward the ionization limit of the atom. It is this remoteness of the Rydberg electron from the ion core, with the correspondingly weak interaction with the core, that makes the Rydberg atom particularly susceptible to external forces.

There is particular interest in the study of Rydberg states in the case of the complex heavy atoms, primarily because studies of this type are essentially impossible by ordinary absorption spectroscopy. The difficulties encountered by the ordinary methods result from the complexity of the electronic structure of the heavy atoms, the weak absorption in transitions between Rydberg states with large principal quantum numbers, the presence of a large number of populated lower-lying levels, and the high density of perturbed valence levels at a high degree of excitation. Before the study of Solarz *et al.*,⁵² which was devoted directly to the Rydberg spectra of uranium, the only work which had been done in this field was on the multistep ionization of hydrogen⁵³ and the collisional properties⁵⁴ and electric-field ionization^{39,40} of the Rydberg states in sodium and xenon.⁴¹

Until very recently, the only atoms which had been studied experimentally were those in groups of elements having comparatively simple electronic configurations: the alkali metals and the inert gases. Wynne *et al.*⁴⁸ recently observed Rydberg series with $n^* > 60$ for the alkaline earths calcium, strontium, and barium. The configurational interactions here are stronger than in the alkali metals, and the quantum defects fluctuate markedly, making it difficult to identify the sequences.

Multistep excitation by several lasers with narrow output lines finds a natural application in the study of highly excited uranium atoms. This method was used previously⁵⁵ to determine the radiative lifetimes and absorption cross sections and to observe and identify high-lying odd levels of the uranium atom. At energies above $49\,000 \text{ cm}^{-1}$, a further increase in the degree of excitation increases the state density by about one level per reciprocal centimeter (the ionization potential of the uranium atom corresponds to about $50\,000 \text{ cm}^{-1}$). In Ref. 52, however, when atoms were excited to energies about 1000 cm^{-1} below the ionization potential, and when the excited atoms were subjected to the beam from a high-power pulsed CO_2 laser ($\nu \approx 1000 \text{ cm}^{-1}$) after a certain delay, only the excited atoms were ionized, and it was possible to distinguish the Rydberg progressions in uranium. This approach made it pos-

sible to distinguish the Rydberg levels from the valence states, i.e., the high-lying states of deeper configurations. The orbital radii of the excited electrons are small for the valence states, and the radiative lifetimes are short (50–100 nsec). A delay of 500 nsec in the ionizing pulse thus made it a simple matter to distinguish the current pulse due to ionization of Rydberg level.

The experimental technique used in Ref. 52 is completely the same as that developed earlier^{8,9,22,26,42} for separation of uranium isotopes, except that the wavelength measurements are more careful and a CO_2 laser is used [the $P(20)$ line of the 001–100 band; power level of 1.5 MW; pulse length of 250 nsec]. These experiments led to the detection of Rydberg series which converge to the ground state of the uranium ion. Several series were identified, with effective principal quantum numbers n^* in the ranges $12 < n^* < 17$ and $38 < n^* < 60$. The corresponding configurations are $5f^3 7s^2 np$, $5f^3 7s^2 nf$, and $5f^3 6d 7s np$. The best value found for the sequence limit is $49\,958.1 \text{ cm}^{-1}$, which corresponds to an ionization potential of $6.1941 \pm 0.0005 \text{ eV}$. Calculations by a modified Hartree–Fock method in Ref. 52, carried out to determine the energy levels of the Rydberg electrons, turned out to agree well with the experimental results. The difference between the calculated and measured values did not exceed 0.9 cm^{-1} for several long series of lines. The measured values of the effective principal quantum number (n^*) differ from the calculated values (n) by an average of 4.8 in the range $42 < n < 52$; the average difference in the range $15 < n < 18$ is 2.1.

Multistep selective photoionization can thus be used to observe the Rydberg sequences for the heaviest of the naturally occurring atoms. Experiments by this method have shown that the computational techniques currently available can accurately take into account the interaction of a highly excited optical electron with the electronic shells of the ion core.

Multistep selective photoionization, combined with time separation of the excitation and ionization pulses, represents a powerful tool for studying high-lying atomic states. It is now possible to study the effect of fields and collisions on the level positions, the level splitting, the ionization rates, the oscillator strengths, and the radiative lifetimes of states which have previously been beyond our reach.

