Laser isotope separation

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A review is given of laser isotope separation methods. Multistep and single-step seaparation methods are discussed. An analysis is given of selective two-step photoionization and photodissociation, multistep selective collisionless dissociation of polyatomic molecules, and formation of charged particles as a result of a strong resonant laser interaction. Such single-step methods as optical pressure, resonant scattering of selectively excited particles, scattering in the strong field of a light wave, deflection of excited molecules in inhomogeneous fields, and heterogeneous separation of vibrationally excited molecules are considered. Selective photochemical laser separation methods are analyzed and the most interesting among these is the selective photopredissociation. The results of experimental investigations are given.

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1. INTRODUCTION

Quantum electronics is becoming increasingly concerned, apart from intrinsic laser action investigations, with studies of the interaction between laser radiation and matter. The ability of lasers to concentrate optical energy in space and time or in a spectral interval can be utilized in two ways. Since the appearance of lasers, attention has been concentrated on nonresonant interaction of high-power laser fluxes with matter under continuous or pulse conditions. Examples of such "brute" force interactions are well known. They include machining of very hard materials, welding, thermonuclear fusion, and many others.

However, the resonant interactions of intense laser radiation with matter are of special interest because they provide an opportunity for selective action on atoms, ions, molecules, and molecular complexes. The high spectral brightness of the radiation makes it possible to ensure selective photodissociation, photo-ionization, photochemical action, and other processes. One should add that the laser method of energy input is characterized by high localization, controlled dose, homogeneity, and sterility.

Clearly, the resonant interaction between high-power laser radiation and matter can be used in the separation of isotopes provided the interaction is made selective. The general idea of using the differences between the absorption spectra of atoms, molecules, and other particles due to the differences between their isotopic compositions in the optical separation of isotopes, i. e., the idea of using the isotopic shift in the absorption spectra for isotope separation, was suggested many years ago and does not require justification. Although mercury isotopes were separated by light emitted from a monoisotopic mercury lamp many years before the appearance of lasers, [1] only the application of lasers made the optical isotope separation method sufficiently universal and productive.

The development of laser technology has now reached a level at which it is possible to carry out systematic studies of the laser separation of isotopes of various elements. The construction of tunable ultraviolet, visible, and infrared lasers emitting highly monochromatic powerful radiation, and the development of methods for measuring and stabilizing laser emission frequency provided the base on which the laser isotope separation can grow.

In the case of molecular systems, the discovery of the means for establishing different vibrational and translational temperatures and for the chemical action of laser radiation[2,3] has led to the accumulation of considerable experimental material and a high degree of understanding of the excitation of higher vibrational states of molecules by infrared laser radiation. [1]

In the case of atomic systems, the subject of excitation of atomic levels has reached a high degree of advancement in classical atomic spectroscopy. Thus, if there are lasers which can excite selectively a sufficiently large number of atoms, one can separate isotopes simply by solving the problem of separating selectively excited particles from those which are not excited in this way.

Thus, the developments in laser technology and the results of studies of resonant interaction between high-power laser radiation and matter have established the necessary base for solving the problem of laser

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[1] Selective (mainly chemical) action of infrared laser radiation is discussed in several reviews (see, for example, [4,7]).

isotope separation.

The growth in energy requirements has made it essential to search for new isotope separation methods, particularly of uranium isotopes. The fission of one U^{235} atom liberates about 200 MeV of energy, i. e., 1 g of U^{235} gives an energy of 7.2×10^6 kJ ($= 2 \times 10^3$ kWh). According to the data reported by the United States Energy Research and Development Administration (ERDA), the energy lost in the separation of uranium isotopes (per one U^{235} atom) by the gas-diffusion method is 3 MeV and in the centrifuge method this energy is 450 keV.[8] In view of the colossal scale and rate of growth of energy consumption, the development of new potentially more cost-effective methods could result in considerable economies in capital and current expenditure. According to ERDA, at the present level of development of laser technology, the economies will amount to 70–80 billion dollars. The potentialities of the laser separation method are such that it should be possible to extract the required isotope from the original mixture more thoroughly and this is desirable not only from the purely economic point of view but because of the better utilization of uranium ores, the reserves of which are naturally finite.

The scale of the requirements in respect of uranium separation can be judged on the basis of the Directives of the Central Committee of the Communist Party of the Soviet Union and of the State Plans of the USSR on the Development of Atomic Power in the Soviet Union.

According to the published data,[9] the total power of the nuclear stations in the Soviet Union by 1980–1982 will be 3×10^4 MW so that the development of the laser method for the enrichment of uranium appears to be a very attractive development. Moreover, the universality of laser isotope separation makes it possible to reduce substantially the cost of preparation of isotopes of all the elements in the Mendeleev table, whose separation by the highly developed methods for uranium is either impossible or undesirable because of the small requirements. Thus, the needs of spectroscopy, chemistry, biology, medicine, agriculture, archeology, etc. also make it essential to develop laser isotope separation methods.

2. LASER ISOTOPE SEPARATION METHODS

A common feature of all the laser isotope separation methods is the selective excitation of the desired isotopic components by laser radiation of sufficient monochromaticity and intensity, followed by physical removal of the excited isotopes based on some aspect of the interaction between selectively excited atoms and molecules with physical or chemical agents. The unique ability of laser radiation to excite atoms or molecules only of the required kind reduces the energy losses in laser isotope separation compared with the conventional methods. Clearly, the subsequent physical or chemical processes in which excited particles participate (and, in general, the process of excitation to a sufficiently high energy, which is sometimes a necessary preliminary to efficient interaction) should ensure minimum possible losses of the excitation selectivity.

The differences between specific laser separation methods lie in the process of physical, chemical, or plasma-chemical interaction of excited particles or their fragments.

An important point is also the difference between the species being separated. The laser methods can be applied to atomic or molecular systems. The line spectra of atoms with a strong isotopic shift, which is usually much greater than the Doppler line width (see, for example, the reviews[10]), are convenient for the resonant laser interaction. However, in the case of many refractory elements, the generation of atomic vapor of sufficient density is a difficult technological problem, which seriously limits the general usefulness of atoms in their pure form. Many chemical compounds of even heavy atoms are more volatile. However, their electronic spectra are highly complicated by the rotational-vibrational structure, which masks the isotopic shift and hinders selective laser action. The use of vibrational spectra of molecules may also be difficult because of the presence of the rotational structure, which represents a practically continuous spectrum in the case of heavy molecules. However, some progress can be made by a strong cooling of a molecular gas, such as that which occurs in gas-dynamic processes and this should "thin out" the rotational spectrum.

The problem of the state of the ensemble of particles subjected to interaction with laser radiation is also important. Clearly, the selectivity of laser radiation is preserved best when a beam of noninteracting atoms or molecules is irradiated. However, the density of beams is low and, therefore, the yield is low. The need to increase the yield makes it necessary to use the gaseous phase and, in principle, condensed phases can also be used. In view of the considerable increase in the intensity of the internal interactions in an irradiated ensemble of particles, we may expect a deterioration in the selectivity of the process of laser separation of isotopes. We must bear in mind that the conflict between the requirements of a high separation coefficient and a high yield (as is well known,[11] this applies to any isotope separation method), which can be solved only by a compromise.

Laser isotope separation methods are also characterized by the fact that one can use single-step or multistep interaction with radiation. In single-step processes, one laser photon excites selectively one energy level of an atom or a molecule. Then, the required isotope is removed, employing the interaction between the selectively excited state and some physical or chemical agent. This can be done using the pressure of light,[12,13] resonant scattering of a beam of excited particles by similar but unexcited particles,[14] scattering in a strong field of a resonant standing wave,[15] deflection of a beam of vibrationally excited molecules by an inhomogeneous electric field,[16] and heterogeneous separation of vibrationally excited molecules.[17] It is well known from chemical kinetics[18] that excited atoms and molecules are much more reactive than unexcited species. The activation energy of chemical reactions is usually high. Therefore, single-step excitation is
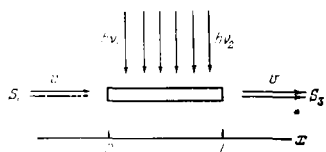
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FIG. 1. Two-step interaction of laser radiation with a particle beam.

generally acceptable for atoms but one should mention the successful laser separation of the hydrogen isotopes in single-step processes involving selective photobromination of methanol[19] and selective photopredissociation of formaldehyde.[20]

In multistep processes, the excitation of particles to a sufficiently high energy and a subsequent drastic change in the structure of physical properties require several and sometimes many photons. Clearly, the excitation should be selective in at least one of the steps. In the case of atoms, an interesting process is the selective two-step photoionization[21] applied successfully in the first studies of the laser separation of uranium isotopes.[22] In the molecular case, use has been made of two-step selective photodissociation[23] employed in the separation of nitrogen molecules[24] (ammonia molecule NH_3) and boron isotopes[25] (boron trichloride molecules BCl_3).

