New methods of isotope separation

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A review is given of methods involving two fundamentally different approaches to the problem of isotope separation. The first approach is based on selective action on definite isotopic modifications of atoms and molecules. These are primarily laser methods of isotope separation: separation by means of light pressure in two-step schemes of excitation of atoms and molecules, and so forth. Special attention in the review is devoted to the second approach to isotope separation, which is based on selective action on the conditions of occurrence of processes in which a difference in the properties of isotopic molecules appears. The possibility is demonstrated of efficient separation of isotopes in processes with participation of nonequilibrium (vibrationally) excited molecules. In this case the isotopic selectivity of the processes is associated with the specific properties of the exchange of vibrational energy between isotopic molecules.

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INTRODUCTION

At the present time investigative programs are being carried out all over the world with the aim of developing more efficient means of isotope separation. In addition to satisfying the growing requirements for isotopically pure materials in scientific research, medicine, the chemical industry, power generation, and so forth, reduction of the energy expenditure required for isotope separation may open new possibilities for use of isotopes of a number of elements in various fields of science and industry in which they are not presently used or are used to a limited extent in view of their high cost.

In the entire set of investigations of isotope separation, two approaches to solution of this problem are evident.

In the first case, means are being developed to act only on definite isotopic modifications of atoms and molecules. We are speaking here principally of selective photoexcitation. Any scheme of isotope separation based on selective photoexcitation in isotopic atoms or molecules must satisfy the following requirements[1, 2]:

1) The radiation must be highly monochromatic, to assure excitation only of definite isotopic modification of the atoms and molecules.

2) Nonoverlapping isotopic lines must be present in the absorption spectra.

3) There must be a physical or chemical process which permits separation of the excited particles from the unexcited particles.

4) The relaxation processes must occur slowly, since these not only lead to loss of excitation, but also (and this is often most important) to transfer of excitation to undesirable isotopic atoms and molecules.

The most promising source of excitation of atoms and molecules which satisfies condition 1) is unquestionably laser radiation. Lasers are finding extensive application in numerous isotope separation schemes: isotope separation by light pressure, selective stimulation of chemical reactions, two-step schemes for excitation of atoms and molecules, and a number of others. At the present time most studies of selective excitation of isotopic atoms and molecules are part of the new field of application of lasers—laser separation of isotopes. [3, 4]

Requirements 2) and 4) impose restrictions on the temperature and pressure of the medium excited by laser radiation, since it is necessary to minimize both the widths of the spectral lines and the rate of exchange of energy between isotopic molecules, which is almost a resonance process. The search for possibilities of reducing these restrictions is a problem of practical importance, since these limitations lead primarily to a reduction of the productivity of the separation process.
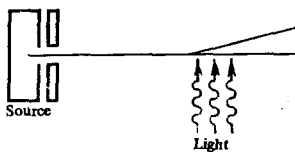
FIG. 1. Deflection of particles from the main beam on resonance absorption of laser radiation. [9]

In regard to requirement 3), it must be noted that the process of separation of excited particles from unexcited ones must itself be isotopically selective. In particular, in the chemical bonding of excited isotopic atoms and molecules the complex mechanism of a reaction can lead to the mixing of isotopes in secondary processes and complete loss of the selectivity achieved in the stage of excitation by laser radiation. (In this case the "isotopic selectivity" of the chemical reaction appears in its being directed toward the natural content of isotopes in the final products.)

In the second approach to the problem of isotope separation, investigations are being made of the conditions of occurrence of processes in which a difference appears in some physical and chemical properties of the isotopes. These investigations include the traditional methods involving various forms of diffusion processes in distillation, electrolysis, evaporation, chemical isotopic exchange reactions, and so forth. The traditional methods are well known (see for example the reviews by Aston and by Peterson and Wheeler[5]) and are not discussed in the present review. We note only that as a rule these methods provide low enrichment per cycle of the separation process, since the physical and chemical properties of the isotopes are extremely similar.

In this review we devote special attention to studies of isotope separation in processes occurring in thermodynamically non-equilibrium conditions, when the supply of vibrational energy substantially exceeds the equilibrium value. These studies evidently also must be grouped with the second approach to the isotope separation problem; however, here this approach is receiving its own development: Selective action on the conditions of occurrence of physical and chemical processes is carried out, which permits a substantial difference to be obtained in the properties of the isotopic modifications of the atoms and molecules. In nonequilibrium excitation of a mixture of isotopic molecules the difference in the properties is brought about by transfer of vibrational energy to molecules containing the heavy isotope in the course of vibrational–vibrational (V-V) relaxation. Thus, the separation of isotopes is produced by energy exchange between isotopic molecules—a process which is most harmful in laser methods of isotope separation.

The requirements on selective excitation are also considerably reduced. Although the possibility of separation of isotopes in nonequilibrium excited molecular mixtures has been noted in study of the kinetics of laser-stimulated chemical reactions, [6] it is possible to use for excitation of the molecules not only laser radiation, but any relatively wide-band source which efficiently excites molecular vibrations.

1. ISOTOPE SEPARATION BY LIGHT PRESSURE

Methods of laser separation of isotopes by means of light pressure are based on the change in the momentum of the atoms or molecules interacting with the radiation. The phenomenon of recoil due to light radiation was observed back in the thirties, [7] but practical use of light pressure for the purpose of isotope separation became possible only with the appearance of lasers.

It is easy to find in the two-level model the average force F acting on an atom in the resonance scattering of light. Let the frequency of laser radiation be equal to the frequency of the atomic transition, and let n_1 and g_1 and n_2 and g_2 be the populations and degeneracy factors of the ground and excited levels. As a consequence of the conservation of momentum in the absorption (or radiation) of a photon of frequency ν, the atom receives (or gives up) a momentum $h\nu/c$; here only absorption and induced radiation lead on the average to a change in momentum of the atom. The average force acting on an atom, due to the last two processes, is limited by the rate of spontaneous decay of the upper level and is numerically equal to the momentum isotropically scattered from the incident light beam per unit time[8]:

$$F = \frac{h\nu}{c} A \frac{n_1}{n_1 + n_2} = \frac{h\nu}{c} \frac{A \cdot x}{1 + [Ax/B_{12}W(\nu)]}, \qquad (1)$$

where $W(\nu)$ is the spectral energy density of the radiation, A and B_{12} are the Einstein coefficients, and $x = [1 + (g_1/g_2)]^{-1}$.

The simplest arrangement, [9] which permits atoms or molecules to be deflected from the main beam by resonance radiation (Fig. 1), has an important disadvantage—as soon as the transverse velocity of the atoms becomes sufficiently large, they no longer absorb radiation (because of the Doppler effect), and therefore the beam can be deflected by this means only by a small angle.

Much greater deflection can be achieved in the light velocity analyzer described by A. Ashkin. [8] He considered a radial cylindrical beam of light (Fig. 2). If the light intensity is sufficiently high, an atom experiences at all points of its trajectory a central force which, on the average, is constant. The trajectory of the atom is a circle, the force acting on it in this case is always perpendicular to the velocity, and there is no Doppler effect. Therefore it is possible to achieve large deflection angles of the atoms from their initial direction and to obtain a spatial separation of a definite isotope. According to Ashkin's estimates[8] in the case of
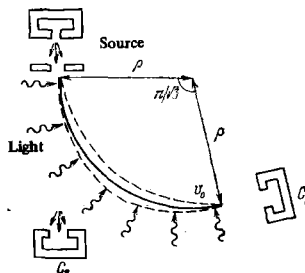

FIG. 2. Arrangement avoiding limitations due to Doppler effect. [8] Collectors: C_1—particles interacting with light, and C_2—particles not interacting with light.
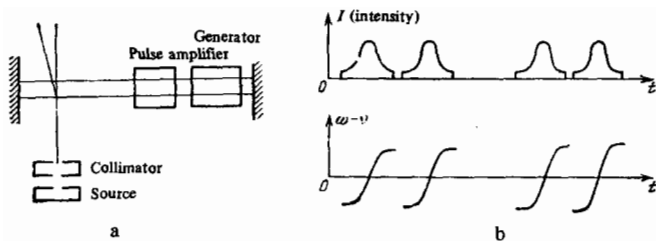
FIG. 3. a) Experimental arrangement for deflection of atoms from a beam on adiabatically fast passage of the light frequency through the frequency of a resonance transition; b) sequence of pulses with which the atoms are "seen" (Ref. 11).

complete scattering of the incident radiation from a beam of sodium atoms moving with a velocity $v_0 \sim 2 \times 10^4$ cm/sec it is possible to obtain ~ 30 mg of the isotope per kilowatt-hour of light energy. Separation of isotopes by light pressure by the simplest method, which is schematically shown in Fig. 1, has been accomplished by Bernhardt et al. [10] A beam of barium atoms with a divergence of 2 μrad was irradiated with a dye laser with wavelength 5535 Å and line width ~ 10 MHz. This permitted selective excitation of a definite Ba isotope, since the isotopic shift was ~ 30 MHz. The presence of the $6s5d\,^1D_2$ metastable state reduces the efficiency of isotope separation, since atoms from the $6s6p\,^1P_1$ excited state drop down with a probability 1/25 not to the ground state, but to the metastable level and no longer absorb the laser radiation. To remove this difficulty, use was made of a second laser tuned to the frequency of the transition $6s5d\,^1D_2 \to 6p5d\,^1P_1$. From the $6p5d\,^1P_1$ state, atoms were transferred with a high probability to the lower level. This scheme permits about 1 mg of the isotope to be obtained per day. [10] Use of this scheme requires good collimation of the atomic beam, so that the initial transverse velocities of the atoms are less than the velocity obtained in the light beam. The latter is limited in principle by the Doppler effect; as we have already pointed out, atoms with a large transverse velocity do not interact with the radiation.