Corresponding experiments have recently been carried out for the lanthanides.⁵⁶ These experiments have revealed both autoionization Rydberg sequences converging toward an excited state of the corresponding ion and sequences converging toward the ground state of the ion. The convergence limit of the sequence is chosen such that the quantum defect $\mu_l(E) = n - n^*$ changes as little as possible with change in the principal quantum number n . This method is quite sensitive. A change in the value adopted for the convergence limit by $\pm 1 \text{ cm}^{-1}$ changes the difference $n - n^*$ by ± 1 for n between 40 and 60. For the final choice of convergence limit, the change in $n - n^*$ was usually ± 0.25 . The convergence limits for the Rydberg sequences determined

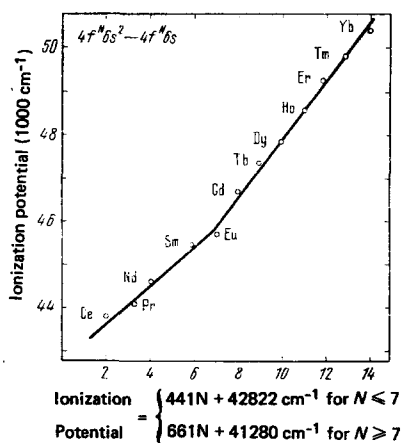


FIG. 10. Ionization potentials of the lanthanides.⁵⁶

in this manner yielded the ionization potentials of the corresponding elements. For most of these elements, the ionization took the form of the loss of one s electron from the $4f^N 6s^2$ configuration ($N=2-4$). Figure 10 shows the ionization potential as a function of N . We see a clearly defined piecewise-linear behavior with a slope change at the half-filled shell ($N=7$). The experimental data in Fig. 10 can be approximated by

$$U_{\text{ion}} = \begin{cases} 441N + 42822 \text{ cm}^{-1}, & N \leq 7, \\ 661N + 41280 \text{ cm}^{-1}, & N \geq 7. \end{cases} \quad (6)$$

This behavior can be explained qualitatively on the basis of the Pauli principle and the Hund rule; a quantitative agreement with the experimental results can be found by the Hartree-Fock method. So far, the determination of the convergence limit of the Rydberg sequence is apparently the most accurate method for determining atomic ionization potentials.

The spectroscopic data obtained in all these experiments are required for further study of the interactions of the optical electron with the ion core and with external agents. It should be noted that the method of this work is quite general in nature and can be used for all elements in the periodic table. For example, spectroscopic data on the Rydberg states in potassium and sodium found by multistep photoionization have recently been published.^{57a}

The interaction of Rydberg atoms with external electric fields was discussed above. Corresponding experiments can be carried out with magnetic fields or with a combination of electric and magnetic fields. An interesting application is the rf spectroscopy of highly excited Rydberg levels.^{57b} Microwave radiation causing transitions between different fine-structure components of the initial and final Rydberg states can be used to obtain more information on the structure of these states. Atoms which have undergone various transitions between Rydberg states are conveniently detected by ionization in an electric field.

The quadratic Stark effect of the Rydberg states and the magnitude of the fine-structure splitting of these states can yield information on the ion core, its polarizability, exchange effects in it, and the penetration of the Rydberg electron into the core.

The size of a Rydberg atom increases with increasing principal quantum number n , in proportion to n^2 . The cross-sectional area of the atom thus increases in proportion to n^4 . Since the electron binding energy falls off rapidly, Rydberg atoms are presumably very sensitive to collisions with other particles. The collisional ionization of uranium Rydberg atoms was used in Ref. 26 in the separation of uranium isotopes at relatively high densities of an atomic vapor. Correspondingly, the chemical activity of atoms should increase markedly when they are excited to Rydberg states.

In general, it is now obvious that selective multistep ionization is a powerful tool for studying Rydberg atomic states. Some important international conferences have recently been held on Rydberg states.^{57c,d} Rydberg states received much attention at the Sixth International Conference on Atomic Physics. Noteworthy here is a study of the fine structure of the $n^2 D_{3/2, 5/2}$ states of sodium by selective multistep ionization.^{57e} A Fourier analysis of the periodic changes in the ion current as a function of the delay time of the pulsed electric field (the ionizing field) with respect to the laser field (the exciting field) yielded values for the splitting between 10.2 MHz and 3.1 MHz for principal quantum numbers from $n=21$ to $n=31$.

