

Selective processes induced by resonance laser radiation at the phase boundary of two media

N. V. Karlov and A. M. Prokhorov

P. N. Lebedev Institute of Physics of the Academy of Sciences of the USSR
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A review is presented of the selective heterogeneous processes that occur on the interface of two media when exposed to laser radiation. These processes can be used for selective chemical reactions and for laser separation of isotopes. Their main attraction is the relatively low activation energy, so that IR laser radiation can be used to act effectively on the surface properties. The review deals with: separation of molecules having different isotopic composition involving adsorption, selective laser-stimulated diffusion, resonant control of surface processes by laser radiation, laser chemistry on the interface of two phases or of two liquids. Experimental results are reported and interpreted.

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1. INTRODUCTION

Among the broad set of phenomena caused by interaction of intense laser radiation with matter, ever more attention is currently being drawn to processes that occur selectively when the laser effect is at a resonance. Resonance interactions of intense laser radiation with matter are of special interest precisely because many photochemical and photophysical processes can proceed selectively at a high spectral density of sufficiently monochromatic laser radiation. Evidently, all of this in turn opens up the possibility of using laser methods for separating isotopes in photochemistry, for preparing superpure materials, and for controlling biophysical and biochemical processes, etc.

Laser methods of separating isotopes are currently being developed actively. Reviews^[1,2] have recently been published on them. The selective photochemical action of laser radiation is also of great interest. Laser initiation and laser control of chemical reactions are extremely important, both on the purely scientific and on the applied level. Since the time of publication of the pioneer studies,^[3,4] much experimental material has accumulated, and a series of reviews has been published.^[5-10] We expediently note that in a number of cases, though far from always, laser separation of isotopes can stem from a selective course of laser photochemical processes.

Moreover, the overwhelming majority of studies of resonance interaction of laser radiation with matter have currently been conducted on homogeneous, mainly

gaseous, media. We must say that the possible achievement of purely homogeneous feed of energy is very important in studying processes of physical and chemical kinetics. Yet difficulties arise for molecular systems that are being excited vibrationally by infrared laser radiation. They involve the fact that the activation energies of various homogeneous chemical reactions generally exceed substantially the energy of the resonance laser quantum, while the anharmonicity of the molecular vibrations impedes the resonance excitation of molecules to high energy (see, e.g., the reviews^[1,7]).

On the other hand, many heterogeneous processes, i.e., processes that run under essentially heterophase conditions, are characterized by a critical energy that is small in comparison with the activation energy of homogeneous chemical reactions. This leads to the high sensitivity of processes that occur at a phase boundary of two media to small changes in the excitation energy of the molecules that participate in the process. The absorption of one infrared quantum by a molecule substantially alters its behavior. Hence the problem is obviated of overcoming the anharmonicity of the molecule, and it becomes possible to operate in a continuous regime at relatively low levels of laser-radiation power. A continuous flux of molecules being irradiated is easily achieved, and a number of restrictions on the type of molecules is eliminated.

In studying selective processes at a phase boundary of two media induced by resonance laser radiation, different realizations of heterogeneous processes are of great interest, such as physical adsorption, chemisorp-

tion, catalytic reactions, solubility of gases in liquids or of liquids in solids, diffusion in porous structures, evaporation from the surfaces of solids and liquids, relaxation in aerosols, ion-exchange adsorption, sorptive extraction, etc.

Since selective heterogeneous processes are extremely interesting *per se*, primarily as a way of studying in a definite manner the physics of interaction of excited particles with surfaces, they are extremely important in the chemistry of catalytic synthesis, in electrochemistry, in biophysics and biochemistry, in cleaning and shaping of surfaces in problems of microelectronics, in epitaxial growth of crystals, and in laser separation of isotopes. Evidently, whenever selective heterogeneous processes are realizable in principle, we obtain analogs of separative sorptive chromatographic columns, fractionating columns, ion exchangers, catalytic reaction columns, etc.