One of the schemes of separation of isotopes by light pressure with use of atomic beams was proposed by Nebenzahl and Szöke. [11] Suppose that a laser emits pulses with a varying frequency which at some moment passes through the atomic transition frequency ν (Fig. 3). If the rate of change of the frequency is sufficiently small, the field is sufficiently large, and the laser pulse is sufficiently short, then an adiabatically fast traversal can be realized. In this case the first light pulse transfers all atoms to the excited state, the atoms receiving a momentum $h\nu/c$. After reflection from a mirror the light pulse returns to atoms to the ground state and again increases their momentum by $h\nu/c$. In this case the average force acting on an atom is no longer limited by the rate of spontaneous scattering and can substantially exceed the value given by Eq. (1). The energy lost by the radiation is equal to the increase in the kinetic energy of the atoms in the direction of deflection (aside from loss to spontaneous radiation and superluminescence), while for transfer to an atom of a momentum ΔP in continuous irradiation an energy $c\Delta P$ is required, i.e., an

energy greater by a factor $\sim c/v$. In addition, in this case the unfavorable effect of metastable levels on the separation process can be reduced substantially.

The same advantages are also possessed by the method of scattering atoms in the strong resonance field of a standing wave. [12] The scattering of electrons in intense light fields has been observed experimentally, [13] and is known as the Kapitza–Dirac effect. The standing electromagnetic wave is a kind of diffraction grating for the electron wave. Kazantsev and his co-workers have shown that scattering of atoms in the field of a standing wave should take place more efficiently than scattering of electrons. Since the force acting on an atom in such a field depends strongly on the frequency detuning $\Delta = \omega - \omega_0$ (ω is the light frequency and ω_0 is the atomic-transition frequency), this effect can be used for separation of isotopes.

Ashkin[14] has proposed a method of isotope separation which may turn out to be efficient for high particle concentrations. Suppose that some volume of gas is illuminated by laser radiation in such a way that it is uniformly filled by it. Then atoms which are resonant to the radiation will be found in the potential field of the force (1), which will lead to a change in their partial pressure along the light beam (the z coordinate). On increasing the pressure of the buffer gas p_b, a more rapid dependence of the partial pressure of the isotope on the z coordinate can be achieved. Here, however, the intensity of radiation required for saturation of absorption[15] increases—first in proportion to the first power of the pressure, as long as the line width of the radiation is less than the Doppler width, and then as p_b^2.

The main advantages of deflection of atoms and molecules by means of light pressure as a method of isotope separation are associated with the physical mechanism of separation of the particles interacting with the radiation. The absence of chemical changes in the system and the homogeneity of the process assure a high purity of the isotope separation methods discussed above. In addition, the simplest schemes are not very different from mass-spectrometric separation of isotopes, both from the point of view of productivity and of cost. Methods which permit an increase in the efficiency of the use of light energy[11, 12] are evidently significantly more promising, although they are substantially more complicated. It should be noted that the field of application of the principles on which most of the methods discussed in the present review are based is not limited to the separation of isotopes. In particular, the resonance deflection of atoms and molecules in the strong field of a standing wave[12] may become the basis of an interesting method of accelerating neutral particles, and also of selection of excited particles for the purpose of producing inverted systems.

2. PHOTOCHEMICAL REACTIONS OF ELECTRONICALLY EXCITED PARTICLES

The first suggestions of the possibility of isotope separation by selective photostimulation of chemical reactions appeared at the beginning of the 1920's. Soon after

the discovery of the isotopes of chlorine the following scheme[16] was proposed for their separation: using a radiation spectrum containing no components absorbed by one of the isotopes (for example, ^{35}Cl), it was proposed to excite the other isotope (^{37}Cl), in this way stimulating an isotopically selective chemical reaction. Experiments on this method gave negative results, but the reason was not that the initial assumptions were invalid, but in the inappropriate choice of a chemical reaction: The reaction chosen was the interaction of chlorine and hydrogen with formation of hydrochloric acid. In the course of this reaction, which occurs by a chain mechanism (which could not be known in 1922) the selectivity achieved in the initiation was completely lost.

Ten years later a similar photochemical method was used successfully for separation of the chlorine isotopes. [17] Filtered light with wavelength 1816.179 Å, corresponding to the intense component in the absorption spectrum of $CO^{35}Cl^{35}Cl$ molecules, preferentially excited this isotopic modification of molecules of phosgene. The excited molecules dissociated in collisions, and the dissociation products turned out to be enriched in the isotope ^{35}Cl.

A similar method was proposed for separation of the mercury isotopes. [18] The source of selective excitation for the mercury isotopes was a mercury lamp whose light passed through a filter consisting of a column with mercury vapor placed in a magnetic field. [19] This filter transmitted only those components of the hyperfine structure of the resonance line which corresponded to the isotopes ^{200}Hg and ^{202}Hg. Stimulation by this light of the mercury oxidation reaction decreased the content of the isotopes ^{200}Hg and ^{202}Hg in the mercury vapor by a factor of four. [20] Photochemical separation of the mercury isotopes was achieved also with use as an initiating source of a monoisotopic mercury lamp (filled with the isotope ^{198}Hg). [21] Selectively excited ^{198}Hg atoms reacted with water vapor and formed mercury oxide enriched 1.5 times in this isotope.

Separation of the carbon and oxygen isotopes has been accomplished by initiating by means of an iodine lamp the formation of the suboxide C_3O_2 from the oxide. [22] Natural iodine is monoisotopic and has a very narrow radiation line at 2062.4 Å. This permits the molecules $^{13}C^{16}O$ and $^{12}C^{18}O$ to be excited preferentially in a mixture of isotopic CO molecules. In particular, the reaction products were enriched 2.68 times in the isotope ^{13}C.

The interest in isotope separation schemes involving photostimulation of chemical processes has risen substantially with the appearance of lasers. The possibility of concentrating large quantities of light energy in narrow spectral regions makes the laser a powerful source for selective stimulation of chemical reactions.

The first attempts at laser separation of isotopes turned out to be unsuccessful. Tiffany and co-workers[23,24] in stimulation of the reaction Br_2 +olefin selectively with respect to the bromine isotopes by the radiation from a ruby laser did not observe any separation of the bromine isotopes. Collisions of the excited bromine

molecules with the molecules of olefin lead preferentially not to a compound, but to dissociation of Br_2. Under the conditions of the experiment the bromine atoms produced a mixing of the isotopes in reactions of the free radicals, apparently mainly in the isotopic exchange reaction $Br^* + Br_2 = Br^*Br + Br$. An additional probable cause of loss of selectively in these experiments is the transfer of energy from selectively excited bromine molecules to unexcited molecules in collisions.

A difference in the excitation of the bromine isotopes was observed in analysis of the vibrational–rotational components of the fluorescence spectrum of Br_2 molecules on bombardment by light at wavelengths of 5145 Å and 5278 Å. [25] The same authors observed selective excitation of different isotopic modifications of Br_2 molecules on selection of different longitudinal types of oscillations of an argon laser at 5145 Å. [26]

Separation of the chlorine isotopes has been accomplished in the laser-stimulated reaction of thiophosgene ($CSCl_2$) with diethoxyethylene. [27] Radiation from an argon laser (4657.84 Å) was absorbed preferentially by $CS^{37}Cl^{37}Cl$ molecules, and laser radiation at 4705.5 Å by $CS^{35}Cl^{35}Cl$ molecules. In the first case the concentration of ^{35}Cl in $CSCl_2$ molecules rose from 75 to 80% as a result of the reaction, and in the second case, it decreased to 64%.

The isotopic filtration method, which has been used successfully to separate the isotopes of chlorine[16,17] and mercury, [20] has been developed with use of laser radiation. [28] A spectrum in which there are no components corresponding to absorption lines of molecules of a definite isotopic composition can be obtained from lasers with an absorbing cell in the resonator. [29] Radiation of such a laser will excite in a gaseous mixture preferentially those molecules which are not present in the resonator. Thus, Ambartsumyan et al. [28] observed a reduction of the degree of excitation of glyoxal molecules ($H_2C_2O_2$) when a cell filled with $H_2C_2O_2$ vapor was placed in the resonator of the laser, the effect increasing with increased vapor pressure of $H_2C_2O_2$.

In all of the studies discussed the selectivity of photoexcitation was based on the existence of an isotopic shift of the frequencies in the absorption spectra of atoms and molecules. Ya. B. Zel'dovich and I. I. Sobel'man considered the fact that, if the nuclear spins of the isotopes are different, selectivity in photoexcitation can be achieved as the result of the difference in the selection rules for radiative transitions. [30] For example, a transition between levels for which the total angular momentum of the electron shell is zero is absolutely forbidden if the nuclear spin is zero. For isotopes with spin different from zero this forbiddenness is weakened as the result of interaction of the electron shell with the nuclear angular momentum. Estimates show, for example, that in the radiative transition $ns^2 \, ^1S_0 - nsnp \, ^3P_0$ efficient separation of the mercury isotopes ^{199}Hg and ^{201}Hg is possible from the even–even isotopes, for which the nuclear spin is zero. It should be noted that in comparison with other separation schemes based on selective excitation of a definite isotope, here the channel of selectivity loss in
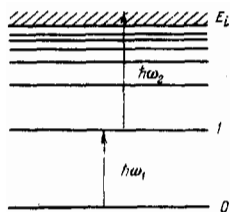
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FIG. 4. Two-step photoionization of atoms: $A \xrightarrow{h\nu_1} A* \xrightarrow{h\nu_2} A^+ + e$.

transfer of excitation between isotopes in resonance collisions is substantially suppressed, since the cross section for this process for multipole interactions is significantly smaller than for dipole–dipole interactions.