An emission line of neutral hydrogen at a wavelength of 3.4 cm (the transition $n=91-n=90$) was detected by radio astronomers in an accumulation of ionized hydrogen near the Omega Nebula back in 1965 (Ref. 50a). Since then, microwave transitions have been detected between the Rydberg states of heavier atoms in the interstellar medium.^{50b,c}

An important spectroscopic characteristic of an excited atom is its photoionization cross section. One of the first series of experiments to determine the photoionization and autoionization cross sections of excited atoms was carried out for inert gases.⁵⁸ Stebbings *et al.*⁵⁸ used an electron beam for preliminary excitation of metastable levels along with laser excitation and laser ionization; they found ionization cross sections between 10^{-17} and 10^{-18} cm² for the triplet and singlet states of helium, in good agreement with the results of calculation methods which have been developed. No unusual spectral features were observed when the energy of the ionizing photon exceeded the ionization potential. The situation is sharply different in the case of the heavier inert gases. The photoionization cross sections just beside the ionization threshold are highly frequency-dependent because of autoionization states. Figure 11 shows a typical autoionization structure for the photoionization of the metastable level of xenon (1, 2). For these atoms, the autoionization states are strongly coupled with the continuum and are thus relatively broad. In argon and krypton and autoionization peaks are extremely narrow; the observed width of 0.7 Å corresponds to the line width of the ionizing laser beam. The observed autoionization states are coupled with metastable levels by electric dipole transitions. The parity selection rule forbids configurations in which the optical electron has an orbital angular momentum which is an even multiple of \hbar . Comparison of

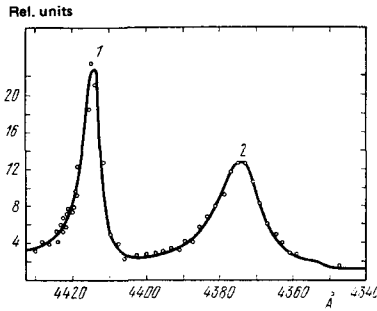


FIG. 11. Autoionization structure of the photoionization transition in xenon at the metastable level of the neutral atom.⁵⁸

the observed line shapes for xenon with the theoretical results of Refs. 59 and 60 yields the values of several characteristics of the corresponding transitions.

Working in this manner, Stebbings *et al.*⁵⁸ compiled a table of valuable spectroscopic data for the ionization of helium, argon, krypton, and xenon. The experiments of Ref. 58 were carried out by exciting relatively low-lying metastable states and using UV light for ionization. For the photoionization of helium from the highly excited $4p^1P_1$ state by a photon with an energy of 1.17 eV ($\lambda = 1.06 \mu$), the cross section is⁶¹ $(3.9 \pm 1.5) \cdot 10^{-18} \text{ cm}^2$, in approximate agreement with the data of Ref. 58, found under different excitation conditions. Among the alkali metals, lithium and rubidium were studied. Among the alkali metals, lithium and rubidium were studied. In the case of lithium⁶² a dye laser excited the known doublet $2P_{1/2, 3/2}$. Ionization was caused by a nitrogen laser ($\lambda = 3371 \text{ \AA}$). The energy of the ionizing photon exceeded the ionization potential (measured from the excited level) by about 1250 cm^{-1} . The ionization cross section estimated for these conditions is $1 \cdot 10^{-17} \text{ cm}^2$. This estimate was based on the ionization current, and it required knowledge of the number of excited lithium atoms in the ionization volume.

Because of the corresponding uncertainty, the value found in Ref. 62 should be taken as an experimental estimate. This is a shortcoming of many methods for determining the absolute photoionization cross sections.

The selective two-step laser ionization of rubidium atoms in Ref. 63 was carried out under conditions such that each excited atom in the volume under study was ionized. Accordingly, there was intensity saturation in the second step, so that the cross section for photoionization from the excited state could be determined without knowledge of the absolute number of excited atoms. For ionization of the rubidium $6^2P_{3/2}$ and $6^2P_{1/2}$ states by a ruby laser, the values $1.7 \cdot 10^{-17} \text{ cm}^2$ and $1.5 \cdot 10^{-17} \text{ cm}^2$, respectively, were found. The same method was used to measure¹⁶ the cross section for photoionization of ytterbium from the excited 3P_1 state. Since the 3P_1 level of the Yb I atom has an energy of $\approx 2.23 \text{ eV}$, while the ionization potential of this atom is 6.2 eV, a UV photon with an energy $\geq 4 \text{ eV}$ is required for photoionization. A XeCl excimer laser ($\lambda \approx 3080 \text{ \AA}$, $h\nu \approx 4.02 \text{ eV}$) was thus used. The photoionization cross section was found to be $1.3 \cdot 10^{-17} \text{ cm}^2$.