In the excitation of vibrational levels of molecules, a promising method is the use of many photons of the same laser radiation, which results in multistep instantaneous (collisionless) dissociation of molecules[26] and formation of ions[27] in the resonant interaction of infrared laser radiation. This instantaneous dissociation effect was used in the isotopically selective reaction of the BCl_3 gas molecules with oxygen[28] and of the SF_6 gas molecules with hydrogen and the walls of a glass cell.[29] In the formation of ions, the electrical removal of isotopes seems to be more attractive than the chemical binding of selectively generated molecular fragments.

Although the multistep laser processes are very promising, particularly in the case of molecules with a strong isotopic shift, we must bear in mind that laser radiation is utilized most effectively in one-step processes.

Finally, in considering the possibility of industrial applications of any specific laser separation method, we must take into account whether the process is continuous or pulsed and whether, in the pulsed case, a high repetition frequency can be achieved.

We shall conclude this section by pointing out the self-evident urgent need for tunable lasers at all the frequencies employed in quantum electronics. This important problem is dealt with in several reviews.[30—33]

One of the first reviews on tunable optical parametric oscillators[31] has mentioned the important application of these oscillators in selective excitation of certain bonds in molecules.

We shall now consider the most interesting (in our opinion) methods and give the results of laser isotope separation experiments.

3. SELECTIVE PHOTOIONIZATION OF ATOMS

Up to now, the potential applications of infrared lasers have been largely limited by the absence of sufficiently powerful continuously tunable lasers in many parts of the infrared spectrum. Such lasers are available in the visible, near infrared, and ultraviolet range. These are the dye lasers employed at the fundamental emission frequency or as harmonics of this frequency. Therefore, the two-step photoionization of atoms becomes particularly important. In this case, one of the resonant absorption lines of an atom is excited by sufficiently monochromatic tunable laser radiation and the excited atoms are ionized by the radiation of a second laser or noncoherent source. This method was used successfully in the separation of the uranium isotopes[22] and of the calcium isotopes.[34]

In an analysis of the selective photoionization of atoms atoms, one should distinguish between the need to achieve a high degree of separation and removal of all the required atoms from the original mixture, without paying much attention to the quantum efficiency of the separation process and its yield, and the case when the yield of the method and its quantum efficiency are important because of the expense involved in generating laser radiation.[35] An analysis can be made in the latter case, allowing for the processes which result in the loss of selectivity, particularly resonant charge exchange and resonant transfer of excitation.

The first case corresponds to two-step laser interaction with a beam of atoms that do not interact with one another.

We shall now consider the efficiency of two-step selective excitation in a beam of atoms.[36] Let us assume that, in a beam of atoms entering at a velocity v a region of interaction with radiation, the flux density of the atoms of interest to us is S_1. The two-step interaction alters the properties of these atoms significantly and irreversibly: they become ionized and can be sorted out very easily. If, at the exit from the interaction region, the density of the ion flux is S_3, the measure of the efficiency of the interaction is the ratio S_3/S_1. Let the length of the interaction region be L. Assume that this region is illuminated homogeneously and that light is incident on the atomic beam at right-angles to the direction of travel of the atoms and that this beam is an optically thin layer. The problem then becomes one-dimensional. We introduce an axis x which is directed along the beam (Fig. 1) and consider a three-level system (Fig. 2). Let $n_1(x)$ be the density of atoms at the lower level and $n_2(x)$ the density at the excited metastable level; $n_3(x)$ is the density of ions. The volume
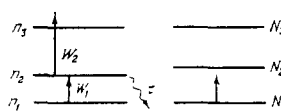

FIG. 2. Energy levels involved in two-step interaction with a particle beam. A formal representation is used to denote the absence of action on a lower isotope (N_i) which goes off resonance as a result of the transition $1 \rightarrow 2$.

densities are related by $n = S/v$ to the flux densities.

Allowance for the gradient of the density of atoms downstream yields the rate equations of the following kind:

$$\begin{aligned}
\frac{\partial}{\partial t} n_1(x) &= (n_2 - n_1) W_1 + \frac{n_2}{\tau} - v \frac{\partial n_1}{\partial x}, \\
\frac{\partial}{\partial t} n_2(x) &= (n_1 - n_2) W_1 - \frac{n_2}{\tau} - n_2 W_2 - v \frac{\partial n_2}{\partial x}, \\
\frac{\partial}{\partial t} n_3(x) &= n_2 W_2 - v \frac{\partial n_3}{\partial x};
\end{aligned} \qquad (1)$$

here, W_1 is the probability of laser-induced selective transitions from the ground to the excited metastable level (first step); τ is the lifetime of the metastable level; W_2 is the probability of ionization in transitions from the excited metastable level to the continuous spectrum under the action of the radiation field of suitable frequency (second step). It is assumed that the degrees of degeneracy of the first and second levels are the same and that no recombination takes place.

Under steady-state conditions (continuous action of laser radiation), the efficiency of the interaction can approach unity if the transit time across the interaction region $\tau_0 = L/v$ exceeds considerably a certain effective lifetime of the excited metastable state τ_{eff}.

If the interaction with radiation is weak, i.e., if it is far from saturation so that $W_1 \tau \ll 1$ and $W_2 \tau \ll 1$, the value of τ_{eff} increases strongly compared with τ because of the repeated pumping of atoms by the $1 \to 2$ transition:

$$\tau_{\text{eff}} = \frac{\tau}{W_1 \tau W_2 \tau}. \qquad (2)$$

To within terms of the second order of smallness, we find that

$$\frac{S_3}{S_1} = 1 - e^{-\tau_0/\tau_{\text{eff}}}. \qquad (3)$$

If the transit time is short $\tau_0 \ll 1/W_2 W_1 \tau$, the efficiency is low and $S_3/S_1 = W_1 \tau W_2 \tau_0$.

Even if the ionization probability is low, the situation improves considerably in the case of strong saturation of the first transition, which ensures the selectivity of the interaction. If $W_1 \tau \gg 1 \gg W_2 \tau$, we find that S_3/S_1 is described by Eq. (3) with

$$\tau_{\text{eff}} = \frac{2}{W_2}. \qquad (4)$$

If the transit time is short $\tau_0 \ll 2/W_2$, we have $S_3/S_1 = W_2 \tau_0/2$.

We shall consider in greater detail the case of strong interaction in the first (selective) step. The condition $W_1 \tau \gg 1$ corresponds to the radiation flux density $I_1 = h\nu_1/\sigma_1 \tau$, where $h\nu_1$ is the energy of the resonant transition quantum and σ_1 is the cross section of the transition. At the wavelength $0.6\ \mu$, for $\sigma_1 = 10^{-13}$ cm^2 and $\tau = 10^{-8}$ sec, the radiation flux density should exceed $2\,\mathrm{W/cm^2}$. The efficiency of the use of saturating radia-

tion in a specific experimental geometry can be increased by the use of a mirror system.

A laser radiation source is usually described not by the flux density but by the radiation power. For a given power, the flux density is governed by the length of the interaction region L if we ignore the divergence of the radiation and the formation of a light spot in the interaction region. The selection of L is governed by the value of τ_{eff} and, in the case under discussion, it is $2/W_2$. The probability is $W_2 = I_2 \sigma_2/h\nu_2$, where $h\nu_2$ is the quantum energy of the photoionization from the excited level, σ_2 is the cross section of this process, and I_2 is the flux density of the ionizing radiation. If the velocity of atoms in a beam is 10^4 cm/sec, the value $L = 2\text{--}3$ cm $[\tau_0 = (2\text{--}3 \times 10^{-4}$ sec] is sufficient for attaining $S_3/S_1 \approx 1$ when $\tau_{\text{eff}} \approx 10^{-4}$ sec. If $\sigma_2 = 10^{-17}$ cm^2 and $h\nu_2 = 6 \times 10^{-19}$ J, this can be ensured if the flux density of the ionizing radiation is $I_2 = 10^3$ W/cm^2. In the case of an atomic beam of transverse dimensions amounting to a fraction of a centimeter, the estimates obtained above indicate that it should be possible to extract completely the required isotope from the irradiated mixture provided the power is a fraction of a watt for the first step and a fraction of a kilowatt for the second.

We shall now consider the more general kinetic scheme of two-step laser photoionization of atoms which can be used to determine such important parameters as the total number of selected ions, quantum efficiency, and separation coefficient; allowance will be made for the principal processes resulting in the loss of selectivity. [37] The most important of these processes are the resonant charge exchange and the resonant transfer of excitation. It is known[38] that the cross sections of these processes are considerably higher than the gaskinetic cross section and they amount to $10^{-13}\text{--}10^{-14}$ cm^2.

Since the Doppler width of the resonant absorption lines of atoms can be of the same order of magnitude as the isotopic shift, allowance has to be made for the loss of selectivity due to the excitation by undesired absorption in the wings of spectral lines.