In the isotope separation methods which we have discussed in Sec. 2, the principle of selective photoexcitation receives its most direct use. However, the simplest approach turns out to be not the most efficient. In addition to limitations imposed by the fast de-excitation of the electronic states, the competitiveness of these methods is substantially affected by the lack of sources of selective photoexcitation with high energy efficiency in the visible and ultraviolet regions of the spectrum.

3. TWO-STEP EXCITATION OF ATOMS AND MOLECULES

We have considered the simplest case of photochemical separation of isotopes, where the excited molecules of a definite isotopic composition are bound by some acceptor. The choice of a chemical reaction for binding the electronically excited atoms or molecules is difficult in the general case; because of the high probability of spontaneous radiation in the optical region, the particles rapidly lose their excitation energy. Use of metastable levels, as occurred in separation of the mercury isotopes, is not always possible. A possible way out of this situation is the two-step ionization of atoms or dissociation of molecules. [31-33] The particles formed here in a stable state—ions and radicals—are comparatively simple to bind. Separation of isotopes occurs according to the following scheme (Figs. 4 and 5). Laser radiation with a frequency ω_1 excites an electronic level of an atom or a vibrational–rotational (or electronic) level of a molecule. Then auxiliary radiation of frequency ω_2 ionizes (or dissociates) just the excited atoms (or molecules). This assures selectivity of the process. The duration of the laser pulse obviously must be shorter than the time of transfer of excitation between isotopic
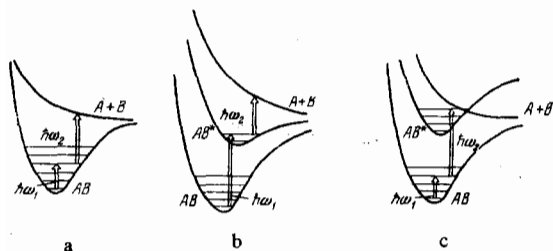

FIG. 5. Two-step photodissociation of molecules: $AB \xrightarrow{h\nu_1} AB* \xrightarrow{h\nu_2} A + B$—in excitation of an intermediate vibrational level (a), an intermediate electronic level (b), and two-step photopredissociation of molecules (c).
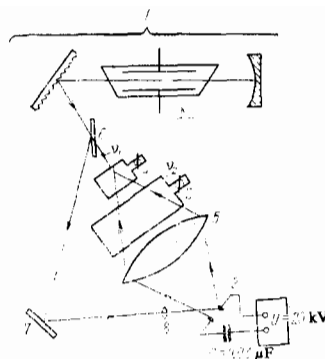

FIG. 6. Experimental arrangement for separation of nitrogen isotopes in two-step photodissociation of ammonia molecules. [37] 1—pulsed CO_2 laser with tunable radiation frequency, 2—source of ultraviolet radiation, 3—absorbing ammonia filter, 4—cuvette with gas studied, 5—lens, 6—plane-parallel plate, 7—rotating mirror, 8—focusing lens.

particles. The probability of spontaneous radiation from an intermediate level does not play a fundamental role—for a sufficiently high intensity of the auxiliary radiation the time spent by the particle in this level is significantly less than the natural lifetime. The two-step photoexcitation method can be used not only for isotope separation, but also for separation of isomeric nuclei [34] and for control of chemical reactions. [35,36]

Laser separation of isotopes by selective two-step dissociation was first accomplished experimentally by Ambartsumyan et al. [37] Their arrangement is shown in Fig. 6. The cuvette was filled with a mixture of $^{14}NH_3$ and $^{15}NH_3$ in equal quantities to a pressure of 20 torr. The source of radiation providing selective excitation of molecular vibrations of $^{15}NH_3$ was a pulsed CO_2 laser with a pulse energy of 60 joules and a duration of 300 nsec. The excited molecules were then dissociated by a spark discharge in air. An ammonia absorber removed from the spark spectrum the region absorbed by unexcited NH_3 molecules. It turned out that the molecular nitrogen, which is one of the final reaction products obtained in dissociation of the radicals NH_2 and H, contained 80% ^{15}N and 20% ^{14}N. The presence of ^{14}N in the dissociation products is explained by the transfer of vibrational excitation from $^{15}NH_3$ to $^{14}NH_3$. [38] On addition of oxygen, which serves as a buffer gas, the amount of energy transferred decreased, and the NH_3 dissociation products contain at least 95% ^{15}N atoms. [38]

Separation of the calcium isotopes by the two-step laser photoionization method is reported by Brinkmann et al. [39,40] The source permitted a substantial flux of atoms in the $4s4p\,^3P_2$ state to be obtained. Radiation from a dye laser ($\lambda = 6162$ Å) of power 2 mW was in resonance with the frequency of the transition $4s4p\,^3P_2 \rightarrow 4s5s\,^3S_1$. For the subsequent photoionization, radiation from a 2.5-W argon laser was used. The ions obtained were extracted from the interaction volume by an electrostatic field. The dependence of the current on the tuning of the laser indicates separation of isotopes in the experiment, but as a consequence of the background current, which did not disappear even when the argon laser was turned off, the separation coefficient could be mea-
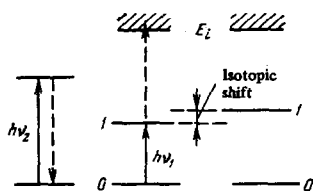
FIG. 7. Diagram of two-step photoionization with use of ioniz-ing collisions. The dashed arrows show the transfer of energy in collisions. Ionization occurs only in previously excited par-ticles.[53,54]

sured only mass-spectrometrically. This was not done in the studies. The dependence of the ion current on the wavelength of the argon laser radiation has a sharp peak near $\lambda = 4880$ Å, which is apparently explained by a reso-nance with the frequency of the transition to the auto-ionized state $5d5p^3P_1$. The yield of ions was up to 10^{-2} of the number of atoms in the $^3P_2$ state.

There is substantial interest in the problem of sepa-rating uranium isotopes by the two-step excitation meth-od.[41–47] As the first step it is proposed to use both ex-citation of vibrations of uranium hexafluoride[41,42] and excitation of electronic states of neutral atoms[42–46] in a beam.[1] So far the progress has been insignificant, and the method is far from suitable for industrial use.[47] (We note that although the development of a cheap method of separating uranium isotopes will have a large econom-ic effect,[47] nevertheless the expenditures on separation of isotopes are only an insignificant fraction of the total cost of nuclear energy.[48]) Application of various laser methods to the separation of light element isotopes is extremely promising. In particular, separation of the boron isotopes is of interest for nuclear technology. A partial enrichment of 14% in the isotopes of this element in the two-step dissociation of BCl_3 has been achieved at the Los Alamos Scientific Laboratory.[46,49]

Following the estimates made by Ambartsumyan *et al.*,[1,50] the efficiency of isotope separation in two-pho-ton selective excitation has been studied theoretically by several authors.[51–55] In the simplest model which per-mits tracing the dynamics of the change in the popula-tions N_i ($i = 1, 2, 3$) of three states coupled by radiation, transitions between these states induced by radiation (W_1 and W_2 are the probabilities of the transitions $1 \to 2$ and $2 \to 3$ per unit time) and the relaxation of the inter-mediate and upper states (relaxation time τ_2 and τ_3, re-spectively) are taken into account. From analysis of this type of kinetic model it follows that the intensity of radiation in the $2 \to 3$ transition must be sufficiently high to avoid reduction of the separation efficiency as the re-sult of saturation of the $1 \to 2$ transition.[51] This re-quirement is extremely important in view of the small-ness of the photoionization and photodissociation cross sections (transition $2 \to 3$). Yung's conclusion[51] that reduction of the separation efficiency as a result of sat-uration of the $1 \to 2$ transition can be avoided by decreas-ing the relaxation time τ_2 of the intermediate level is subject to question. Actually, in this case the number of

[1] Nebenzahl and Levin[44] used three-step photoionization.

molecules which can be raised to the upper state and then chemically bound, decreases. This circumstance is particularly important in the model considered by Yung,[51] in which the molecules which have left level 2 as the result of relaxation are irreversibly lost for the separation process.

Karlov and Prokhorov[52] discuss in detail the question of isotope separation in two-step laser action on an atom-ic or molecular beam. The use of molecular beams in isotope separation schemes permits the selectivity of the laser action to be retained better, since particle colli-sions and consequently energy transfer between isotopes are practically absent. From the result obtained by these workers[52] it follows that for high efficiency of isotope separation (practically all particles of a given isotopic composition are excited to state 3) it is neces-sary that the time of flight through the interaction region $\tau_0 = L/v$ be much greater than some effective time τ_{eff}. In the particular case of saturation of the $1 \to 2$ transition and low intensity of the radiation of frequency ν_2 ($W_1\tau_2 \gg 1 \gg W_2\tau_2$) the effective time is $\tau_{eff} = 2/W_2$. This situa-tion is most realistic for two-step ionization, because of the large difference in the absorption cross sections σ_1 and σ_2. If $\lambda = 0.6$ μ, $\sigma_1 = 10^{-13}$ cm^2, and $\tau_2 = 10^{-6}$ sec, the condition $W_1\tau_2 \gg 1$ corresponds to intensities $I_1 > 2$ W/cm^2. For a velocity of atoms in the beam 10^4 cm/sec, a length of the region of interaction with radiation $L = 10$ cm ($\tau_0 = 10^{-3}$ sec), $\sigma_2 = 10^{-17}$ cm^2, and $h\nu_2 = 6 \times 10^{-19}$ joules, effective separation of isotopes can be achieved with a flux density of the ionizing radiation $I_2 = 10^3$ W/cm^2 ($\tau_{eff} = 10^{-4}$ sec). The great difference in the intensities of radiation at frequencies ν_1 and ν_2 is due to the low ionization cross section, which is apparently the most important limitation of the efficiency of the two-step separation methods.