Excimer lasers, which can be tuned over a narrow

range, can be used to seek and study narrow autoionization states like those studied in Ref. 58. Since the cross sections for photoionization from excited states are equal in order of magnitude for such different atoms (He, Ar, Kr, Xe, Li, Rb, Yb) away from the autoionization resonance, the value $\sigma_{\text{ion}} \approx 10^{-17} \text{ cm}^2$ can apparently be used for estimates in all cases. For uranium, according to Ref. 25, with ionization by light at 3609 Å of atoms excited beforehand at 4266.325 Å, the ionization cross section is $2 \cdot 10^{-17} \text{ cm}^2$, again in agreement with the estimate above. We emphasize that a detailed study of the cross sections for photoionization from excited states should be carried out, first, with tunable lasers and, second, by the method of ionization-current saturation. Table II summarizes the published data on the cross sections for photoionization from excited states.

Selective multistep photoionization is a very convenient tool for determining the lifetimes of excited states. If pulsed lasers are used in all steps of the process, and a time delay is inserted between the exciting and ionizing pulses, the lifetime of the excited level can easily be determined from the variation of the ionization current with the delay time. Experiments of this type have been carried out for uranium.^{25, 55, 64} The most complete data compilation is in Ref. 55, where the radiative lifetimes are tabulated for 14 high-lying odd levels and five even levels. For the even levels, the observed lifetimes are in the range 200–400 nsec, while for the odd levels the scatter is much larger: from 40 to 800 nsec.

The cross sections for transitions between the levels of the second step were measured at the same time. For the odd upper levels at about 32000 cm^{-1} , and for transitions at wavelengths in the range 6000–6200 Å, these cross sections are $(0.6 - 4) \cdot 10^{-14} \text{ cm}^2$.

Carlson *et al.*⁵⁵ took measures to eliminate possible photoionization of cascade-populated levels: The photoionization was arranged in a three-step scheme, and the third, ionizing laser was tuned to the autoionization

TABLE II. Cross sections for photoionization from excited states.

Atom	Excited transition	Wavelength of excited transition, Å	Wavelength of ionizing radiation, Å	Photoionization cross section, cm^2	Width of autoionization peak, Å	Reference
Helium	$^3S_1 - ^3p$	3688.6	3688.6	$(8.7 \pm 0.2) \cdot 10^{-18}$		58
	$^3S_1 - 4^3p$	3187.7	3187.7	$(2.1 \pm 0.4) \cdot 10^{-18}$		58
	$^3S_1 - 5^3p$	2945.1	2945.1	$(8.6 \pm 1.8) \cdot 10^{-19}$		58
Lithium	$^2S_{1/2} - ^2P_{1/2, 3/2}$	6708	3371	10^{-17}		62
	$^2S_{1/2} - ^2P_{1/2, 3/2}$	4216	6943	$(1.7 \pm 0.3) \cdot 10^{-17}$		63
Rubidium	$^2S_{1/2} - ^2P_{1/2, 3/2}$	4203				
	$^2S_{1/2} - ^2P_{1/2, 3/2}$	4216	3472	$(1.9 \pm 0.3) \cdot 10^{-18}$		63
Magnesium	$^1S_0 - ^1P_1$	2852	3009	$5 \cdot 10^{-16}$	35	21
Calcium	$^3P_0 - ^3S_1$	6162	4880	$1.1 \cdot 10^{-17}$		10
Neodymium	$^5I_8 - \text{undetermined}$	5888	2537	10^{-18}		14
Samarium	$^7F_1 - \text{undetermined}$	5916	3371	10^{-17}		14
Europium	$^8S_{7/2} - ^6P_{7/2}$	5765	3371	10^{-17}		14
Gadolinium	$^9D_5 - ^9F_5$	5856	2537	10^{-18}		14
Dysprosium	$^5I_8 - \text{undetermined}$	5988	2537	10^{-18}		14
Erbium	$^3H_6 - \text{undetermined}$	5827	2537	10^{-18}		14
Ytterbium	$^1S_0 - ^3P_1$	5556	3081	$1.3 \cdot 10^{-17}$		14
Uranium	$^5L_6 - \text{undetermined}$	5915	2537	10^{-18}	3	42

transition. The success of this procedure is demonstrated by the fact that the observed time dependences are simple curves which can be described by a single exponential function.