The Doppler width can be reduced and the influence of collisions can be minimized by the use of well-collimated atomic beams but this limits the usefulness of the two-step selective photoionization method to the range of low densities. This restricts the yield of the method if the laser radiation power is sufficiently high. Optimization of the whole separation process makes it necessary to determine the degree to which it is possible to increase the density of atoms from the point of view of efficiency and selectivity of the process.

We shall consider the kinetics of the populations of the energy levels in a mixture of A and B isotopes which are in the gaseous phase (Fig. 3). The moment $t = 0$ corresponds to the beginning of illumination with radiation which is in resonance with the spectral line of atoms A and whose spectral width is sufficient for the excitation of all the atoms within the Doppler profile. This radiation may extend to the wing of the spectral line of atoms B. In addition to the resonant
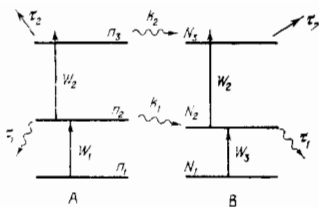
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FIG. 3. Energy level scheme of two-step selective photoionization of a gas of A and B atoms.

$$
\left.\begin{aligned}
n &= \frac{n_0}{1 + k_2 N_0 \tau_2}, \\
\alpha &= \frac{1}{1 + k_2 N_0 \tau_2} = \frac{n}{n_0}, \\
\eta &= \frac{1}{k_2 n_0 \tau_2}.
\end{aligned}\right\} \tag{5}
$$

radiation, atoms are also subjected to radiation whose absorption causes ionization of excited A and B atoms. These excited A and B atoms can give up their excitation energy to unexcited A and B atoms in a resonant process whose rate constant is k_1. Similarly, ionized atoms of each kind may exchange electrons with atoms of another kind in the process of resonant charge exchange characterized by a rate constant k_2. Let us assume that the concentration of A atoms is less than that of B atoms, $n_0 \ll N_0$, which corresponds to the most important case of the separation of rare isotopes. The relative concentrations of the excited (N_1/N_0) and ionized (N_2/N_0) B atoms can be regarded as low and the charge exchange experienced by the B atoms as well as the resonant transfer of the excitation energy from B to A can be ignored, which simplifies the analysis considerably. It should be noted that these processes play a positive role. The radiative lifetime τ_1 of the excited atoms, which is the same for A and B, is assumed to be equal to the total lifetime of these atoms. The average time for the removal of ions from the interaction region of atoms with radiation is τ_2. An analysis shows that all the characteristics of the separation process deteriorate with increasing number of charge-exchange events during the separation time. The separation time is usually fairly long, $\tau_2 \gtrsim 10\tau_1$. Therefore, the most undesirable process is the charge exchange and the influence of the transfer of excitation can be ignored. It should be noted that even a relatively weak excitation of B the atoms in the wings of their absorption lines may considerably reduce the separation coefficient.

The quantum efficiency $\alpha \approx 1$ can be achieved if the rate of photoionization $W_2 \tau_1 \gtrsim 1$ is high. Since the photoionization cross section is small, $\sigma_2 = 10^{-17}$–10^{-18} cm^2, this means that the ionizing radiation power has to be high and the energy of this radiation is hardly absorbed by atoms. The position can be improved somewhat by resonant ionization through autoionization states. [38] The ionization cross section may then be $\sigma_2 = 10^{-15}$–10^{-16} cm^2 but the optical thickness of the gas for the ionizing radiation is still 4–5 orders of magnitude less than for the resonant radiation ($\sigma_1 = 10^{-11}$–10^{-13} cm^2). Nevertheless, in view of the stringent requirements that the resonant radiation must satisfy, it is desirable to determine the quantum efficiency of ionizing radiation.

In the case of high values of $W_2 \tau_1$ and on the assumption that the excitation of B atoms in the wing of their resonant absorption line can be ignored, we find that the total number of extracted ions n, quantum efficiency α, and separation coefficient η are described by the relationship

Then, at low densities, when $k_2 N_{02} \ll 1$, the separation coefficient is high, the quantum efficiency tends to 100%, and practically all the type A atoms are transformed into separable ions, as shown above for a collisionless atomic beam. However, the mass yield is low.

When ions are removed by an external electric field in the case of low gas densities, the average transit times of ions to the cathode is independent of the density. When the density is increased, the yield of ions increases proportionally to n_0 and the separation coefficient falls proportionally to $1/n_0$. If $k_2 N_0 \tau_2 \gtrsim 1$, the collisionless motion of ions changes to a drift, in which case we have $\tau_2 \propto N_0$ and the yield of ions decreases with increasing density. The optimal density from the point of view of yield is that for which $k_2 N_0 \tau_2 \approx 1$. Then, $n = n_0/2$, $\alpha = 1/2$, and $\eta = N_0/n_0$ and ions of the A and B atoms are present in the separation products in approximately the same amounts, $n \approx N$, whereas the original mixture obeys the inequality $n_0 \ll N_0$. If $k_2 = 5 \times 10^{-10}$–10^{-9} cm^3/sec, $\tau_2 = 10^{-5}$ sec, the condition $k_2 N_0 \tau_2 \approx 1$ corresponds to an atomic vapor density $N_0 \approx 10^{14}$ cm^{-3}, which is several orders of magnitude higher than in a collisionless beam.

In the removal of ions by plasma-chemical reactions, it is necessary to introduce into a gas atoms and molecules which react chemically with ions and the cross section of this reaction should be considerably greater than the gaskinetic cross section (the reaction rate constant should be $k_3 \gg \langle \sigma V \rangle_{gk}$). The quantity $k_2 N_0 \tau_2$ is then independent of the density but, for a given density, there is an optimal (from the point of view of yield) density of the atoms being separated and of the "impurity" (N_i) particles introduced for the purpose of the reaction $(N_0/N_i)_{opt} = \sqrt{k_3/k_2}$. In this case, the yield of ions of the required kind is maximal and amounts to $n_0/(1 + \sqrt{k_2/k_3})$. The total density of the particles is then limited by the need to retain the excitation selectivity because an increase in the density increases the collisional line width and the isotopic shift should be greater than this width. If it is necessary to ensure a high content of the isotope being separated in the reaction products, the condition $k_3 N_i \gg k_2 N_0$ should be satisfied. This reduces the yield. Clearly, the plasma-chemical method of the removal of ions obtained as a result of selective two-step photoionization is quite promising.

The considerations put forward above, based on different approaches, both allowing and ignoring the processes which result in the selectivity of the interaction, demonstrate the possibility of effective separation of isotopes by selective two-step photoionization in an atomic beam and in the gaseous phase, and they also yield formulas suitable for calculations. These considerations also show that the weakest link in the two-step method (from the energy point of view) is the sec-

ond one, involving the photoionization of excited atoms and this is due to the smallness of the ionization cross section of the excited states.

For example, in the case of uranium, the results[8] averaged over the wavelength range 2100–3100 Å (second step) show that the value of σ_2 is 10^{-17} cm^2, whereas, in the case of resonant absorption (first step) at the wavelengths of 6056.8 Å, 5915.4 Å, and 5758.1 Å, the values of σ_1 are 5.9×10^{-15} cm^2, 1.1×10^{-13} cm^2, and 1.6×10^{-14} cm^2. The autoionization levels, which arise (according to the results of a preliminary analysis) due to the interaction of the metastable configurations f^3dp^2, f^3dsp, f^3s^2p, and f^4s^2 of the neutral atom with the configuration of the ion f^3ds, are located 500 cm^{-1} higher than the ionization limit of the atom. (The ionization potential is 6.11 ± 0.02 eV. [39]) The cross sections of the autoionization transitions are 10 times higher. A better theoretical estimate gives $\sigma_2 = 5 \times 10^{-16}$ cm^2.

Although values such as $\sigma_2 = 5 \times 10^{-16}$ cm^2 make it possible to consider seriously the competitiveness of the method of selective two-step photoionization for the enrichment of uranium with the U^{235} isotope, [8] it is preferable to search for methods which avoid the obstacle mentioned above.

A direct generalization of the two-step photoionization method is the N-step procedure in which successive resonant excitation of the uranium atom is performed by four lasers with emission wavelengths of about 0.6 μ and this is done until the energy reaches a value close to the continuum. The ionization is then performed by an infrared laser whose photons are relatively "cheap" compared with the ultraviolet photons. [8] Thus, infrared radiation may be provided by a CO$_2$ laser ($\nu \approx 1000$ cm^{-1}) whose efficiency may reach 30%.

A promising procedure is the chemical ionization of selectively excited atoms, in accordance with the scheme

$$U^* + M = UM^+ + e^-, \qquad (6)$$

where M is a metal (cesium, barium, thallium, or aluminum), or in accordance with

$$U^* + SF_6 \begin{array}{l} \longrightarrow U^+ + SF_6^-, \\ \longrightarrow UF_2^+ + SF_4^-. \end{array} \qquad (7)$$

It is proposed to use the method of intersecting beams in a study and utilization of these reactions. [8] Particularly interesting is the intermetallic chemical ionization in the Cs + U* reaction (excited at the wavelength 4352 Å) since the probability of the reaction of cesium with unexcited uranium is relatively low.