As applied to isotope separation, selective heterogeneous processes can sharply enhance the efficiency of molecular-kinetic separation methods by combining the high throughput of a well-developed known process with the high selectivity of laser excitation. As is well known,^[11] a conflict arises in analyzing any method of isotope separation between the requirements of high throughput and high separation coefficient. The solution of this conflict can be only a compromise, but the level of compromise sharply differs in laser isotope separation from that characteristic of the traditional methods. Therefore selective heterogeneous processes are of interest for laser isotope separation.

Analogously, in synthetic chemistry as in chemistry in general, reactions play a large role that occur at the phase boundary of two media. A large fraction of the catalysts used in chemical industry are porous structures having a well developed surface above or on which the desired reactions run. In chemical extraction also, the separation of the required compounds involves formation of molecular complexes of the extractant and the substance being extracted in the boundary layers of the phase surface of two media. Evidently laser stimulation of chemical reactions that occur at such surfaces is of great interest.

This review is mainly concerned with discussing the experimental and theoretical results obtained recently along the lines mentioned in the last two paragraphs. The first proposal to use selective heterogeneous processes for laser separation of isotopes was made in 1975.^[12] Rather encouraging experimental results were soon obtained.^[13-15] Stimulated chemical extraction at the phase boundary of two liquids under the action of CO₂ laser radiation was also first observed in 1975.^[16] A preliminary review of these results was presented at the 9th International Conference on Quantum Electronics, and in part at the 1st All-Union Conference on Laser Isotope Separation.^[17] Laser chemistry at the surface of a solid in which the vibrations of adsorbed molecules are excited with an infrared laser was observed experimentally in 1976,^[18] while it was observed somewhat earlier^[19] in a gas excited near the surface of a solid

with the radiation of a high-power argon laser ($\lambda = 4880 \text{ \AA}$).

Some interesting theoretical studies of the problem have also been published recently.^[20-23]

2. SEPARATION OF MOLECULES OF DIFFERENT ISOTROPIC COMPOSITION INVOLVING ADSORPTION

In laser isotope separation an important problem is how many laser quanta must be absorbed by one particle to alter its properties enough that it can become physically (spatially) removed. The advantages of one-step processes in which the absorption of only one quantum suffices are obvious. Therefore selective heterogeneous processes whose activation energy (critical energy) is comparable with the energy of a laser quantum are of great interest. We have noted above the great variety of heterogeneous processes that merit attention as the object of selective laser effects. Yet it is expedient to treat first the simplest of the selective heterogeneous processes: the process of physical adsorption, which allows one to carry out the most complete analysis, though not, of course, attractive from the practical standpoint.

In the first approach to the problem, on the level of the suggestion^[12] of separating selectively excited molecules in selective adsorption processes, it is expedient to limit the treatment to the following.

As we know, the probability of nonattachment of a molecule in an adsorption process at a wall, i.e., the reflection coefficient of the molecule, is determined by the specific energy of interaction E_c of the molecule with the wall and the energy E of the molecule:

$$R = 1 - S = e^{-E_c/E}, \quad (1)$$

Here S is the attachment coefficient. Analysis^[12,13] of the experimental data on adsorption of a gas in thermodynamic equilibrium while being cryogenically pumped^[24] leads to the conclusion that the quantity E must include the vibrational energy of the molecule. Moreover, the invariance of E_c as the ratio between the temperatures of the wall and of the gas molecules is varied over a wide range allows us to assume that the attachment coefficient S^* in the presence of non-equilibrium vibrational excitation of the molecules is determined by a relationship of the same type:

$$S^* = 1 - e^{-E_c/E^*}. \quad (2)$$

Here E_c remains invariant, while E^* includes the energy of vibrational excitation, $E^* = E + h\nu_{\text{vib}}$. We should immediately emphasize that the abovesaid is a hypothesis, but a convenient one that allows one perspicuously to trace the further consequences. Within the framework of this hypothesis, the ratio of the reflection coefficients of the vibrationally excited and the equilibrium molecules is given by the simple formula:

$$\frac{R^*}{R} = \left(\frac{1}{R}\right)^{h\nu_{\text{vib}}/(h\nu_{\text{vib}}+E)}. \quad (3)$$