At the present time two means of increasing the effi-ciency of two-step ionization have been proposed—two-step ionization with use of ionizing collisions[53,54] and selective ionization of atoms by light and an electric field.[55] In the first case one adds to the mixture of isotopes a third gas (optical catalyzer) which resonantly absorbs radiation of frequency ν_2 (Fig. 7) sufficient for ionization of the excited atoms. Selective ionization oc-curs as the result of ionizing collisions due to long-range forces. As estimates by Harris and Lidow[54] have shown, the cross section for ionizing collisions can be three orders of magnitude greater than the photoioniza-tion cross section. This permits a substantial reduction in the intensity of radiation at frequency ν_2 and permits it to be utilized more completely than in the case when there is no optical catalyzer.

Another possibility of increasing the efficiency of two-step ionization lies in excitation of atoms in states close to the ionization limit with their subsequent ionization by an electric field.[55] In the absence of an electric field the levels of the discrete spectrum closest to the ioniza-tion potential fall into the continuum, while the remain-ing levels become auto-ionized. Excitation of molecules to these auto-ionized states can be accomplished effi-ciently by certain lasers of comparatively low power, since the absorption of the light occurs between discrete
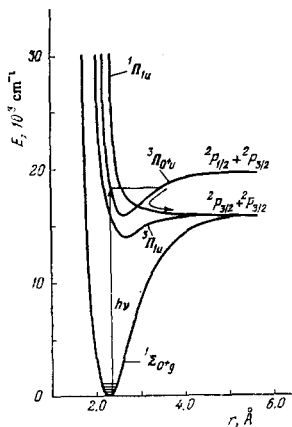
FIG. 8. Approximate potential diagram of Br_2 molecules. [61]

levels (and consequently with a large absorption cross section). In order that practically all excited atoms be ionized, it is necessary that the probability of auto-ionization decay from the upper level exceed the probability of radiative decay. An electric field strength of the order 3×10^4 V/cm is necessary for this purpose.

Two-step excitation methods are currently among the closest to practical application. They are being investigated in many laboratories with application to a wide range of purposes. We have already noted that the main problem in realization of these methods is the matching of the intensities of radiation at frequencies ν_1 and ν_2. A new spurt in the development of studies involving two-step excitation of atoms and molecules apparently can be provided by excimer lasers (see for example Ref. 108). Use of these lasers as a source of ionizing radiation will permit, for example, broader use of auto-ionized states. An important feature of two-step methods of isotope separation is the fact that the rates of excitation in the two stages of the process are determined by the intensity of the radiation. This fact assures the possibility of relatively flexible control of isotope separation processes.

4. SELECTIVE PHOTOPREDISSOCIATION

As we have already mentioned, the chemical binding of electronically excited molecules often turns out to be extremely difficult as a result of the high rate of radiative decay of the electronic terms. To carry out selective photochemical processes in this case it is possible to use, in addition to two-step excitation schemes, the photopredissociation process. [56,57] The essence of this separation method is as follows. If the lifetime of a molecule in an excited state is sufficiently long, greater than 10^{-10} sec, the isotopic structure will appear clearly in the absorption spectrum. On the other hand, if this excited state turns out to be short lived with respect to dissociation, i.e., dissociation occurs in times less than the radiation times (10^{-5}–10^{-8} sec), the dissociation products can be enriched in one isotope or another.

This type of isotope separation was first accomplished by Yeung and Moore[56] in the photopredissociation of formaldehyde. An equimolar mixture of H_2CO and D_2CO at a total pressure of 3 torr was irradiated by light from the second harmonic of a ruby laser at 3472 Å. Photochemical studies[58] indicated a high dissociation quan-

tum yield of the order of one dissociated molecule per absorbed photon. The composition of the dissociation products was $H_2 : HD : D_2 : CO = 0.5 : 0.2 : 3.3 : 3.9$. This result is quite satisfactorily interpreted on the basis of the absorption spectra of formaldehyde at 3472 Å. The absorption coefficients in D_2CO and H_2CO at this wavelength actually differ by about a factor of five, which explains the obtained enrichment of the dissociation products in deuterium. The substantial quantity of HD molecules indicates the relative importance of the radial mechanism of dissociation. Therefore, for separation of the isotopes of the heavier elements carbon and oxygen by this scheme it is necessary to study in detail not only the spectroscopy but also the photochemistry of formaldehyde. [58]

Use of the highly monochromatic radiation of a helium–cadmium laser at 325.03 nm has permitted achievement of a 14-fold enrichment of the formaldehyde dissociation products in deuterium. [59] In these experiments the initial concentration of deuterium in the mixture of formaldehyde isotopic molecules was close to the natural value (0.015%–5%). For separation of the hydrogen isotopes in a mixture $H_2CO : D_2CO = 1 : 1$, incoherent light[60] has been used successfully; however, only a two-fold enrichment was achieved here. The photolysis was carried out with a mercury lamp, radiation from which passed through a cuvette-absorber filled with H_2CO or D_2CO. The dissociation products were enriched in the isotope corresponding to the content of the cuvette-absorber.

Selective photopredissociation of bromine has been accomplished by Leone and Moore. [61] Molecules of Br_2 were excited by light at 558 nm or 532 nm to the state $^3\Pi_{0^+u}$, from which they predissociated or dissociated in collisions (Fig. 8). The dissociated bromine atoms were bound by HI molecules. While the content of the isotopes ^{79}Br and ^{81}Br in natural bromine is identical, the reaction products contained 80–85% $H^{81}Br$. The concentration of HI was chosen such that the bromine atoms reacted with HI faster than the isotopic exchange $Br^* + Br_2 = Br + Br^*Br$ occurred. As we have noted above, the opposite situation occurred in experiments[20,21] where Br_2 molecules were excited by ruby laser radiation to the state $^3\Pi_{1u}$, from which they dissociated in subsequent collisions.

As mentioned above, the selectivity of excitation could be lost as the result of energy transfer from the excited molecules to unexcited molecules in collisions. To weaken this channel of selectivity loss, Letokhov and Lozovik[62] proposed to carry out predissociation of excited molecules by acting on the position of the paramagnetic terms of the molecules with a strong magnetic field. For example, if the stable and unstable terms of the molecule do not cross, the paramagnetic terms are split in the magnetic field, crossing of the components of stable and unstable terms becomes possible, and consequently also predissociation of molecules from the upper vibrational levels of the stable term. According to the estimates of the authors,[62] magnetic predissociation of vibrational levels of the Br_2 molecule into $^3\Pi_{1u}$ states (see Fig. 8) lying below the dissociation limit by 50–1000 cm^{-1} occurs in fields of 150–300 kG as the re-
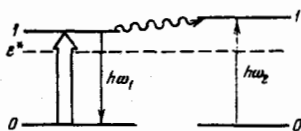
FIG. 9. Separation of isotopes in chemical reactions with low activation energy, stimulated by laser radiation. The straight arrow shows the transition produced by the radiation, and the dashed line is the location of the activation energy. The transfer of excitation between isotopic molecules (wavy arrow) reduces the selectivity of the process.

sult of crossing of the upper branch split from the $^3\Pi_{1u}$ term and the lower branch split from the unstable $^1\Pi_u$ term.

The isotope separation method discussed in Sec. 4 is applicable apparently to a relatively narrow range of objects. This is due both to the relative rarity of molecules with an appropriate spectrum and to the necessity in each specific case of having a laser with sufficiently high energy efficiency. However, the high efficiency in use of radiant energy in selective photopredissociation (practically every absorbed photon is active) is an extremely attractive advantage of this method of isotope separation.

5. EXCITATION OF MOLECULES BY INFRARED RADIATION

In the Introduction we formulated the requirements imposed on isotope separation schemes based on selectivity in action of laser radiation on isotopic molecules. In particular, the difficulties in satisfying requirement 3) in excitation of electronic states—the choice of a process for binding the excited molecules—are responsible for the complexity of the separation schemes in this case (multistep excitation by several lasers, high radiation intensity, use of auxiliary electric and magnetic fields, and so forth). Those few cases where metastable states are used, where the electronically excited molecules could be chemically bound, are the exception rather than the rule.

The infrared region has much greater possibilities for creation of simple laser isotope separation schemes. The large natural lifetimes of molecules in excited vibrational states allow considerable freedom of choice of acceptors for the excited molecules. In principle, in this case for isotope separation it is sufficient to have radiation of comparatively low power at the resonance frequency and to have an acceptor in the gaseous mixture of isotopic molecules.

The simplest scheme of laser isotope separation by infrared radiation is illustrated in Fig. 9. The energy of a vibrational quantum is usually substantially greater than kT at room temperature, and the upper vibrational levels of isotopic molecules unexcited by radiation are practically unpopulated. Thus, only molecule 1, which has absorbed the laser radiation, is bound by the acceptor. Some loss of selectivity may result from transfer of energy to isotopic molecules of another type, not excited by laser radiation, and as a consequence the reac-

tion products will contain, in addition to the isotope 1, also a certain amount of isotope 2. However, if the rate of reaction of the excited molecules is significantly greater than the rate of cross relaxation, the efficiency of isotope separation can be quite high. This situation occurred in the first work on photochemical isotope separation by infrared laser radiation, [63] where the hydrogen isotopes H and D were separated by irradiation with a laser of a mixture of methanol and deuterated methanol with bromine. The radiation from an HF laser (90 W, $\lambda = 2.7\ \mu$) initiated only the reaction of H_3COH with Br_2. After continuous irradiation for 60 seconds of a mixture with a total pressure 39 torr and equal concentrations of H_3COH, D_3COD, and Br_2, the gas which had not reacted contained 95% D and 5% H, and in this way a twenty-fold enrichment of the gas in deuterium was achieved in one cycle.