In view of the known fact that the rates of many endothermal bimolecular reactions increase strongly when either the vibrational or the electronic energy of the system is increased, it would be interesting to consider such fairly common reactions as

$$U^* + CO \rightarrow UO + e. \qquad (8)$$

It is likely[8] that reactions of the (8) type will be preferable to reactions (6) and (7) because, in the former case, the isotopic exchange is less likely and the products are removed more easily.

Another interesting possibility is the use of ionization of selectively excited atoms in a strong electrostatic field which deforms considerably the electronic terms of atoms. [40]

In this case, the essential point is that the selective ionization of atoms is possible as a result of selective excitation to a state close to but lower than the ionization limit followed by subsequent ionization of highly excited atoms by an electric field. Laser radiation makes it possible to populate readily and quite efficiently the states of atoms with large values of the principal quantum number n. The applied electric field modifies the electronic terms in such a way that some of the terms in the discrete spectrum adjoining the ionization limit reach the continuum and the other levels become of the autoionization type. The probability of autoionization decay rises rapidly with the principal quantum number n. Since an effective filling of the states with high values of n requires three or four tunable lasers emitting sufficiently monochromatic radiation, the method is basically similar to the N-step photoionization mentioned above. An important difference is the use of an electric field for ionization rather than infrared laser radiation. According to the estimates given in[40], the field required for rubidium atoms need not exceed 30 kV/cm.

The autoionization of high atomic states in an electric field was achieved experimentally in the case of sodium atoms. [40b] The two-step excitation was provided by two dye lasers (rhodamine 6G and POPOP), excited by a pulse nitrogen laser. The emission wavelengths of these lasers were 5895.9 Å (first step) and 4210–4140 Å (second step). In the first step, the laser radiation saturated the $3^2S_{1/2} - 3^2P_{1/2}$ transition. The second step involved the excitation of high S and D states of Na with a quantum number n varying from 13 to 18. The electric field was within the range 10–20 kV/cm. It was found that the photocurrent increased strongly and the effect was resonant. Although the monoisotopic nature of sodium was unsuitable for testing the suitability of this isotope separation method, this experiment demonstrated the possibility of a considerable extension of the range of applications of the method of selective photoionization of atoms.

Essentially, the methods described in the preceding paragraphs are intended to avoid the principal difficulty in two-step photoionization, which is the smallness of the value of σ_2, and to make this a single-step process. However, up to now, the only experimentally realized laser method of enriching uranium[22] has been the selective-step photoionization. In the early part of 1975, this separation was achieved not only at the microscopic level but also at a level at which considerable amounts of uranium were produced. A fourfold enrichment of natural uranium with the U^{235} isotope was achieved and the yield was 1 mg/h. [41] (An atomic

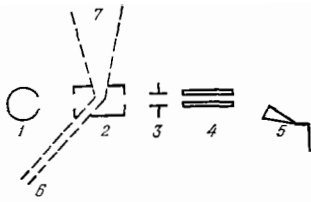N. V. Karlov and A. M. Prokhorov

FIG. 4. Schematic diagram of the experimental arrangement used in selective two-step photoionization of uranium in an atomic beam: 1) furnace; 2) interaction chamber; 3) ion lens; 4) quadrupole mass filter; 5) ion collector; 6) laser beam; 7) ultraviolet radiation.

power station with an output of 3×10^{10} W consumes[9] U^{235} at a rate of 4 g/sec.) This experiment was carried out using two lasers, one krypton (Kr III, $\lambda = 3507$ Å) and the other xenon (Xe II, $\lambda = 4606$ Å), producing a total photon energy of 6.25 eV, which was 0.14 ± 0.02 eV higher than the ionization potential of uranium atoms and, consequently, it should be possible to use the auto-ionization transition in the second step.

The first reported experiment[22] was carried out using a cw tunable rhodamine 6G laser (first step) and a continuously operating mercury lamp. The laser and ultraviolet radiation were oriented at right-angles to one another and to a collimated beam of uranium atoms. The experimental arrangement was as shown in Fig. 4. The laser separation of uranium atoms was successful because of the development of a uranium alloy which acted as a source of uranium vapor of sufficiently high pressure. (Liquid uranium is very active and, at temperatures exceeding 2100 °K, there are practically no technological materials which would not be "eaten away" by uranium at a high rate.) It was found that uranium-rhenium alloy with the stoichiometric formula URe_2, kept in contact with tungsten up to temperatures exceeding 3100 °K, formed a dense protective film which prevented the attack of uranium on tungsten. The uranium vapor pressure was close to what one would expect at the temperatures involved.

This experiment was carried out at 2400 °K and the heating was ohmic. The density of the uranium atomic flux was 10^{12} cm^{-2} · sec^{-1}. The cross section of the atomic beam after passing through several apertures was 3×7 mm and the density of the atoms in the interaction region was 5×10^{10} cm^{-3}. Bias voltages were applied to the crucible, thermal screens, and apertures so as to free the beam from charged particles of thermal origin before it entered the interaction region.

The wavelength of the laser radiation was 5915.4 Å. The isotopic shift at this wavelength was 8 GHz. The Doppler width of the absorption line was 1 MHz. The width of the laser radiation spectrum was less than 50 MHz. The rhodamine 6G laser was pumped by a cw argon laser and the output power of the dye laser was 40 MW. The dye laser resonator included a Fabry-Perot interferometer controlled by piezoelectric means. A small proportion (~1%) of the laser power was deflected for frequency monitoring and stabilization with the aid of an absorption cell containing enriched uranium iodide in which a microwave discharge was established.

The arc mercury lamp with an output power of 2500 W performed the ionization of the excited uranium. A quartz filter removed radiation of wavelengths shorter than 2100 Å so as to avoid ionization of the unexcited uranium. The intensity of the ultraviolet radiation in the 2100–3100 Å range was 8 W/cm^2.

An ion beam produced by this selective ionization method was slightly focused by an ion lens before it entered a quadrupole mass filter mounted in the same vacuum chamber. The ions which were transmitted by the filter were removed from the beam by a collector cone to which a bias voltage of 3100 V was applied.

When the dye laser was tuned to the U^{238} absorption line, the mass spectrum of the ion current consisted only of U^{238} photoions. When the laser was tuned to a U^{235} line, only ions of mass 235 were obtained. When uranium with a natural mixture of isotopes was employed, the ion current for tuning to U^{235} was 1000 times smaller than for tuning to U^{238}. This was due to the relative abundances of U^{235} and U^{238} (0.071%) and the presence of eight hyperfine structure components in the spectrum of U^{235}.

An additional confirmation of the attainment of separation was provided by an experiment in which the mass filter was tuned to the 235 mass and the absorption spectrum of uranium was scanned with the laser. All eight hyperfine structure components of the absorption spectrum of U^{235} appeared in the photocurrent of ions of mass 235; the shape of the peaks, their positions, and intensities agreed exactly with the known optical spectrum (Fig. 5).

These experiments demonstrated that, in principle, it should be possible to perform laser isotope separation even on such a heavy element as uranium. Moreover, these experiments provided valuable spectral information and made it possible to formulate the requirements which lasers should satisfy for an industrial unit performing laser separation of uranium isotopes by the selective photoionization method.

It should be pointed out first that the number of uranium atoms in the ground state depended strongly on temperature. At 2600 °K, 44.5% of all the atoms were in the ground state and 27% at the 620 cm^{-1} metastable level. Many lasers would be required to interact with all the atoms but, clearly, two lasers differing in frequency by 620 cm^{-1} would be needed for the first step. At 2800 °K, the use of the two lasers almost doubled
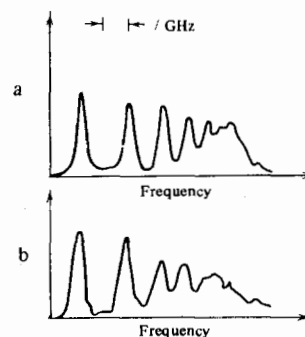

FIG. 5. Hyperfine structure of the spectra of the U^{235} isotope in the 5915 Å range: a) emission spectrum in a hollow-cathode lamp; b) spectrum of photons emitted by U^{235} as a result of scanning of a dye laser frequency.

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the output parameters of the separation system.

Rough estimates[8] based on the experimental results indicated that one unit for the separation of uranium isotopes with a yield of 2.5–10 tonnes per year of uranium enriched with U^{235} to 3.2% would require lasers with an output power of 10–40 W in the visible range (100–400 W/cm^2 intensity) and ionizing radiation sources of 20–40 kW power (10^4 W/cm^2 intensity). The monochromaticity of the lasers should be at least 100 MHz (0.03 cm^{-1}), the frequency stability should be at least 1 GHz (cm^{-1}), and the divergence should be 10^{-4} rad. For an overall laser efficiency of 0.1%, the total power consumption of such a unit would be 250–1000 kW and, clearly, the laser efficiency would have to be increased considerably.