When $h\nu_{\text{vib}} \gg E$ and $E \rightarrow 0$, then $R^* \rightarrow 1$, while $S^* \rightarrow 0$. This seemingly purely speculative conclusion has been con-

firmed experimentally^[13] in separations of the isotopes of boron (vibrational excitation of BCl₃ molecules). Moreover, direct experiment^[25] on the interaction of vibrationally excited CO₂ molecules with a refrigerated surface revealed a serious divergence in the sorptive properties of excited and unexcited particles. The experiment was performed with a molecular-beam generator with cryogenic pumping.^[26] A molecular beam of flow rate 0.1 g/sec was obtained at pumping speeds of 10⁶ L/sec. The molecular beam was incident normal to a metallic screen. When the screen was not cooled, no difference was found between the numbers of reflected molecules for a beam having excited and unexcited molecules. Cooling of the screen with liquid nitrogen led to a sharp difference, practically an order of magnitude, in the number of reflected molecules. Direct observation^[25] confirms well the hypothesis of Ref. 12.

Evidently the difference in reflection coefficients of excited and unexcited molecules allows one to separate them selectively under conditions of selective excitation.

As an example, let us study a gas contained in a vessel whose characteristic dimensions are much greater than the mean free flight path. Then laser radiation acts on molecules of only one type. The rate equations in the two-level approximation have the form

$$\left. \begin{aligned} \frac{dn_1}{dt} &= (n_2 - n_1)W - S \frac{n_2 - n_0}{\tau}, \\ \frac{dn_2}{dt} &= -(n_2 - n_1)W - S^* \frac{n_2}{\tau}, \\ n_1 + n_2 &= n; \end{aligned} \right\} \quad (4)$$

here W is the probability of induced transitions, τ is the mean flight time to the wall, n_0 is the equilibrium number of molecules in the volume without irradiation, n is the number of molecules in the gas phase when acted on by the radiation, and n_1 and n_2 are their distributions over the first and second energy levels. Under steady-state conditions and with saturation ($n_1 \approx n_2 \approx n/2$), the number of molecules in the gas phase substantially differs from the equilibrium value:

$$n \approx 2n_0 \frac{S}{S^* + S} \quad (5)$$

and it becomes doubled when $S^* \ll S$.

This example, which pertains essentially to the elementary cell of a selective-adsorption laser method of isotope separation, is not only illustrative in nature. Consider an adsorbent that is macroscopically finely but microscopically coarsely porous, while the adsorbate gas flows slowly through the thickness of the laser-irradiated adsorbent. Then the equilibrium in each of the pore cells can shift in precisely this way upon excitation of a molecular component. Of course, evidently the entire diffusion system of this type needs more thorough analysis.

Selective adsorption of vibrationally excited molecules can be used effectively in passage of a continuous gas flow through a cylinder having refrigerated walls.^[12,13] Under conditions of Poiseuille flow, the concentrations of excited and unexcited molecules upon saturation by a

laser-radiation field will decline exponentially along the direction of flow with substantially differing decay coefficients. Such a laser chromatographic column can show a high separation coefficient at substantial mass flows, as has been confirmed experimentally.^[13] We can expediently emphasize here that experiment has shown the need of relatively deep (to 160 °K) cooling of the column walls.

Experiments^[13,25] confirm that adsorption can actually be used for developing heterogeneous methods for separating vibrationally excited molecules, and they are stimulating the development of the pertinent theoretical analysis.

Vibrational relaxation of the excited molecules plays a substantial role in physical adsorption processes. Vibrational relaxation in heterogeneous systems plays a large role in quantum electronics. Relaxation in aerosols has recently been studied as applied to the problem of gas-dynamic lasers.^[27] The same authors have analyzed the possibility of adsorptive separation of isotopically substituted molecules by an aerosol beam.^[28]

We can expect to get qualitative or semiquantitative estimates in the theoretical analysis^[22] of the efficiency of the elementary event of adsorption separation of molecules having differing isotope compositions. Unfortunately, detailed description of the studied objects is practically impossible owing to their complexity.