Another study in which separation of isotopes also occurred in reactions initiated by infrared radiation of vibrationally excited molecules was carried out by Freund and Ritter. [64] Here a mixture of BCl_3 and H_2S was irradiated by radiation from a CO_2 laser tuned to the absorption frequency either of $^{11}BCl_3$ molecules or $^{10}BCl_3$ molecules. An enrichment of 49% of the unreacted gas in the isotope ^{10}B was achieved when the light was absorbed by molecules of the heavy isotope. In the opposite case the ^{10}B content was changed by a smaller amount, from 19.5% to 14.5%. In both experiments the repetition frequency of the laser pulses was 10 Hz, the energy per pulse was 0.1 J, and the pulse duration 300 nsec. The rather low isotope separation coefficient can be explained by the transfer of energy between isotopic molecules and also by thermalization of the energy and subsequent thermal excitation of molecules of the other isotopic composition. This suggestion is favored by the fact that in continuous irradiation no isotope separation was observed, and in addition no isotope separation was observed with operation of the laser with an increased pulse length of 1 msec. It is also possible that the energy of the radiation quantum was insufficient to stimulate the reaction, and the molecules reacted with the high vibrational levels, then dropping down as the result of vibrational–vibrational exchange of energy, thus partially losing the initial selectivity of the laser excitation.

Cases of high activation energy are apparently quite common. A number of experiments on laser stimulation of chemical reactions, not considering the dissociation of molecules by infrared radiation, indicate that an important part of the initiation of laser reactions is excitation of molecules in collisions to an energy comparable with the reaction activation energy. [65] The isotopic effect in the reaction rate in this case is determined mainly by the details of the exchange of vibrational energy between molecules when the "temperature" of molecular vibrations is much greater than the temperature of the medium. [6,66] To produce a substantial difference in these temperatures it is possible to use both laser pumping and other methods of excitation of molecular vibrations, and therefore this question will be considered in the next section, which is devoted to separation of isotopes in chemical reactions occurring in the

absence of thermodynamic equilibrium.

In addition to excitation of high vibrational levels in the exchange of energy between molecules, initiation of chemical reactions and dissociation of molecules by infrared radiation can take place also in collisionless cascade excitation of molecular vibrations in a strong light field. It has been observed[67, 68] that on focusing a high power pulse of radiation from a CO_2 laser in a molecular gas (BCl_3, SiF_4, etc.) the signal from luminescence of radical fragments of the molecules occurs with a delay relative to the laser pulse substantially less than the V-V exchange time. It has also been established that these radicals differ from those formed in dissociation of the same molecules by ultraviolet radiation. The results obtained indicate that in a high-power infrared field molecules in a collisionless process can accumulate a large energy, sufficient to break several bonds. It is natural to suppose that with a well resolved isotopic shift the dissociation must be isotopically selective, with a high degree of selectivity as the result of the collisionless excitation mechanism.

The selective dissociation of molecules by infrared radiation, first obtained experimentally by V. S. Letokhov and his colleagues,[69] is being studied in a number of laboratories at the present time. Considerable attention is being given to these studies not only as an efficient method of isotope separation, but also in connection with the purely scientific interest in understanding the physics of the process. Selective dissociation by infrared radiation of high intensity has made possible achievement of partial separation of the isotopes of boron,[69, 70] sulfur,[31] and osmium.[72]

A ten-fold enrichment of the dissociation products of BCl_3 in the boron isotopes was obtained in irradiation of a mixture of boron trichloride with nitrogen and oxygen by the focused radiation of a CO_2 laser with an energy per pulse of 0.5 J and a pulse duration of 100 nsec. The degree of enrichment of the dissociation products was measured by means of the intensity of the luminescence spectrum of BO radicals formed as a result of reaction of these products with oxygen.

Separation of the sulfur isotopes has been accomplished in the selective dissociation of SF_6 by CO_2 laser radiation[71] (2 J per pulse, pulse duration 90 nsec). The laser beam was focused onto a cuvette containing SF_6 of natural isotopic composition. On tuning the laser to the $^{32}SF_6$ absorption band, these molecules practically completely disappeared.

In regard to the separation of isotopes of heavy elements, at the present time encouraging results have been obtained on separation of osmium isotopes by CO_2 laser radiation.[72] Experiments with different acceptors of the radicals formed in dissociation of OsO_4 gave approximately similar results: 8—15% enrichment of the undissociated gas. The pressure of OsO_4 was varied over the range 0.1–0.24 Torr. The authors[72] explain the low degree of enrichment, in particular, by the low intensity of radiation at the focus of the lens ($\sim 7 \times 10^7$ W/cm²).

Isotopically selective dissociation in SF_6 has been observed in action on weak compound vibrations of the molecule.[73] This result extends the choice of molecules to which one can apply a given method of separation based on existing high power infrared lasers.

The main difficulties in application of molecule dissociation in a strong infrared field for separation of isotopes are apparently associated with the need for high intensity of radiation ($\sim 10^9$ W/cm²). For this reason the process occurs mainly in the region of the focus and encompasses a small volume of gas.

In description of the collisionless dissociation of molecules in the field of intense quasiresonance infrared radiation, the two-stage model of excitation of high vibrational levels is invoked.

In polyatomic molecules the vibrational spectrum is extremely rich and, beginning with some vibrational energy appreciably below the dissociation potential, the level density becomes so high that the levels form almost a continuum of absorption. Molecules which fall into this region are capable of resonance absorption of laser radiation right up to the dissociation limit. The participation in absorption in this region of practically all types of vibrations can explain the effect of collection of a high energy by a molecule, since in each of them it is possible to have a supply of energy of the order of the corresponding dissociation energy.[74]

However, we may ask how it is possible for molecules to fall into the continuum, and how is it possible to overcome the anharmonicity of molecular vibrations in the first vibrational levels? Various models of this process have been proposed. It is assumed, for example, that resonance absorption in the first vibrational levels of molecules is provided by compensation of the anharmonicity as the result of broadening of the levels in a strong field: If the broadening of the transition by the field is of the same order as the maximum shift in these levels as the result of anharmonicity, the molecule will remain in resonance with the field right up to the transition to the continuum (see, for example, Refs. 70, 75–77). As another possible way of compensation of anharmonicity in the first vibrational levels, it is proposed that molecules are excited to the continuum by a sequence of resonance vibrational–rotational transitions.[74,78] Thus, for the molecule SF_6 this sequence is as follows: ($v = 0$, J_{res})→($v = 1$, $J_{res} - 1$)→($v = 2$, $J_{res} - 1$)→($v = 3$, J_{res})→quasi-continuum. For $2BJ_{res} = \Delta\nu_{anh}$ the frequencies of all transitions are identical.

In terms of the proposed models for overcoming the anharmonicity of the first molecular transitions, it is not possible to avoid contradictions with various experimental results. In particular, the threshold intensities of laser radiation necessary for sufficient broadening of the vibrational levels, evaluated by Bloembergen,[76] turned out to be significantly higher than in experiment. It is undoubtedly necessary to carry out still more theoretical and experimental studies of this complex quantum process of the interaction of a multilevel molecular system with a quasiresonance field.

A report[79] has recently appeared on the first obser-

vation of selective dissociation of SF_6 molecules, isolated in low-temperature matrices of argon and carbon dioxide, by CO_2 laser radiation. Studies of the interaction of molecules in the solid phase with high power infrared radiation apparently open broad possibilities for detailed study of the collisionless dissociation process.

High-power infrared radiation can produce not only dissociation, but also selective ionization of polyatomic molecules.[80] In polyatomic molecules the potential well of a higher excited electronic state often lies inside the well of a lower excited state, so that a quasicontinuous sequence of vibrational–rotational levels is formed right up to the ionization limit. It is therefore possible to accomplish by this means the ionization of molecules by infrared radiation, with selectivity in the isotopic composition.

The fact that at the present time the highest energy efficiency is possessed by infrared lasers makes the isotope separation methods discussed in this section some of the most interesting ones from the practical point of view. In this connection it is here that the record degrees of isotopic enrichment in one cycle of the separation process have been observed (enrichment of SF_6 dissociation products in the isotope ^{32}S by more than 10^3 times in comparison with the initial mixture[71]). We again emphasize that dissociation of molecules in a high-power infrared field presents independent scientific interest, independently of its use for isotope separation. In addition, enormous possibilities of detailed study of the physics of this effect are undoubtedly to be found in the course of its invesitgation as a method of isotope separation.

6. ISOTOPIC EFFECT IN CHEMICAL REACTIONS OCCURRING UNDER THERMODYNAMICALLY NONEQUILIBRIUM CONDITIONS

As we have noted previously, in reactions with high activation energy (or the order of several $h\nu$), stimulated by infrared radiation, the isotopic effect is determined not by the selectivity of action of the laser radiation but by the exchange of vibrational energy between isotopic molecules. The role of laser pumping reduces here mainly to vibrational heating of the reagents. It is therefore clear that use of any other means of heating molecular vibrations leaves the general picture of the isotope separation process unchanged.