The above results were obtained for the laser separation of isotopes of an important element such as uranium. However, it is clear that the method described here and its analysis are of general application and can be used in every case in which an atomic beam can be formed.

4. SELECTIVE DISSOCIATION OF MOLECULES

The most general method for the selective dissociation of molecules is the two-step photodissociation. This method is fully analogous to the two-step photoionization of atoms and it has the same advantages and shortcomings as the former. An undoubted advantage is, in principle, the universality of the method. It arises from the fact that the molecules absorbing resonantly infrared laser radiation are subjected at the same time to this radiation and visible or ultraviolet light of photon energy sufficient for photodissociation from an excited vibrational state of the ground electronic state but too small for dissociation from the ground vibrational state. On this basis, the photodissociation is best performed by lasers with a suitable wavelength. However, one can also use wide-band light sources and filters for establishing a suitable violet edge to the radiation spectrum. However, in the latter case, the efficiency is lower. If thermal population of the selected vibrational level can be avoided,

$$h\nu_{vib} \gg kT, \tag{9}$$

and if the red edge of the molecular continuous absorption spectrum corresponding to the photodissociation is sufficiently steep,

$$h\nu_{vib} \gg \Delta E_{diss}, \tag{10}$$

this method can utilize the high selectivity of the vibrational excitation to even higher energies.

As in the case of photoionization of atoms, the shortcomings of the method are related to the differences between the resonant absorption and dissociation cross sections, which makes it difficult to utilize fully photons of very different wavelengths. Moreover, the smallness of the infrared photon energy results in difficulties in the spectral filtration of the dissociating light with a sufficiently high degree of contrast.

Nevertheless, this method has been applied successfully in the separation of nitrogen[24] and boron[25] isotopes as a result of CO_2 laser irradiation of NH_3 and BCl_3 molecules, respectively. In both cases, the photodissociation was performed by ultraviolet radiation with a continuous spectrum passed through an absorption filter formed from vibrationally unexcited NH_3 and BCl_3 gases, respectively.

Selective photodissociation of molecules, in which the elementary event produces a large number of identical infrared quanta in resonance with the 0↔1 vibrational transition in a molecule, has attracted considerable interest. In this case, the selectivity of the dissociation is observed when the intensity of the laser radiation is high and the energy is supplied rapidly.

The basis of this method is the nonthermal action of high-power infrared laser radiation on a molecular gas, first reported in[2]. Continuous illumination of a gas whose molecules have a vibrational spectrum in the frequency range of the laser radiation results in an increase of the vibrational temperature above the translational temperature[2] and causes dissociation of the affected molecules. Collisions play an important role in this process and they can result in the loss of the selectivity of the molecular excitation. However, the "instantaneous" dissociation of molecules resulting from pulse resonant excitation of gases in a time short compared with the interval between gaskinetic collisions—which is, consequently, a purely radiative process—was discovered later.[26] This collisional (instantaneous) dissociation is characterized by an intensity threshold (10^8–10^9 W/cm^2) and by a total energy threshold.

The instantaneous dissociation effect has been used in isotopically selective reactions of gas molecules BCl_3 with oxygen[28] and of SF_6 with hydrogen.[29]

The boron isotopes were separated experimentally using a pulse CO_2 laser (energy per pulse 0.5 J, pulse duration 100 nsec). The experiment was carried out on a natural mixture of $B^{10}Cl_3$ and $B^{11}Cl_3$. When air was added to BCl_3, the instantaneous luminescence spectrum exhibited an intense system of bands of the BO radical. When the laser frequency was tuned to the vibrational band ν_3 of the $B^{11}Cl_3$ molecule (938.7 cm^{-1}) or to the absorption band of the $B^{10}Cl_3$ molecule (978.5 cm^{-1}), the instantaneous luminescence spectrum had evidence of the appearance of the $B^{11}O$ or $B^{10}O$ radicals. The experiment was carried out at a pressure of 4 Torr BCl_3 and 20 Torr air in a small cell.

The separation of sulfur isotopes by the interaction of pulse CO_2 laser radiation with SF_6 molecules, characterized by a high enrichment coefficient, was a considerable step forward. The experimental arrangement was similar to that used for BCl_3. The collisionless dissociation of the SF_6 molecule was achieved when the laser radiation intensity was $(1-2) \times 10^6$ W/cm^2 at pressures of 0.1–0.5 Torr. At low pressures, the enrichment coefficient reached 10^3. Irradiation for 1 min (100 pulses with an energy of 2 J) resulted in macroscopic separation of the isotopes with a yield of 10^{-4} g SF_6 with a twelvefold enrichment compared with $S^{34}F_6/S^{32}F_6$.

Clearly, in these two experiments, the irreversibility of the instantaneous dissociation of the SF_6 molecules was due to the uncontrolled reactions of the molecular fragments with the cell walls. The addition of hydrogen did not alter significantly the results obtained.

Significant amounts of enriched BCl_3 (a few milligrams) were obtained[41b] when a chemical reaction was initiated between strongly excited boron trichloride and hydrogen sulfide. The enrichment disappeared when the duration of the laser pulses was increased from 300 nsec to 1 μsec.

The collisionless dissociation effect was also used in the separation of osmium isotopes by interaction of CO_2 laser radiation with the OsO_4 molecule.[41c] Although 10^4 pulses produced only a small enrichment of 15%, this experiment was interesting because heavy molecules with a small isotopic shift were separated.

Clearly, the selectivity of the reactions is due to the collisionless nature of the acquisition of energy by molecules. The dissociation energy is reached selectively if an individual molecule subjected to the field of strong infrared laser radiation absorbs 30–50 photons in a time shorter than the vibrational–vibrational (VV) time and if it accumulates the absorbed energy as the number of absorption events increases. The anharmonicity of the vibrations makes the radiation which is resonant with the first vibrational level, nonresonant with higher vibrational levels. Therefore, without allowance for the VV exchange, the process of acquisition of the vibrational energy in a strong radiation field resonant with the first vibrational level should, apparently, terminate. Thus, the instantaneous dissociation mechanism is obviously a nontrivial effect and its understanding will be extremely important for the future development of this multistep method for isotope separation.

It is known[42] that, because of the dynamic Stark effect, a strong radiation field broadens the energy levels. This makes possible nonresonant absorption in a strong field when the Stark broadening exceeds the shift due to anharmonicity. This mechanism is considered in[43] for the case of chemical activity of laser-excited diatomic molecules. However, the anharmonicity can be overcome throughout the process of accumulation of energy in higher vibrational levels, right up to the dissociation limit of molecules such as BCl_3, SF_6, N_2F_4, etc., by the use of infrared radiation fields several orders of magnitude higher than those found sufficient experimentally and these high fields would correspond to a nonresonant infrared breakdown. Thus, this mechanism cannot account entirely for the instantaneous dissociation of molecules.

On the other hand, one may take into account the processes of fast migration of excitation energy within an individual molecule, similar to those observed in long one-dimensional molecules of organic "superconductors,"[44] in large organic dye molecules,[32] or in large coordination compound complexes.[45] However, these processes are unlikely in the case of the relatively simple molecules of the type considered. Moreover, they

are not of threshold nature.

The multiphoton nature of the processes can explain the threshold nature of the dissociation,[46] but, in the present case, the number of photons involved is so high (30–50) that, for reasonable values of the radiation intensity, the probability of simultaneous participation of this number of photons is low.

It is useful to mention here that the interaction of gas molecules with an external electromagnetic field, whose frequency varies adiabatically with time, may result in the selective excitation of a given high vibrational level of a molecule.[47] When the adiabatic condition is fulfilled and if, during the time needed for field inversion of the populations of two neighboring vibrational levels, the change in the field frequency is much less than the separation between neighboring rotational sublevels and detuning due to anharmonicity, then consecutive complete transitions of a molecule from a lower to the next higher level may take place in field pulses of duration much shorter than the relaxation time. At the end of this process practically all the molecules should be concentrated in a given level N. If the dipole moment of the vibrational transition is 0.3 D, anharmonic and rotational detuning is ~ 5 cm^{-1}, and $N = 10$, the estimates obtained in[47] give $\sim 3 \times 10^5$ W/cm^2 when the frequency varies at a rate of $\sim 1.5 \times 10^8$ cm$^{-1} \cdot$ sec^{-1}. During a pulse of 0.3×10^{-6} sec duration, a combined anharmonicity of ~ 50 cm^{-1} may be compensated. This excitation mechanism is undoubtedly of intrinsic interest but its realization requires construction of lasers in which frequency can be varied rapidly over a wide range.