The work by Carlson *et al.*⁵⁵ is also interesting because it clearly demonstrates the potential of multi-step selective photoionization as a method for purely spectroscopic research. Using three pulsed dye lasers and a quadrupole mass filter, Carlson *et al.*⁵⁵ were able to observe more than 100 new high-lying odd levels of uranium atoms in the energy range 32 600–34 600 cm^{-1} (the ionization potential is $\approx 50\,000\ \text{cm}^{-1}$). In these experiments the spectral resolution was 0.5–1.0 cm^{-1} , and the time resolution was 5 nsec. This method is of quite general applicability, although the extremely high density of highly excited states of heavy atoms makes it difficult to distinguish and identify them.

This method was subsequently modified⁶⁵ to determine the absolute probabilities for transitions beginning from the ground-state levels in neutral uranium vapor (UI). The same ground-state sublevel served as the starting point for both the multistep photoionization and the radiative transition to the level under study, which was not involved in the ionization. When the laser activating the transition under study was turned on, the photoionization current dropped off because of the decrease in the population of the starting level. The use of pulsed lasers with an adjustable delay between pulses made it possible to determine the branching ratios and radiative lifetimes of the levels independently. These experiments revealed the probabilities gA for transitions between the $5f^36d7s^2$ and $5f^36d7s7p$ configurations. For example, the transitions $J=6 \rightarrow J=7$ and $J=6 \rightarrow J=6$ have gA values of $1.76 \cdot 10^{-8}$ sec and $1.36 \cdot 10^{-8}$ sec, respectively. This method can be used to determine small branching ratios, and it measures the absolute transition probabilities accurately (within an error as small as 1%). It can also be used to study the radiationless relaxation of excited states and—a very important point—to study the strengths of transitions between excited levels. Its basic advantage is its independence from the state population densities.

It is thus clear from these results that selective multistep ionization is a powerful and quite general method for spectroscopic research; it is particularly noteworthy that this method can even be used to study the highly excited states of heavy atoms.

4. MEASUREMENT OF THE CROSS SECTIONS FOR RESONANCE TRANSFER OF EXCITATION ENERGY

Working against the selective multistep photoionization of atoms are interatomic collisions and, especially, the resonance transfer of excitation energy which occurs in collisions. In the discussion of laser isotope separation it was shown how this effect influences the selectivity of the separation. For spectroscopic problems we must obviously also take into account the possible loss of selectivity which occurs as the atomic vapor density increases. Especially dangerous in this regard is the transfer of excitation between isotopes in a dense atomic vapor of complex isotopic composition. The transfer of excita-

tion-transfer processes in a gas of like atoms, which have been studied in some detail in the physics of atomic collisions. The corresponding theory and experimental methods have been worked out well (see, for example, Refs. 19 and 66). Nevertheless, there is essentially no information in the literature on the magnitudes of the cross sections, especially for heavy atoms.

Excitation transfer in a gas of like atoms occurs at relatively high densities of the colliding atoms. The direct experimental study of these processes by ordinary spectroscopic methods is complicated by radiation capture. The development of methods for high-resolution laser spectroscopy and the use of the experimental techniques developed for laser isotope separation of heavy atoms have made it possible to study excitation transfer between isotopes, to observe them directly, and to measure the corresponding cross sections.^{67,68}

The product of this cross section and the relative velocity of the atoms gives us the transfer constant K_1 , which appears in Eq. (3) and which determines the selectivity of the isotope separation: $K_1 = \sigma_{AB}^* v$ (the atoms of species A are selectively excited). In inelastic collisions, the atoms of species A transfer energy to the atoms of species B . The atoms of species B excited in this manner can in turn either transfer energy back to an atom of species A or revert to the ground state through the spontaneous radiative decay of the excited state. The transition to the ground state is accompanied by the emission of a luminescence line of the corresponding wavelength. At the same time, there is a radiative decay of the excited state of the atoms of species A , accompanied by corresponding luminescence. Since the ratio of the luminescence intensities of the atoms of species A and B is equal to the ratio of the densities of the corresponding excited atoms, $a = N_A^*/N_B^*$, it is possible to study excitation exchange by measuring the luminescence lines of the two atoms.

For heavy atoms, a convenient object for studying excitation transfer is the excitation transfer between different isotopes in an atomic vapor. In this case the conditions for a resonance of the excitation transfer are well satisfied, since the energy defect of the interacting atoms is negligibly small and the atoms are very nearly identical. The isotopes are quite distinguishable by spectroscopic means, so that it is possible to study the excitation transfer independently on the basis of the isotopic structure of the atomic spectrum.

In the experiments of Refs. 67 and 68, the first step was to record the isotopic structure of the optical transition of interest at low densities of the atomic vapor. Then the laser was tuned to one of the isotopes of interest, and the luminescence spectrum was recorded with a scanning Fabry-Perot interferometer. When the density of atomic vapor was increased, changes were observed in the luminescence spectrum: a broadening of the luminescence line, a frequency shift of the line, and the appearance of lines corresponding to other isotopes.