It is known[61] that the difference in the reaction-rate constants of isotopic molecules

$$\gamma_i = A_i \exp\left(-\frac{\varepsilon^*}{kT}\right),\tag{2}$$

where the subscript i refers to an isotope of a definite type, T is the temperature of the gas, and ε^* is the activation energy of the chemical reaction, is determined by the difference in the pre-exponential factors A_i, since the activation energy does not depend on the isotopic composition of the reagents. Usually the values of A_i are nearly the same, and the isotope separation coefficient

$$\beta = \frac{r}{r'} - 1,\tag{3}$$

where r' and r are the isotopic ratios before and after separation, rarely reaches values of ~0.1.[81]

The above refers to the case of equilibrium distribution of energy among the degrees of freedom of the gas. If the supply of energy in one of the normal vibrations, which is active in the chemical reaction, substantially exceeds the equilibrium value, the difference in the reaction rates can be quite significant. Physically this effect is due to the fact that under these conditions the vibrational degrees of freedom of the isotopic molecules correspond to their temperature T_i, the difference between them being greater, the lesser the translational temperature of the gas.

We shall assume that these conditions are satisfied, i.e., that in some way a significant excess of the vibrational temperatures T_i over the temperature of the translational and rotational degrees of freedom T has been created (for example, by action of resonance laser radiation, by excitation of molecular vibrational in an electric discharge, by fast adiabatic cooling of a previously heated gas). We shall assume also, and this is natural for the high activation energies considered here, that as a consequence of quasiresonance exchange of vibrational energy, equilibrium between the vibrational degrees of freedom of the isotopic molecules is established practically instantaneously (on the time scale of a chemical reaction).

Vibrational energies of molecules in a number of cases can play a decisive role in chemical reactions[82]; having this in mind, we can generalize Eq. (2) for $T_i \gg T$ as follows:

$$\gamma_i = \exp\left(-\frac{\varepsilon^*}{kT_i}\right),\tag{4}$$

where, generally speaking, $T_i \neq T_j$.[2]

It follows from Eq. (4) that even with a small difference between T_i and T_j $(i \neq j)$ the reaction-rate constants may differ rather significantly; their ratio is determined already by the exponential factors.

Let us now consider the kinetics of the relaxation processes in a gas, taking into account in more detail the isotopic composition of the molecules. Establishment of thermodynamic equilibrium in the medium occurs in several stages. The first and most rapid stage is the exchange of vibrational energy between molecules of identical isotopic composition; next is the stage of cross relaxation, which establishes equilibrium between vibrations of different types. These two stages occur mainly before the beginning of the chemical reaction, and we consider them completed. Finally, the vibrational-translational (V-T) exchange of energy leads to thermodynamic equilibrium between all degrees of freedom of

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[2] In the general case the quantity ε^* in Eq. (4) exceeds the activation energy of the reaction measured for an eqiulibrium distribution of energy over all degrees of freedom of the molecules.[83]

the gas. If the molecules enter into the reaction before the beginning of V-T relaxation, a difference exists between the vibrational temperatures T_i and, consequently, between the rates of reaction of the isotopic molecules.

For simplicity we shall consider only two isotopes, to which we assign indices 1 and 2, and in addition we shall neglect vibrational–translational relaxation. In the harmonic model of molecular vibrations the vibrational–vibrational (V-V) relaxation processes establish the Boltzmann distribution of the molecules over the vibrational levels with different vibrational temperatures T_1 and T_2,

$$n_v^{(i)} = n_0^{(i)} \exp\left(-\frac{vh\nu_i}{kT_i}\right), \tag{5}$$

where $n_v^{(i)}$ are the populations of the v-th level of molecules of type i. The flux of molecules of type 1 from level v to level $v-1$, due to V-V exchange with molecules of type 2, can be described as follows:

$$J_v^{(1)} = \sum_k (P_{v,\,v-1;\,1}^{k-1,\,k;\,2} n_v^{(1)} n_{k-1}^{(2)} - P_{v-1,\,v;\,1}^{k,\,k-1;\,2} n_{k-1}^{(1)} n_k^{(2)}), \tag{6}$$

where the probabilities of vibrational exchange are related by the principle of detailed balance,

$$P_{v-1,\,v;\,1}^{k,\,k-1;\,2} = P_{v,\,v-1;\,1}^{k-1,\,k;\,2} \exp\left(-\frac{h\nu_i - h\nu_2}{kT}\right). \tag{7}$$

After establishment of a stationary distribution, all partial fluxes comprising $J_v^{(1)}$ are zero. From this it follows that the relation between the temperatures of molecular vibrations due to V-V processes[84–86] is

$$\frac{\nu_i}{T_1} - \frac{\nu_2}{T_2} = \frac{\nu_i - \nu_2}{T}. \tag{8}$$

With this equation it is not difficult to calculate the ratio of the reaction rate constants of isotopic molecules. Aside from a factor close to unity, we find

$$\frac{\gamma_2}{\gamma_1} = \exp\left[\frac{\nu_i - \nu_2}{\nu_2} \frac{\varepsilon^*}{k}\left(\frac{1}{T} - \frac{1}{T_i}\right)\right]. \tag{9}$$

It follows from this that for a significant excess of the vibrational temperature of the gas over the translational temperature ($T_1 \gg T$) the isotope separation efficiency could be very high. For example, for $T = 100\,°K$, $\varepsilon^* = 2.5$ eV, $(\nu_1 - \nu_2)/\nu_2 = 1/40$ (isotopes with mass number of the order 20) we obtain $\gamma_2/\gamma_1 = 1.5 \times 10^3$. Here the heavier molecules, which have a lower vibrational quantum energy and consequently, according to Eq. (8), a higher vibrational temperature, react more rapidly.

In the developed elementary theory of isotope separation in nonequilibrium chemical reactions[66] we have not taken into account the influence of the reaction process itself on the distribution function, which can be appreciable,[87] and in addition we have neglected the anharmonicity of molecular vibrations, vibrational–translational relaxation, and spontaneous radiation. The first factor has practically no effect on the result presented above.[6] Anharmonicity of molecular vibrations is unimportant at least as long as the minimum of the Treanor

distribution function[84] lies above the activation energy of the reaction, i. e., for comparatively low levels of excitation.[66,88] In the more general case the problem of isotope separation under nonequilibrium conditions has been discussed by Gordiets and Mamedov.[89] It is shown that for a high degree of excitation of molecular vibrations, as the result of anharmonicity and V-T relaxation the isotope separation coefficient can be smaller than follows from Eq. (9). In the limiting case, according to Gordiets and Mamedov,[89] the coefficient is practically independent of the temperature of the medium and is determined by the temperature of the first vibrational level. If this is the case, there should evidently exist optimal conditions for isotope separation—a strong buildup of molecular vibrations increases the yield of reaction products, but at the same time the degree of enrichment in a given isotope drops. At the present time this question has not yet been well studied. We can only, following Ref. 89, estimate the limit below which the decrease in initial gas temperature for a given vibrational temperature is ineffective.

According to Eq. (9) for the condition $T_i \gg T$ the isotope separation coefficient does not depend on the degree of excitation of vibrational levels; the value of the vibrational temperature T_i determines only the rate of the process. If the separation process is considered in more detail, a high degree of vibrational excitation will unnecessarily reduce the separation coefficient. In fact, since the ratio of the reaction rates of different isotopic molecules, and consequently also the isotope separation coefficient, depend exponentially on the translational temperature T, comparatively small changes in T will substantially affect the degree of isotope separation. Since the temperature T can change appreciably during a reaction, the reaction is characterized by some average separation coefficient, smaller than its initial value. The change in the temperature T is due to vibrational–translational relaxation processes and the thermal effect of the reaction itself, and the rates of these processes increase with increasing vibrational temperature.

The separation coefficient characterizing the process as a whole, with allowance for the change in temperature T and reaction rate with time, has been calculated by Belenov et al.[90] The problem was solved for pulsed pumping and a harmonic model of the vibrational motion of the molecules; it was assumed also that the molecules contain mainly isotope 1 and a small admixture of isotope 2. After the pumping pulse the change in the vibrational and translational temperatures was described by the system of equations

$$k\frac{dT_i}{dt} = -(\varepsilon^* - kT_i)\gamma_i - \frac{kT_i}{\tau_{VT}},$$
$$\varkappa k\frac{dT}{dt} = \varepsilon_0 \gamma_i + \frac{kT_i}{\tau_{VT}}, \tag{10}$$

where the first terms in the right-hand sides correspond to the change in temperature as the result of the reaction (ε^* is the activation energy, ε_0 is the energy released in a single reaction event, $\gamma_1 = -(1/N_1)dN_1/dt$ is the reaction-rate constant for molecules of type 1, and
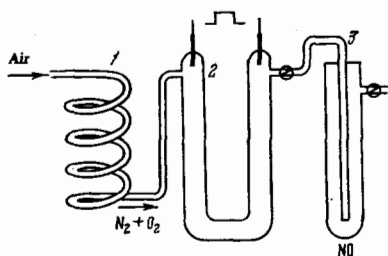
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FIG. 10. Diagram of experimental apparatus of Ref. 91. 1, 3—nitrogen traps, 2—reactor.

$\varkappa$ is the heat capacity per molecule of the rotational and translational degrees of freedom of the gas), and the second terms correspond to vibrational–translational relaxation. Taking into account the change in the isotope separation coefficient during the reaction permits better agreement to be obtained with the experimental results[66,68,91,92] and also makes possible estimation of the role of a number of parameters in the separation process: For high vibrational temperatures of the molecules the separation coefficient decreases; the exothermal nature of the reaction at high reaction rates has little effect on the separation coefficient but appreciably decreases the reaction yield; at low values of the translational temperatures the separation coefficient may be increased by the effect of increasing heat capacity as the result of addition of a buffer gas.