At present, the most thoroughly investigated is the two-step collisionless (instantaneous) mechanism of the dissociation of gas molecules as a result of resonant interaction with high-power laser pulses.[48] It is assumed that the excitation of the lower vibrational levels is due to allowed transitions and the detuning due to the anharmonicity of the vibrations is compensated by level broadening in the strong laser field (first step). The subsequent excitation of molecules right up to the dissociation limit occurs due to, generally speaking, forbidden transitions in a quasicontinuous sequence of levels (second step). This situation is shown schematically in Fig. 6.

The point is that, in the case of polyatomic molecules, the deviation from resonance in the excitation of higher vibrational levels may be compensated by the greater
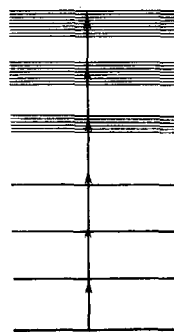
FIG. 6. Schematic representation of two-stage excitation of higher vibrational levels of diatomic molecules.

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complexity of the energy levels. In molecules such as BCl_3, SF_6, etc., the total number of vibrational levels, including combination levels corresponding to the excitation of s vibrational quanta for l vibrational modes, is given by the binomial coefficient C_{s+l+1}^s and is fairly large when the degree of excitation is high. Allowance for the rotational structure reduces, at the rate of excitation corresponding to $(3-4)h\nu$, the average separation between the levels to a value comparable with the homogeneous width of a rotational level so that the levels merge into a single quasicontinuous background. It should then be possible to excite radiatively these levels in steps equal to the energy of the laser photons $h\nu$, which is in resonance with the transition from the ground to the first excited vibrational state. In view of the anharmonicity of the molecules, the next two–three levels are no longer in resonance but it is possible to excite them with sufficiently strong laser radiation because of the field broadening of the levels.

In the first stage of this process involving the excitation of a vibrational level whose energy is equal to the energy of n laser photons, the excitation efficiency is proportional to I_n, the effect should have a threshold, and the threshold excitation intensity of the first two or three vibrational levels should be approximately

$$I \approx \frac{c}{4\pi} \left(\frac{h\Delta\omega}{d} \right)^2, \qquad (11)$$

where $\Delta\omega$ is the detuning due to anharmonicity and d is the dipole moment of the vibrational transition. In the specific case of the BCl_3 molecules, characterized by $d \approx 3 \times 10^{-19}$ cgs esu[49] and $\Delta\omega \approx 3$ cm^{-1}, the threshold intensity is 10^8 W/cm^2, in agreement with the published experimental results. [26,28,50]

In the second stage of the process, the detuning in the quasicontinuous sequence of levels is small and the excitation of increasingly higher levels occurs in a manner similar to that in coherent effects of the photon echo type. [49] The main difference lies in the fast, compared with the relaxation rate, excitation of molecules under the action of radiation. In this case, the important quantity is the threshold of the integral of the pulse envelope and not the intensity threshold

$$\int_{-\infty}^{\infty} \varepsilon(t)\, dt \approx \frac{\hbar}{d_{\text{forb}}}. \qquad (12)$$

where $\varepsilon(t)$ is the envelope of the laser radiation pulse field and d_{forb} is the dipole moment of the generally forbidden transitions between combination levels forming a quasicontinuous sequence. When the intensity is given by Eq. (11), the above condition imposes a minimum of the exciting pulse duration. If $I = 10^8$ W/cm^2 and $d_{\text{forb}} = 10^{-2}$ D, the minimum pulse duration is 10^{-8}–10^{-9} sec, which agrees with the experimentally determined durations of luminescence emitted from dissociated molecules.

This radiative dissociation mechanism has a number of characteristic features. Firstly, the specific nature of the molecular coupling is lost in the excitation of higher vibrational levels: all the levels are "identical" and form one quasicontinuous background. A molecule becomes overexcited and behaves like an atomic nucleus in the drop model. [51] Secondly, the bottleneck now lies in the lower vibrational levels, where the gap between the rotational sublevels is large so that there is still selectivity in respect of molecules of different isotopic compositions. Thirdly, the dissociation may be controlled by varying not only the power but also the duration of the exciting radiation pulses. The dissociation may occur at low pressures when the level broadening needed for the effective achievement of the second stage is ensured not by collisions but by a strong field present because of the first stage. Clearly, the dissociation selectivity is highest at low pressures. At high pressures, the radiative–collisional cascade processes of the excitation of higher vibrational levels may play an important role. An analysis of these processes deserves special attention.

The existence of a quasicontinuous sequence of levels in highly excited polyatomic molecules leads to the conclusion[27] of the possibility of "instantaneous" formation of ions as a result of the action of strong infrared laser radiation on molecules. Clearly, this effect can be utilized in isotope separation.

Above the dissociation limit, there lies a range of electronic–vibrational–rotational (rovibronic) levels characterized by a high density of states. The number of electronic terms in polyatomic molecules such as BCl_3, SF_6, etc. exceeds 100. These terms can be divided into bonding and dissociating. The dissociating terms are very likely to have a structure in which a higher potential well overlaps a lower well, as is found in several diatomic molecules. [38] This gives rise to a quasicontinuous sequence of vibrational–rotational levels right up to the ionization limit. Then, if allowance is made only for bonding terms, radiative excitation becomes possible as a result of resonant transitions in a quasicontinuous sequence of levels similar to that which occurs in a sequence of levels of the ground electronic state. Thus, radiation corresponding to the vibrational quanta of a molecule populates the vibrational levels of excited electronic states. This gives rise to "instantaneous" ionization.

When a molecule reaches one of the dissociating terms (lifetime $\approx 10^{-15}$ sec), it splits up and leaves the radiative excitation channel. This and the nonadiabatic processes involving the bonding terms give rise to unusual products typical of the "instantaneous" dissociation, which can be explained by a strong overexcitation of the molecule, compared with the excitation within the ground electronic state (the analog is again the drop model of the nucleus). The fragments obtained as a result of dissociation of a strongly overexcited molecule ionize readily and both channels then contribute to the "instantaneous" collisionless formation of ions.

Since the process under consideration begins from resonant excitation of the first vibrational level, the selectivity is retained right up to the ionization limit. This can be used in the separation of isotopes by an electric field.
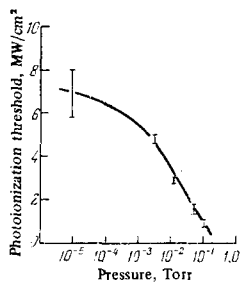
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FIG. 7. Pressure dependence of the photoionization threshold of BCl_3.

The "instantaneous" formation of ions and its analog in the form of "instantaneous" dissociation both have intensity thresholds as well as thresholds of the integral of the pulse envelope. When these thresholds are exceeded, the populations are, on the average, distributed approximately uniformly over all the energy levels which are multiples of $h\nu$. If there is a discontinuity in the quasicontinuous sequence of levels, the crossing of the gap may result in an intensity threshold characteristic of multiphoton processes.

The formation of ions was observed experimentally in a strong infrared laser radiation field applied to a BCl_3 gas under conditions excluding gaskinetic collisions.[52] Use was made of a CO_2 laser ($\lambda = 10.6$ μ, pulse duration 1 μ sec, and energy up to 1.5 J). This phenomenon had a definite threshold of the laser radiation intensity. Figure 7 shows the dependence of this threshold intensity on the pressure. The efficiency of ion formation was considerable. Figure 8 gives the dependence of the total relative density of charged particles in the irradiated gas on the radiation intensity. Preliminary results indicated that the formation of ions was isotopically selective.

At pressures below 10^{-3} Torr, a gas became conducting under conditions which eliminated the influence of collisions during a pulse and during the propagation of the charges obtained, which indicated that the charge formation mechanism was purely radiative. The high relative density of ions indicated that the collisionless resonant infrared photoionization of polyatomic molecules was highly efficient. This process was characterized by a low threshold (≈ 10 MW/cm^2) and it was efficient at intensities (~ 50 MW/cm^2) considerably lower than in the multiphoton photoionization case.

Undoubtedly, the experiment reported in[52] was an important step in the solution of the problems encountered in laser isotope separation. A particularly attractive feature was the possibility of electric removal of the separation products avoiding chemical binding.

The selective multistep interaction methods utilizing the vibrational spectra of molecules are sufficiently promising and interesting. They can be used in the selective interaction not only with one of the fundamental vibrations of a molecule but also with combination vibrations or harmonics (overtones).[26,41c] A shortcoming of these methods is the pulse nature of the interaction and the low quantum efficiency. On the basis of present knowledge, these methods are unlikely to be useful for highly selective laser isotope separation in

the case of molecules whose isotope shift is less than or equal to detuning resulting from anharmonicity.

5. SINGLE-STEP SELECTIVE PROCESSES

The attractiveness of single-step selective processes in laser isotope separation is self-evident. In Sec. 3, we discussed two-step selective photoionization and briefly mentioned the possibility of nonradiative ionization of uranium atoms and of chemical binding of excited atoms. In principle, these are methods of general application but there have been no reports of their realization. Methods based on the pressure of light, scattering of excited particles, and their deflection in electric and magnetic fields are also of single-step nature.