For europium at the intercombinational transition ${}^8S_{7/2} - {}^6P_{7/2}$ ($\lambda = 5765\ \text{\AA}$), measurements at densities

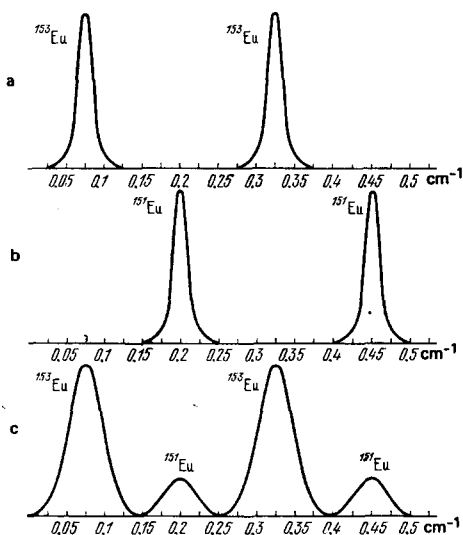


FIG. 12. Appearance of the ^{151}Eu luminescence line as the vapor density of atomic europium is increased and with laser excitation of ^{153}Eu (Ref. 67).

from $5 \cdot 10^{12} \text{ cm}^{-3}$ to $5 \cdot 10^{14} \text{ cm}^{-3}$ yield a value of $1.3 \cdot 10^{-13} \text{ cm}^2$ for the cross section for collisional excitation transfer between the isotopes ^{153}Eu and ^{151}Eu . Figure 12(a, b) shows some recordings of sequential stages in the process of excitation transfer from ^{153}Eu to ^{151}Eu . As the atomic vapor density is increased, the luminescence line of the isotope not excited by the radiation appears. A further increase in the density shifts the center of the luminescence line in the long-wavelength direction, in qualitative agreement with the theory of collisional broadening. It is apparently necessary also to take into account van der Waals forces in the interaction potential of the colliding atoms.

Europium has a simple isotopic structure, a large isotopic shift (0.12 cm^{-1}), and a small hyperfine splitting. In the case of samarium, with a much more complicated isotopic structure (the transition $a^3F_1 - Z_{22}$, $\lambda = 5916 \text{ \AA}$), it has been shown⁶⁸ that the excitation transfer is masked by the overlap of the wings of the absorption lines due to collisional broadening. This method is thus quite applicable for those atoms or those optical transitions for which the isotopic structure in the absorption spectrum is not overlapped by a hyperfine structure. It should also be noted that the accuracy with which the cross sections are determined is governed by the accuracy with which the atomic density in the irradiation volume is determined. Unfortunately, it is necessary to rely on temperature measurements here and on the assumption that the vapor is at thermodynamic equilibrium.

It is pertinent to note that the method developed in Refs. 67 and 68 for direct observation of excitation transfer can be used to study many energy-migration processes, including processes which occur within the Doppler line shapes.

The luminescence technique described above is comparatively simple. It is clear, however, that the selectivity and accuracy of the method can be improved substantially if an ionizing step and a selective mass filter

to measure the ion current are used to supplement the luminescence analysis in the measurements.

With pulsed lasers it becomes possible to study the temporal characteristics of the migration of excitation energy.

Finally, we note that the transfer of excitation energy in collisional processes can be exploited to improve the sensitivity of optical methods for detecting atoms.⁶⁹ The sensitivity of the method of resonance fluorescence is limited by the scattering of the exciting light. A relatively good sensitivity can be achieved if the total pressure of the gas (or vapor) is low. Where it is necessary, as it frequently is, to detect slight impurities in comparatively dense gases, this scattering becomes an essentially insurmountable obstacle. This problem is avoided in the method of nonresonance emission spectroscopy,⁶⁹ in which measurements are made of the emission of atoms which have acquired energy through resonance transfer from atoms excited by a monochromatic laser beam and which emit upon decay at a wavelength different from the wavelength of the exciting laser. If the radiation-excited transition is saturated, this method is insensitive to fluctuations in the laser intensity. Furthermore, this method is linear in the number of detected atoms over a broad range. The use of this method for sodium (for energy transfer in the doublet $D_1 - D_2$) led to a sensitivity of 10 atoms/cm^3 . This method can evidently also be used to study energy transfer on the basis of the isotopic structure of atomic spectra.