In a binary molecular mixture, the efficiency of the elementary event is characterized by the separation coefficient γ per collision of adsorbate molecules on the surface of the adsorbent. The quantity γ is the ratio of the reflection coefficients:

$$\gamma = \frac{R_1}{R_2} \quad (\text{by definition } R_1 > R_2). \quad (6)$$

As we have said, $R = 1 - S$, where the attachment coefficient

$$S = \frac{1}{kT} \int_0^{\infty} P_s(E_z) e^{-E_z/kT} dE_z \quad (7)$$

is defined as the ratio of the number of attached molecules to the number of collisions per unit time per unit surface. Here T is the temperature of the gas, $E_z = mv_z^2/2$, and v_z is the normal component of the velocity of the molecule. The attachment probability $P_s(E_z)$ mainly depends on v_z , since the adsorption potential varies little along the surface. Essentially, $P_s(E_z)$ is the probability that the energy of the molecule will dissipate in the lattice of the adsorbent within the time of motion in the field of the adsorptive forces. In classical mechanics, P_s has the form of a step function^[29-31]:

$$P_s(E_z) = \begin{cases} 1, & E_z < E_c, \\ 0, & E_z > E_c, \end{cases} \quad (8)$$

Here E_c is the critical attachment energy that we have introduced above. In the present case it has the meaning of the maximum possible energy exchange of the molecule with the lattice. Then (cf. Eq. (1)) we have

$$S = 1 - e^{-E_c/kT}, \quad R = e^{-E_c/kT}, \quad (9)$$

which gives

$$\gamma = e^{(E_{c2} - E_{c1})/kT}. \quad (10)$$

The values of E_c depend on the mass ratio m/M , where M is the mass of an atom of the lattice of the adsorbent, and on adsorptive interaction energy, etc. In a crude approximation that treats the collision of the molecule with an atom of the surface as an elastic collision of free particles, and with $m/M \ll 1$, we have

$$E_c \approx 4 \frac{m}{M} D, \quad (11)$$

Here D is the depth of the adsorptive potential (heat of adsorption). Thus the critical energy of attachment of a molecule is directly determined by its mass (direct isotope effect).

The direct isotope effect is rather large for the very light molecules H_2 , HD , and D_2 .

Here we must bear in mind that in practice R_1 must differ appreciably from zero, lest all the molecules generally become adsorbed. As a convenient compromise, we can adopt the condition on the temperature of the gas $kT \approx E_{c1}$; then

$$\gamma = \frac{1}{3} e^{E_{c2}/E_{c1}} \approx \frac{1}{3} e^{m_2/m_1}. \quad (12)$$

While γ is rather large for the very light molecules, the relative variation in mass owing to isotopic substitution for heavier molecules is small, and the separation coefficient that arises from the direct isotope effect differs little from unity:

$$\gamma \approx 1 + \frac{\Delta m}{m}. \quad (13)$$

In a more careful analysis^[22] the surface atom is assumed to be contained in a certain unexcited harmonic oscillator having an intrinsic frequency equal to the Debye frequency, while the adsorptive potential is represented by a Morse potential. For adsorbates of H_2 , HD , and D_2 being adsorbed on such adsorbents as solid Ar, Xe, CO_2 , N_2 , and H_2O , it yields practically the same estimates for the relationships between the critical adsorption energies. This renders the simple above-discussed estimates reasonable.

It is expedient to make two remarks here. First, we must stress that the theoretical analysis^[22] was carried out while assuming a cold wall, which corresponds to the experiments of Refs. 13 and 25. Second, the strong direct isotope effect for adsorptive separation of H_2 , HD , and D_2 molecules may have a certain practical interest for preparing heavy hydrogen, which plays an important role in the program of construction of heavy-water energy reactors based on unenriched uranium.^[32]