We shall first consider the application of laser chemistry methods in one-step laser isotope separation processes. There is no common approach and one has to seek specific reactions which can be catalyzed sufficiently effectively by laser radiation. Nevertheless, the published information[19,20] gives grounds for continuing the search in this direction.

Mayer et al.[19] used a cw HF laser to separate isotopes in the gaseous phase by a selective chemical reaction whose first stage was selective vibrational excitation of the reacting molecule. The separation process was applied to hydrogen and deuterium atoms produced as a result of interaction of 2.7 μ laser radiation with a mixture of methanol CH_3OH and the deuteromethanol CD_3OD, present in a cell at a pressure of ~ 100 Torr at a temperature of ~ 300 °K. The vibrationally excited methanol reacted with Br_2 vapor and was precipitated from the gaseous phase which was thus enriched with the deuteromethanol. As a result of laser irradiation for 60 sec (90 W power), the CD_3OD content increased from 50% to 95%. Illumination with a source characterized by a continuous spectrum gave rise to nonselective photobromination. Since the energy of the HF laser quanta exceeded the activation energy of the bromination reaction, the excitation of the first vibrational level of the O–H bond in methanol accelerated the reaction strongly.

The reaction kinetics was complex and could not be analyzed clearly. It would seem that a large number of collisions which a vibrationally excited molecule should experience before reacting would have prevented high selectivity of the reaction. The results obtained could possibly be explained by a considerable difference be-
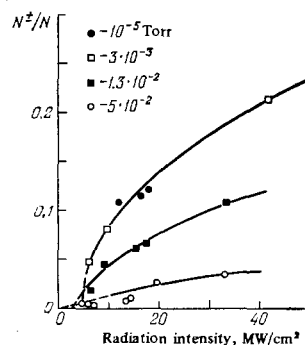

FIG. 8. Relative concentrations of charged particles produced by photoionization of boron trichloride plotted as a function of the intensity of 10.6 μ laser radiation at different gas pressures.
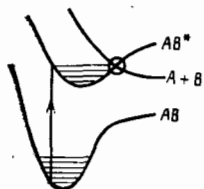
FIG. 9. Schematic representation of the selective photopredissociation method.

tween the chemical properties and vibrational frequencies of the CH_3OH and CD_3OD molecules.

The experiments of Mayer et al.[19] were interesting primarily because they represented the first successful attempt to separate isotopes by laser radiation. The aim of the experiments was also interesting: it was the separation of hydrogen isotopes needed in power reactors (laser generation of heavy water).

However, the selective photopredissociation method,[20] first applied to the separation of hydrogen isotopes, is more promising. This method is also more generally applicable.

In those cases when electronic excitation raises a molecule to a bonding term intersecting a dissociating term, a nonadiabatic transition can take place from one term to the other and this results in what is known as predissociation.[53] The probability of predissociation may be 10^{-7}–10^{-10} sec and it may be greater than the rate of relaxation or transfer of the excitation energy to other molecules. The absorption lines corresponding to weak predissociation are fairly narrow[53] and can ensure isotopic selectivity of the process. As a rule, in the case of polyatomic molecules, one can ensure that the reaction is molecular and not radical predissociation by exciting the lowest possible vibrational level of an excited electronic state.

The advantage of selective photopredissociation is its high quantum efficiency, which approaches unity, and its shortcoming is the need to add other chemical substances for the inhibition of undesirable reactions and for chemical binding of the separation products. The range of applicability of the method is limited by the existence of molecules with suitable spectra. The essence of the method is illustrated in Fig. 9.

The first successful application of selective predissociation[20] was the separation of deuterium from an H_2CO–D_2CO 1:1 mixture kept at a pressure of 3 Torr and subjected to 25 laser pulses of 3472 Å radiation (second harmonic of ruby laser). The duration of each pulse was 15 nsec and the peak power was 8 MW. The spectral width of the radiation employed was 3 cm^{-1}, which accounted for the relatively weak enrichment. The ratio of the concentration of deuterium and hydrogen in the dissociation products was 6:1.

One should also mention another advantage of the predissociation method. In principle, predissociation can be carried out by lasers. The most suitable are tunable frequency-stabilized dye lasers emitting the fundamental or doubled frequency at a high repetition rate.

The method, tested experimentally in the separation of hydrogen isotopes, was applied successfully to for-maldehyde in the separation of carbon isotopes and in the separation of bromine (Br_2 molecule) and chlorine (Cl_2) isotopes. A chemical acceptor had to be selected carefully for each of these molecules. In spite of that, one should regard the method of selective photopredissociation as promising for the attainment of a high mass yield in those cases when suitable spectra are available. The method is promising for the preparation of isotopes of extreme purity and for enrichment with very rare isotopes. Unfortunately, there is only a very small number of molecules which dissociate, on the one hand, sufficiently slowly to have a narrow line in the absorption spectrum and, on the other, sufficiently rapidly to exclude the possibility of the transfer of excitation energy in collisions with unexcited molecules.

In one-step laser action on chemical processes, it is usually very difficult to establish conditions which would eliminate the thermal action of the radiation. The selective photopredissociation method is a successful and promising exception to this rule.

In laser photochemistry, one should seek reactions faster than VV relaxation, resonant transfer of energy in collisions with unexcited molecules of undesired isotopic composition, etc. A direct approach is the use of reactions in intersecting molecular beams when all collisions, except those with molecules of the desired reagent, are excluded. An example is known[52] of the reaction $K + HCl \rightarrow KCl + H$ in which the excitation of the first vibrational level of the HCl molecule by HCl laser radiation increased by a factor of 50 the cross section of the reaction which occurred in intersecting beams.

The shortcomings of methods utilizing atomic or molecular beams, compared with those occurring in gases, are self-evident. Therefore, a particularly interesting case is the dissociation of tetrafluorohydrazine $N_2F_4 \rightarrow 2NF_2$, which is 5–10 times faster compared with the equilibrium thermal dissociation when the vibrational spectrum of this molecule is pumped with CO_2 laser radiation.[55] Since the energy of one CO_2 laser photon is equivalent to the energy input of 2.8 kcal/mole and the activation energy of the reaction is 15 kcal/mole, it is likely that the laser-radiation-induced dissociation includes some mechanism for the accumulation of the vibrational energy. The question of the isotopic selectivity of this reaction has not yet been settled.

On the whole, it is not yet quite clear whether it will be practical to use the laser photochemistry of molecules in one-step isotope separation. Investigations of this possibility should clearly be continued.

Among the physical one-step separation methods, there is considerable interest in selective heterogeneous separation of vibrationally excited molecules[17] by utilizing selective adsorption. The main advantage of this method is that the critical adsorption energy is small compared with the activation energy of homogeneous chemical reactions. This makes the adsorption method highly sensitive to small changes in the excitation energy of molecules and thus the separation of excited molecules can be highly selective. Moreover,

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a distinguishing feature of the method is the possibility of operating in a wide range of gas pressures and the fact that there is no need for subsequent chemical purification.

Since in heterogeneous separation it is sufficient to excite only the first vibration level of a molecule, the excitation conditions become much easier. Firstly, there is no need to overcome the anharmonicity of the molecule and, secondly, isotope separation becomes possible in the presence of gaskinetic collisions and, thirdly, it is possible to operate continuously.

Collisions equalize the relative populations of the vibrational molecules of different isotopic composition when the isotopic shift is small. However, a strong influence of even a small difference between the vibrational energies on the rates of adsorption processes makes the heterogeneous separation highly selective. Clearly, in contrast to the collisionless case, the separation coefficient is lower and the yield is higher. Heterogeneous separation of excited from unexcited molecules can have a high separation coefficient even at high pressures, when the role of the VV resonant exchange processes is weakened by the addition of a thermalizing monatomic gas (gallium).

This method is based on the observation that the rate of adsorption of molecules of a gas in thermodynamic equilibrium on a cooled wall (cryogenic pumping) is given by the sticking coefficient

$$c = 1 - e^{-E_c/E}, \tag{13}$$

where E_c is the critical energy of adsorption which depends on the temperature of the surface and E is the energy of the translational motion of the gas molecules.[56] The results obtained for several polyatomic molecules at different gas temperatures[57] demonstrate that the change in c with the gas temperature can be explained if E is understood to be the total energy of a molecule including its vibrational and rotational components. The question of the dependence of the sticking coefficient c on the degree of vibrational excitation of molecules under nonequilibrium conditions, when the vibrational temperature differs from the translational value, requires special analysis.

It was suggested in[17] that, in the nonequilibrium case, the sticking coefficient c is governed by a formula similar to Eq. (13) in which the value of E_c remains constant and E includes the energy of the vibrational excitation E_V. In subsequent analysis, use was made of the formula for the sticking coefficient of vibrationally excited molecules in the form

$$c^* = 1 - e^{-E_c/(E_V + E_T)}, \tag{14}$$

where E_T is the translational energy of a molecule.