5. SPECTROSCOPIC DIAGNOSTICS OF A VAPOR OF NEUTRAL ATOMS; THE DETECTION OF ATOMS

The various applications of the selective multistep photoionization of atoms discussed above are practicable when a vapor of neutral atoms of an adequate density can be produced. For many refractory metals which are chemically active in their molten state, the simple methods of resistive or rf heating in some sort of crucible are not technically feasible. Among the metals of this type are the rare earths and the actinides. Lee and Zare⁷⁰ have made the interesting suggestion that chemical compounds containing the atom of interest be decomposed to produce the desired vapor. They produced free atoms of uranium through the decomposition of uranocene (bis-cyclooctatetraenyluranium), which yields cyclooctatetraenyl and carbon in addition to the uranium. A study of the temperature dependence of the concentration of uranium atoms produced in the chemical decomposition of the complex compound $(\text{NH}_4)_2\text{UF}_6$, with a subsequent reduction of the decomposition product UF_4 to uranium, has shown⁷¹ that the concentrations achieved in this way are very near the equilibrium concentrations achieved in the evaporation of metallic uranium in the same temperature intervals.

A general disadvantage of the chemical decomposition method is the contamination of the interaction volume with lasing emission of the unwanted decomposition products. Furthermore, in this case it is necessary to study the population distribution among the energy lev-

els of the neutral atoms resulting from the chemical decomposition. This study has been carried out for crucible-free methods of producing high vapor densities of refractory metals.^{30, 31}

In electron-beam evaporation and cathode sputtering, the collisions of the vapor atoms with electrons should affect the population distribution among the metastable levels. Electronic impact excites short-lived upper levels. The excited atoms undergo transitions to lower metastable states, and in these states they leave the volume in which the interaction with electrons is occurring. The resulting distribution among the low-lying metastable levels can be determined by laser-spectroscopy techniques similar to those described above.

This method is essentially one of measuring the luminescence intensity of the atomic vapor as a function of the wavelength of the laser beam exciting the atoms outside the volume in which the interaction with electrons is occurring. The luminescence is recorded during the laser pumping of relatively high-lying levels in transitions which begin from lower metastable levels, which are populated, in the final analysis, by electron impact. The change in the luminescence intensity as the laser is tuned can be used to find the population distribution among the metastable starting levels.

Experiments were carried out for gadolinium. Results found for both electron-beam evaporation and cathode sputtering are shown in Table III. Shown for comparison here are data corresponding to thermal-equilibrium heating at $T = 2000$ °K. We see that there is a very nonequilibrium population of the level a^9D_5 (999.11 cm^{-1}), where about 50% of the particles are concentrated. Interestingly, the distributions corresponding to the electron-beam evaporation by electrons with energies up to 8 keV and corresponding to cathode sputtering in a krypton atmosphere are essentially the same. Then in all cases in which methods other than purely thermal-equilibrium methods are used to produce refractory metal vapors (for spectroscopy, isotope separation, or selective photochemistry) it is necessary to carry out a luminescence-spectrum diagnostic study of the population distribution among the ground-state sublevels of the resulting atoms.

Being essentially an auxiliary method, this spectroscopic technique for the diagnostics of atomic vapor determines whether the vapor is suitable for the studies with which we are concerned in this review.

A problem closely related to the effort to produce

TABLE III. Population distribution among the metastable levels of the a^9D ground term of gadolinium during evaporation.

Level	Energy, cm^{-1}	Relative population		
		Cathode sputtering	Electron-beam evaporation	Thermal-equilibrium evaporation at 2000°K
$a^9D_5^0$	0	1	1	1
$a^9D_4^0$	215.13	1.2	0.7	1.49
$a^9D_3^0$	532.98	4.3	4.3	1.48
$a^9D_2^0$	999.11	8.3	8.0	1.43
$a^9D_1^0$	1719.06	1.2	4.2	1.15

neutral atoms is that of detecting atoms, which was touched on briefly at the end of the preceding section in connection with the resonance transfer of excitation energy. When laser-spectroscopy techniques are combined with multistep ionization it is possible to detect a single atom of the desired species selectively against a background of 10^{19} atoms of a different species.⁷² Here it is important to attain saturation conditions, such that each ground-state atom is converted into an ion pair. The most important point here is to saturate all the resonance transitions, and this is easily done at moderate laser pulse intensities. As in the general case of multistep ionization, the photoionization rate of the excited levels must exceed the overall rate of all types of energy loss due to collisions and spontaneous level decay. Line broadening degrades the selectivity, but on the other hand this broadening can be exploited to study the interaction of the atoms of interest with their surroundings.