In the first experiments on separation of isotopes in chemical reactions occurring with selective excitation of molecular vibrations, electrical discharges were used as pumps.[88] As is well known,[93] for a definite relation between electric field strength and gas pressure for a number of molecules the vibrational degrees of freedom are mainly heated in the discharge; the vibration heating process is particularly efficient in such molecules as H_2 and N_2.[93] The discharge was excited in a quartz cuvette cooled with liquid nitrogen and filled with air at a pressure ~20 torr. Separation of the nitrogen isotopes occurred in the oxidation reaction

$$N_2 + O \rightarrow NO + N,$$
$$O_2 + N \rightarrow NO + O. \qquad (11)$$

The first of these reactions requires an activation energy of at least 3.3 eV, and the second occurs practically without activation.[82] Since the frequency of vibrations in the molecule $^{15}N^{14}N$ is lower than in $^{14}N^{14}N$, according to Eq. (9) we can expect an enrichment of the reaction products in the heavier isotope of nitrogen. The reaction was stimulated by a series of pulses of duration 5 $\times 10^{-6}$ sec with a period of 15 sec. A mass-spectrometric analysis of the gas showed that approximately twentyfold enrichment of NO in the isotope ^{15}N was achieved.

Refinement of the experimental technique permitted a substantial increase in the efficiency for separation of nitrogen isotopes in the reaction $N_2 + O_2 = 2NO$ stimulated by a discharge.[91] In Fig. 10 we have shown a diagram of the experimental apparatus. Air at a pressure of ~5 Torr enters a nitrogen trap 1 in which impurities are

frozen out (water, CO_2, and so forth). Then it enters a reactor 2 which is immersed in a cooling agent. The reactor consists of a U-shaped tube of diameter 20 mm and length 600 mm in which a series of discharge pulses are excited (pulse duration several microseconds, repetition frequency 0.5–0.3 Hz, energy 4 J). At the exit from the reactor is placed a trap 3 in which the reaction products are frozen out. Analysis of the composition of the mixture is carried out in a mass spectrometer.

On cooling the reactor with liquid nitrogen a 130-fold enrichment of NO in the isotope ^{15}N was obtained—6.5 times higher than in the first experiments. Experiments at dry ice temperature and room temperature were also carried out. The isotope separation coefficient at these temperatures was respectively 20 and 3. The mass spectra of the mixture after the reaction, with the reactor walls cooled to various temperatures, are shown in Fig. 11. The rapid dependence of the separation coefficient on temperature is in qualitative agreement with the theory (see Eq. (9)).

Separation of the nitrogen isotopes in a nonequilibrium chemical reaction has been obtained also with laser pumping of molecular vibrations.[66,92] Since the excitation of molecules which have no dipole moment by infrared radiation is impossible, the "hot" molecules of nitrogen were obtained in simultaneous action on the mixture $N_2 + O_2$ of the radiation of a ruby laser and a strong Stokes component obtained beforehand by stimulated Raman scattering in liquid nitrogen or gaseous nitrogen at high pressure (60–100 atm).[94] Approximately 100-fold enrichment of the reaction products in ^{15}N was obtained on cooling a cuvette with air (200–500 Torr) by liquid nitrogen.

As we have already mentioned, the means of excitation of molecular vibrations is not important for the separation of isotopes in chemical reactions with a large activation energy; it is sufficient that the temperature of the vibrational degrees of freedom be significantly above the translational temperature. The required temperature difference can be produced not only by excitation in some manner of molecular vibrations, but also
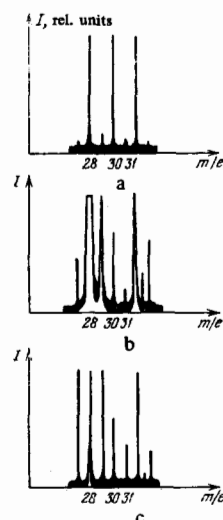

FIG. 11. Mass spectra of a mixture after reaction on cooling the reactor walls to the following temperatures: (a) room temperature; (b) dry ice temperature; (c) liquid nitrogen temperature. The intensities of the peaks $m/e = 30$ and $m/e = 31$ are proportional to the concentrations of ^{14}NO and ^{15}NO. The natural ratio of the concentration of the nitrogen isotopes is $^{14}N/^{15}N \approx 250$.[91]

by cooling the translational and rotational degrees of freedom of a previously heated gas. Naturally, here the rate of cooling must exceed the rate of relaxation. In particular, for fast cooling, flow of the gas through a nozzle can be utilized.[95] The main advantage of this scheme of isotope separation is the possibility of cooling the gas to a temperature significantly lower than the liquefication temperature and, consequently, substantially increasing the isotope separation coefficient.

On expansion of the hot gas through the nozzle, two isotope separation schemes can be realized.[95]

1) A gas of isotopic molecules heated to a high temperature passes through the nozzle. Its translational temperature drops sharply, while the vibrational temperature changes insignificantly. If we now add to the gas a cold reagent which binds the "hot particles," molecules containing the heavier isotope will enter into the chemical reaction with a higher rate.

2) The reaction mixture is prepared before the flow through the nozzle. Suppose that separation of the isotopes of element A occurs in a reaction of the type

$$A_iC + BD \rightleftarrows A_iB + CD \qquad (i = 1, 2). \qquad (12)$$
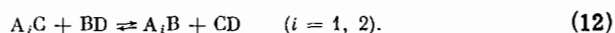
The stationary concentrations of the molecules of the reagents and reaction products are determined from the relation

$$k_{1i}[A_iC][BD] = k_{2i}[A_iB][CD], \qquad (13)$$

where k_{1i} and k_{2i} are the rate constants of the forward and reverse reactions. If the vibrational temperature of the reagent molecules changes sufficiently slowly with time, a quasistationary state can be achieved in which Eq. (13) is satisfied at each moment of time. Suppose that the molecular vibration energy of AC is responsible for the forward reaction. If the activation energy ε_2^* of the reverse reaction is significantly less than the activation energy ε_1^* of the forward reaction, or the rate of vibrational–translational relaxation for molecules AB and CD is significantly greater than for AC, then for a separation of the vibrational temperature of the molecules AC from the translational temperature and for constants k_{1i} and k_{2i} the following relation is satisfied:

$$\frac{k_{11}}{k_{12}} = \exp\left(\frac{\Delta v}{v}\frac{\varepsilon^*}{kT}\right), \quad k_{21} \approx k_{22}, \qquad (14)$$

where $\Delta\nu/\nu$ is the relative shift of the vibrational frequencies of AC molecules. From this it follows that the reaction products—the molecules AB—will be enriched in the heavy isotope of the element A.

The separation of nitrogen isotopes on cooling of the reagents in an ultrasonic flux has been obtained experimentally in explosion of the mixture $H_2 : O_2 : N_2(N_2O)$ $(0.1 : 0.15 : 0.4$ atm); the gas temperature reached $2500-3000\,^\circ K$. Then the gas mixture was expanded through a nozzle into a low pressure chamber, so that its translational temperature was reduced to $300-350\,^\circ K$. The reaction products—NO molecules—were frozen out in a nitrogen trap. The concentration ratio of ^{14}NO and

^{15}NO of the order 100 indicates a more than two-fold enrichment of NO in the isotope ^{15}N in comparison with its natural content.

In this section we have discussed the separation of isotopes in chemical reactions with a quasistationary distribution of the molecules in their vibrational levels. In the initial period of the reaction the quasistationary distribution is not yet formed; in particular, this refers to the initial period of laser reactions. Here the distribution of the molecules over the vibrational levels is determined to a significant degree by the spectral composition and intensity of the laser radiation, and Eq. (9) for the ratio of the reaction rate constants is no longer valid. This question has been investigated in detail by Kudrin and Mikhaĭlova.[96] In particular, it has been shown that for small durations of the radiation pulse (of the order of the exchange time of vibrational energy in collisions) one can hope for an appreciable isotopic effect. This is quite natural from a physical point of view, since the excitation of the component which does not absorb the laser radiation is still insignificant. We note that the case of low concentrations of the excited component in the quasistationary regime, discussed in Ref. 96, is not of practical interest, since in this case the isotopic effect is determined mainly by the exchange of vibrational energy, while from the point of view of achieving higher vibrational temperatures it is necessary to excite the most abundant isotope. The disadvantages of the nonstationary separation of isotopes include the short duration of the separation process and, consequently, the low yield of the reaction products.

In conclusion of this section we would like to dwell on one interesting consequence of Eq. (8), which describes the jump in vibrational temperatures in the V-V exchange process.[97] The jump in temperatures is due to the pumping of vibrational energy from the lighter molecules to the heavier ones. It is evident that for a given supply of vibrational energy in the molecules the "temperature" of the heavier isotope will be higher if its relative concentration in the isotopic mixture is lower. If the temperature is low, the heavy molecules can enter into the reaction, even in the case when the supply of vibrational energy is insufficient for occurrence of the reaction under equilibrium conditions. This approach to the problem of isotope separation appears to us very promising for elements at the beginning of the periodic table. Actually, in compounds of these elements the natural content of the heavy isotope is extremely small, and the difference in the vibrational quanta is rather significant, so that a comparatively modest cooling of the gas is already sufficient for efficient separation of the isotopes.