Recent experiments[58] demonstrate the validity of the above assumptions at least for the BCl_3 molecules when the wall temperature is 160 °K. Separation was achieved under conditions of strong VV exchange between the $B^{10}Cl_3$ and $B^{11}Cl_3$ molecules. In this case,

the ratio of the densities of the excited molecules of different composition is equal to the ratio of their partial pressures in the original mixture. Then, heterogeneous separation is due to the difference between the vibrational energies of the excited molecules of different isotopic compositions. In accordance with Eq. (14), the gas mixture is enriched with molecules whose vibrational level lies higher, i.e., with the lighter molecules. The parameters of the separation process are then clearly governed by the magnitude of the isotopic shift.

In the experiments, a BCl_3 gas with a natural isotopic composition flowed through a stainless-steel tube cooled to 160 °K. The tube was illuminated with cw CO_2 laser radiation of 30 W power. At the exit of the 30-cm long tube, the enrichment of boron trichloride with $B^{10}Cl_3$ was characterized by the enrichment coefficient $\eta = 1.57 \pm 0.2$. The amount of enriched BCl_3 accumulated in 2h was 2.2 mg.

In control experiments carried out in the absence of laser illumination, there was no change in the isotopic composition of the gas, which was in agreement with the experimental results,[59] according to which the separation coefficient of boron isotopes in the case of equilibrium evaporation of BCl_3 at $T = 160$ °K was 1.0035.

A theoretical analysis of the operation of this "laser chromatographic column" was carried out by solving the the steady-state transport equation under standard boundary conditions[60] using Eq. (14). Under Poiseuille flow conditions in the case of saturation by a laser radiation field, the concentration of molecules with different values of the vibrational energy decreases exponentially downstream but the rate of decrease varies considerably from one molecule to another. An estimate of the separation coefficient for the reported experimental conditions gives $\eta = 1.65 - 1.45$, in good agreement with the experimental value.

The separation coefficient η can be increased considerably by adding a thermalizing gas such as helium. Although it is easy to separate helium from the enriched mixture, we must bear in mind that a strong dilution with helium requires a considerable increase in the laser power needed to saturate the resonant transition.

These results are of considerable interest. They show that it should be possible to carry out one-step laser separation of isotopes in continuously flowing streams. In this connection, there are very interesting realizations of heterogeneous processes such as chemisorption, dissolution of gases in liquids, diffusion in porous adsorbents, relaxation of gases on aerosols,[61] etc. Heterogeneous selective processes may be applied also to selectively excited atoms. Investigations of the interaction between excited particles and surfaces are of great interest from the physical point of view.

The method of pressure exerted by light,[12,13,62,63] in which the elementary event reduces to the acquisition by an atom (or molecule) of a momentum $h\nu/c$ in the direction of propagation of light after the absorption of a photon, can be regarded as a one-step laser isotope

separation method. In spontaneous emission of light, the direction of the recoil momentum is accidental, whereas in a laser radiation field the repeated absorption and emission of photons imparts a resultant directional motion to resonant atoms. Unfortunately, the deflection of the selected atoms (even through a small angle) out of an atomic beam interacting with laser radiation would require the absorption of a large number of photons which would make this method essentially of multistep type and inefficient from the energy point of view. The use of stimulated radiation of excited atoms passing through a system of mirrors between which a laser pulse with a "swept" emission frequency is traveling[62] may improve somewhat the separation efficiency but will complicate greatly the system. Sweeping of the radiation frequency in this method should be very accurate so that the Doppler effect is avoided for photons in the forward and reverse directions of propagation, which interact with an atom (or molecule) simultaneously.

It is possible that, in practical applications of selective optical pressure, the most convenient laser isotope separation technique will be an optical pump[64] in which use is made of the difference between the rates of diffusion of atoms along a laser beam parallel and antiparallel to the direction of propagation of light.

The optical pressure method was used experimentally in the separation of barium isotopes.[13] The selected atoms were deflected out of an atomic beam by utilizing the absorption of radiation of a tunable dye laser emitting highly monochromatic radiation. The $6s^2 {}^1S_0 \to 6s6p\,{}^1P_1$ resonant transition (wavelength 5535 Å) was selected for this purpose. The lifetime of the excited state, amounting to 8.4×10^{-9} sec, governed the rate of dissipation of the laser energy by a beam of particles when the transition was saturated. Isotope separation was observed both visually and mass-spectroscopically. Tuning to the required resonance peak resulted in a deflection of the beam in the direction of propagation of the laser radiation. The deflected part of the beam reached a suitably located slit of a mass spectrometer. The peak due to the selected isotope was twice as high as all the other peaks.

As mentioned earlier, the smallness of the photon momentum makes the optical pressure method insufficiently effective in the separation of selectively excited particles from a molecular (atomic) beam. In this connection, it is interesting to consider the probability of selection of vibrationally excited molecules in a strong inhomogeneous electrostatic field.[16]

The sorting of molecules in accordance with their inverted energy states in an inhomogeneous electric field was used in the first ammonia beam maser.[65] In this case, the separation mechanism was essentially the quadratic Stark effect.[42] In the case of vibrational spectra of molecules, the quadratic Stark effect does not ensure a sufficient degree of separation for reasonable values of the electric field.

Symmetric molecules such as XY_4 of the T_d symmetry, which do not have a dipole moment in the ground vibrational state, require a permanent dipole moment when the vibrations are excited and this moment is of the same order as the dipole moment of the second-harmonic vibrational transition. Vibrationally excited molecules are then deflected by an inhomogeneous electric field due to the linear Stark effect.

The appearance of a permanent dipole moment in vibrationally excited molecules is due to mechanical and electro-optic anharmonicity of the molecules. The effective permanent dipole moment is[16]

$$d = \frac{1}{2}\left(\mu_{02} + a\mu_{01}\right), \qquad (15)$$

where a is the dimensionless cubic anharmonicity constant; μ_{01} and μ_{02} are the matrix elements of the $0 \to 1$ and $0 \to 2$ vibrational transitions, respectively. The order of magnitude is $a \approx \sqrt{\Delta\omega/\omega}$, where $\Delta\omega$ is the frequency shift due to the mechanical anharmonicity. In the case of XY_4-type molecules, the $0 \to 2$ transition is allowed sufficiently and we can assume that $\mu_{02} \approx 0.1\mu_{02}$. Hence, it follows that, in the case of molecules of this class, the value of d may reach a few tenths of a debye.

In accordance with these estimates, which were confirmed experimentally[66] for CF_3, CCl_4, SiF_4, $SiCCl_4$, $GeCl_4$, TiF_4, $TiCl_4$, and VF_4, the angle of deflection may reach $10°$ for reasonable values of the electric field gradient ($\nabla E \approx 10^4$ cgs esu)[67] acting over a distance of 10–20 cm.

The method of deflection of vibrationally excited molecules in an inhomogeneous electric field is of fairly general validity. It is not related to multiple absorption of laser photons by molecules and its quantum efficiency is fairly high. However, the mass yield of this method is clearly limited by the need to use a well-collimated essentially collisionless molecular beam.

One-step laser isotope separation methods, i.e., processes in which the elementary event involving selective separation of the required isotope is the absorption of one laser photon, are characterized by the highest energy efficiency. Their realization requires a search for interactions with low critical energies. The most promising are selective heterogeneous processes and selective photopredissociation, which have the widest range of applicability and the highest yield.

6. CONCLUSIONS

There is now no doubt that the unique ability of laser radiation to interact only with selected isotopes in a natural mixture rather than with the mixture as a whole, which is true of all the other isotope separation methods, is a very important advantage of laser isotope separation methods. These methods are still in their infancy. The first promising results have been obtained. A major step has been the separation of isotopes of such an important (from the power generation point of view) element as uranium. Laser isotope separation, which is one of the successes of quantum electronics, is becoming a major area laser application comparable in its importance with laser fusion.

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In principle, laser isotope separation can be applied to any element in the Mendeleev table.

We have considered here some of the laser isotope separation methods of the widest applicability. One may expect suggestions and developments of new methods which are particularly effective in the case of a specific element.

Investigations of laser isotope separation are not only of intrinsic interest but of great importance in the scientific sense because they give valuable information on the physical and chemical kinetics of basically nonequilibrium systems and on the wide spectrum of interaction mechanisms of excited atoms and molecules. Laser isotope separation studies will further stimulate quantum electronics by presenting fairly stringent demands in respect of new laser systems. These demands include, particularly, high efficiency, tunability, monochromaticity, stability, and high average output power.

The advantages of laser isotope separation methods are so great and they are now so reliably grounded both theoretically and experimentally aspects that we can expect these methods to play an important role in physics, chemistry, and power engineering in the near future.

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