The first experiments in this direction^{73, 74} showed that each helium atom in the 2^1S metastable state can be ionized in a two-step process in which the atom is initially excited from the 2^1S state to the 3^1P state by light at 5015 \AA and then ionized by light at the same wavelength. This approach has been used to measure the absolute helium population in the initial state resulting from pulsed proton bombardment and to study the time evolution of this population. It was later shown⁷⁵ that this technique can be used to detect ground-state atoms. For example, it was shown that each cesium atom in the irradiated volume can be detected at any time during the laser pulse. Hurst *et al.*⁷⁶ recently measured the number of cesium atoms produced in the photodissociation of CsI molecules and found the cross section for photodissociation of this molecule at the wavelength of 3175 \AA to be $2.9 \cdot 10^{-17} \text{ cm}^2$. They showed that all the molecules can be dissociated, and since a single cesium atom can be detected it is thus possible to detect a single molecule. It should be emphasized that it is important here to attain saturation with respect to all the laser beams used, both those used for photodissociation and those used to excite and ionize the atoms.

With a technique for detecting individual atoms and molecules it becomes possible to study some interesting physical processes. Hurst *et al.*,⁷² for example, have used this method to study the diffusion of cesium atoms in pure argon and to study the kinetics of cesium oxidation in an argon atmosphere. They produced the cesium vapor by evaporation from a container holding a cesium-iodine melt. To produce the atomic cesium, the vapor, consisting primarily of cesium-iodine dimers, was illuminated with the UV beam from a tunable dye laser ($\lambda = 3175 \text{ \AA}$) with a photon energy sufficient to dissociate the CsI dimer. The illuminated volume was also subjected to the beam from a second dye laser, at $\lambda = 4593 \text{ \AA}$. This beam excited cesium atoms to the $7^2P_{1/2}$ state, which lies approximately halfway between the ground state of the cesium atom and its continuum. In this arrangement it was possible to achieve cascade ionization of the excited atoms by light at the same wavelength, $\lambda = 4593 \text{ \AA}$. The ioniza-

tion was detected by observing the free electrons resulting from the ionization. By varying the time delay between the laser pulses producing the cesium atoms and ionizing them, it was possible to measure the diffusion coefficient of cesium atoms in argon ($0.12 \text{ cm}^2 \text{ atm/sec}$). The admission of oxygen into the reaction vessel reduced the number of ionization electrons, because some of the cesium atoms took part in an oxidation reaction. The rate of a chemical reaction under conditions of three-particle collisions were measured in experiments carried out at oxygen pressures $0.001\text{--}0.3 \text{ torr}$, at a cesium atom density $3 \cdot 10^6 \text{ cm}^{-3}$, and at buffer gas pressures $25\text{--}150 \text{ torr}$.

Again we wish to emphasize that the ionization technique using dye lasers has been refined⁷²⁻⁷⁶ to the point at which it can reliably detect a single impurity atom in a buffer gas. The most convincing example is the detection of cesium in argon at atmospheric pressure.⁷⁶

This technique has some interesting applications for detecting atoms, including chemically active atoms which are produced in chemical reactions; atoms which are the products of radioactive decay, slow evaporation, or slow transport processes; etc.

Again we note that by taking careful measures to suppress light scattering it is possible to detect essentially single atoms by the method of resonance laser fluorescence.⁷⁹ A discussion of these methods goes beyond the scope of this review.

6. CONCLUSION

In summary, it has been reliably established that multistep photoionization of atoms is a feasible and highly selective method in applications such as laser isotope separation and ultrahigh-resolution spectroscopy. Since selective photoionization of atoms is a universal method, it can be used for all isotopes of all elements in the periodic table, including rare and unstable items.

The further development of selective photoionization will presumably take the form of a refinement of known applications and a search for new applications. One application is the production of beams of polarized electrons and nuclei.^{77,78,80-82} Delone and Fedorov⁷⁷ have recently reviewed this application of multistep photoionization of atoms in nuclear physics, which has been made feasible by developments in quantum electronics. It should also be noted that it is possible to determine the products of nuclear reactions immediately with a sensitivity of essentially a single atom, without removing the sample from the experimental vessel. In nuclear physics there may be an interesting analogous application of selective photoionization, to measure neutron velocities.⁸³

We can undoubtedly expect new suggestions and the development of many new applications of the selective photoionization of atoms into molecules. In the isotope-separation application there are many problems still to be solved, involving the removal of charged particles from the relatively dense plasma produced through the selective photoionization of atoms.

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