Chemical separation of isotopes in a system of vibrationally excited molecules has been observed so far only in the reaction $N_2 + O_2 = 2NO$. In use of this separation method for the nitrogen isotopes, it appears most promising to us to carry out the process in a cooled gas discharge, since electron impact is one of the simplest and most efficient sources of vibrational excitation of nitrogen molecules. For molecules of other elements of the periodic table this means of excitation may turn out to be unsuitable; however, since the only fundamental require-
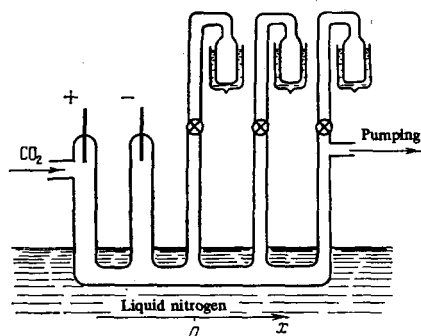
FIG. 12. Diagram of experiment to freeze out vibrationally excited molecules.[98]

ment is to produce a separation of the vibrational temperature of the molecule from the translational temperature, it will evidently be easy to choose an appropriate excitation scheme for a number of reagents.

7. CONDENSATION OF A GAS OF VIBRATIONALLY EXCITED MOLECULES, AND OTHER HETEROGENEOUS METHODS OF ISOTOPE SEPARATION

As we have noted above, one of the requirements imposed on isotope separation schemes based on selectivity in excitation of isotopic modifications of molecules is the existence of a physical or chemical process separating the excited and unexcited molecules. Up to this time, as a rule, we have discussed chemical binding of excited or dissociated particles. However, in a number of cases the selectivity achieved in excitation can be lost in the course of a stimulated chemical reaction. The mixing of isotopes is particularly important in the case of reactions occurring with participation of free atoms and radicals. This fact is one of the causes of the search for other processes for binding selectively excited atoms and molecules.

One of these processes is the condensation of an excited gas. The dependence of the condensation rate on the degree of vibrational excitation of molecules was pointed out by us in another article[66]; it is natural to expect that unexcited molecules should be frozen out first. In particular, in a vibrationally excited gas at low translational temperatures the first molecules to freeze out should be the light isotopes, which have a lower vibrational temperature. Our experiments[98] qualitatively confirm the expected dependence of condensation rate on vibrational temperature of a gas. The diagram of the apparatus is shown in Fig. 12. Carbon dioxide gas at a pressure of ~1 torr was pumped through a cuvette placed in liquid nitrogen with a velocity of $(2-3) \times 10^3$ cm/sec. In the first section of the cuvette a glow discharge was maintained. Vibrationally excited CO_2 molecules produced in the discharge were frozen out in the second, third, and fourth sections. As can be seen from Fig. 13, in correspondence with the slower freezing of the heavy molecules $^{13}CO_2$ their relative concentration increases along the cuvette. For CO molecules, which are formed in the discharge as a result of the reaction $2CO_2 = 2CO + O_2$, an increase in the relative content of the isotope ^{13}C is also observed with increasing

distance from the discharge. The difference in the ratios $^{12}CO/^{13}CO$ and $^{12}CO_2/^{13}CO_2$ at $x = 0$ can be explained by the isotopic effect of the CO-formation reaction itself.

The physical absorption process is essentially similar. In this case we should expect qualitatively the same result—the relative concentration of heavier isotopic molecules should increase on passage of a vibrationally excited gas along the adsorbent.[98] Use of an adsorption process for separation of selectively excited molecules was proposed by A. M. Prokhorov and his colleagues.[99,100] Konyukhov and Faizulaev[101] proposed use of an aerosol as adsorbent for a particle beam to increase the efficiency in separation of excited and unexcited molecules. Experiments[98,100] have revealed some features of the kinetics of condensation and adsorption for vibrationally excited molecules. The separation coefficients achieved here are small and the interpretation of the results obtained has apparently not been adequately proved. However, regardless of the promise of using these and other heterogeneous processes for isotope separation, the study of nonequilibrium systems of this type presents undoubted interest.

Karlova et al.[102] observed a displacement of the chemical equilibrium in the resonance action of CO_2-laser radiation on the separation boundary of organic and water solutions of uranyl nitrate. No selectivity in the isotopic composition of the uranium compounds was achieved, but the nonthermal mechanism of the effect of laser radiation on chemical equilibrium permits us to suppose that this is possible.

A report appeared recently on the selective evaporation of a frozen gas by laser radiation.[103] It was observed that in a thin film (100–500 molecular layers) of molecules of boron trichloride frozen at liquid nitrogen temperature the ν_3 bands of the $^{10}BCl_3$ and $^{11}BCl_3$ molecules were shifted by practically identical amounts (about 20 cm^{-1}) toward the low-frequency region in comparison with gaseous BCl_3, although with some broadening. The preservation of the isotopic structure of the spectrum on freezing permitted a resonance action on $^{10}BCl_3$ or $^{11}BCl_3$ molecules, resulting in their preferential evaporation.

At the present time it is difficult to discuss the promise of use of heterogeneous methods of isotope separation. We have shown only the basic possibility of separation by these methods, and the positive results obtained in individual studies, generally speaking, cannot serve as the basis for concluding that such schemes are applicable to a wide range of purposes. In particular,
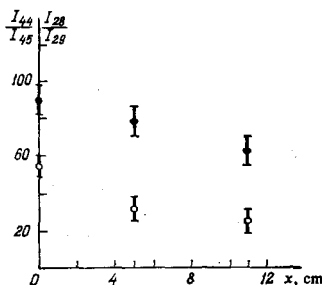

FIG. 13. Dependence of isotopic ratio in frozen-out-molecules on the length of the freezing zone. Solid circles— $^{12}CO_2/^{13}CO_2$, hollow circles— $^{12}CO/^{13}CO$.[98]

the possibility of isotope separation in selectively occurring condensation and adsorption processes is determined by the mechanism of vibrational deactivation of the molecules on the surface of the solid phase, and this method depends substantially both on the type of molecular gas and on the state of the surface of the condensate or adsorbent.[107] In Refs. 98 and 100 the interpretation of the experimental results was carried out on the basis of a model in which the entire vibrational excitation energy of the molecules in the surface layer of the condensate (adsorbent) is transferred to energy of translational motion of the particles. Apparently this situation is nowhere near always realized.[107] (In addition, the data on these experiments indicate that in the study of the heterogeneous relaxation of vibrational energy of molecules the isotopic composition of the gas may have an appreciable effect on the results obtained.)

Brauman et al.[104] and Alimpiev et al.[105] discuss two additional processes which can be used to separate selectively excited molecules. Shawlow and others[104] have proposed, for the purpose of retaining the selectivity achieved in the excitation, to use for separation of the excited molecules the process of monomolecular photoisomerization, for example, cis-trans isomerization. The monomolecular nature of the process permits remixing of the isotopes to be avoided in the transformations. Alimpiev et al.[105] consider a method of selection of vibrationally excited molecules symmetric in the ground state by deflection of a beam of molecules in a nonuniform electric field. The authors showed that symmetric molecules which do not have a dipole moment in the ground state acquire it in a strong electrostatic field on excitation of degenerate vibrations.

In conclusion we note the work of Namiot,[106] who has suggested a method of separation of isomers and isotopes for materials consisting of paramagnetic atoms. The separation mechanism consists of separation in a nonuniform magnetic field of a beam of atoms with a given electron-spin direction and subsequent resonance change of the spin direction only in atoms with isomeric nuclei (or only in definite isotopes). These atoms can be separated by again passing the beam through a nonuniform magnetic field.

CONCLUSION

The development of new methods of isotope separation, to which this review has been devoted, is just beginning to go beyond the framework of purely scientific studies, but already the first experiments have demonstrated a separation efficiency which is orders of magnitude greater than that of traditional methods. The characteristic feature of the new methods of isotope separation, which provides high enrichment coefficients, is the use in them of sources of selective action on isotopic modifications of atoms and molecules, including isotope separation in processes occurring in thermodynamically nonequilibrium conditions (Sec. 6). Actually the vibrational excitation of molecules plus V-V exchange provide a source of selective action on heavy isotopic molecules. The assignment of the methods considered to the two approaches to the problem is to a significant degree arbitrary.

It should be noted that in any isotope separation scheme in selection of the conditions for carrying out the process one necessarily encounters a contradiction between the requirements of high productivity and high separation coefficients. Thus, to increase the productivity of laser methods of isotope separation it is necessary to increase the gas pressure, but here the spectral lines are broadened and the transfer of excitation to undesirable molecules in collisions is accelerated. The separation coefficient for isotopes in reactions of vibrationally excited molecules increases exponentially with increase of the activation energy (see Eq. (9)), but the absolute reaction rate falls exponentially. Therefore, depending on the requirements on the isotopically enriched final products, the optimal conditions for carrying out a separation process also change.

The possibility of action by laser radiation not on the entire isotopic mixture, but only on definite isotopic modifications of the atoms and molecules, permits in principle use of each laser photon for the separation. The use of light energy with such high efficiency requires high monochromaticity, stability, and smooth tuning over a wide range of frequency of the laser radiation. The powers, energy efficiencies, and cost of existing laser installations do not yet permit isotope separation methods with selective photoexcitation of atoms and molecules to compete with traditional methods over the entire visible and infrared range of wavelengths. However, the advantages of laser separation of isotopes are so great that this area of quantum electronics cannot fail to have a stimulating effect on the further development of laser technology.

In contrast to laser methods, selectivity in participation of different isotopic modifications of molecules in processes occurring in thermodynamically nonequilibrium conditions is determined not by selectivity in the excitation, but by the nature of the interaction of the molecules. The modest requirements on the source of vibrational excitation and the high efficiency of separation make these methods promising for a relatively wide class of molecules, particularly for compounds of the light elements, where the resonance vibration defect $\Delta\nu/\nu$ is greatest. In the transition to heavier elements of the periodic table the efficiency of the method, like selective laser-excitation methods, drops. Nevertheless, the diversity of isotope separation methods proposed and developed and the undoubted progress in this direction is a guarantee of an increase in the efficiency of the separation process for practically all elements of the periodic table.

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