In order to increase the separation coefficient for heavier molecules, the pathway remains of selective excitation of vibrations in the molecules having the required isotopic composition.^[12] As an excited molecule moves in the field of the adsorptive forces, it can relax vibrationally so as to increase the energy of trans-

lational motion of the molecule. This diminishes the probability of attachment of the molecule, which can be represented in the form

$$P_s^*(E_z) = P_s(E_z) - p(E_z) [P_s(E_z) - P_s(E_z + h\nu_{\text{vib}})]; \quad (14)$$

Here $p(E_z)$ is the relaxation probability per flight through the field of the adsorptive forces. The difference $P_s(E_z) - P_s(E_z + h\nu_{\text{vib}})$ varies sharply the region $E_z \approx E_c$. When the following condition is obeyed:

$$E_z < E_c < E_z + h\nu_{\text{vib}} \quad (15)$$

the probabilities of attachment of excited and unexcited molecules differ strongly. Quantum corrections blur the edge of the classical stepwise dependence of $P_s(E_z)$ of Eq. (8), but they play no role when $kT \approx E_c$. Then, upon transforming from the attachment probability to the reflection coefficient, we can derive the following expression for the separation coefficient:

$$\gamma = \frac{R^*}{R} = 1 + p(E_c) (e^{\min(E_c, h\nu_{\text{vib}})/kT} - 1), \quad (16)$$

Here

$$\min(E_c, h\nu_{\text{vib}}) = \begin{cases} E_c, & E_c < h\nu_{\text{vib}}, \\ h\nu_{\text{vib}}, & h\nu_{\text{vib}} < E_c. \end{cases}$$

In principle γ can differ strongly from unity, and the concentration of molecules in the gas phase that have been preliminarily excited at resonance increases. In actual practice one should be interested in the mass throughput of the method as well as the value of γ . While not discussing this problem, we shall assume again as a convenient compromise the requirement that R should not be small. Then $kT \approx E_c$, and

$$\gamma = 1 + p(E_c) (e^{\min(E_c, h\nu_{\text{vib}})/E_c} - 1). \quad (17)$$

Thus the estimate of the efficiency of the elementary event of adsorptive separation of vibrationally excited molecules is reduced to determining the relaxation probabilities and the critical adsorption energy.

Theoretical determination of E_c is difficult for heavy molecules. Estimates of it based on approximating the surface atom with a harmonic oscillator give E_c values far exceeding the binding energy of the surface atoms. Therefore this approximation is inadmissible. Moreover, at the high energy transfers characteristic of heavy molecules, the bottleneck may be the removal of the excitation energy of the surface atoms into the adsorbent lattice. Then the role of lattice defects of the adsorbent increases, and they greatly decrease the efficiency of attachment owing to the impaired conditions of energy removal.^[33] A quantitative account for the role of defects is very complicated. Moreover, the size of the critical attachment energy can be obtained from experimental data on cryogenic pumping.^[24] Since the direct isotope effect is small for heavy molecules, we can assume that E_c enters into the formula as a constant empirical parameter. Then in order to estimate the separation coefficient of vibrationally excited and unexcited molecules, we must know only the probability of vibrational relaxation in the field of the adsorptive forces.

We should expect this probability to correspond somewhat to the probability of VT-relaxation of the studied adsorbate molecules in a gas of molecules (or atoms) of the adsorbent.^[27] The latter has been well studied for a large number of molecular gases,^[33,34] and the pertinent experimental data can be useful in estimating the sought probability.

If the electronic state is not altered in the collision of a molecule with any other particle, then we can use the model of a harmonic oscillator colliding with the particle for estimating the vibrational relaxation. Here the interaction potential of the particle with the atom of the molecule incident on the particle that undergoes the collision can be conveniently represented as a Morse potential. It turns out^[22] that, when the translational energy is much less than the depth of the pairwise interaction potential D_0 and when $m \ll M$, the relaxation probability in the flight to the wall exceeds the relaxation probability in pairwise interaction by a factor of $\exp(D/D_0)^{1/2}$. The heat of adsorption D can exceed the depth of the pair-interaction potential D_0 by a factor of 5–7. Then one can realize a tenfold enhancement of the sought probability over the probability of pairwise interaction.

Evidently we can easily get the probability of vibrational relaxation in the gas phase from measurements of the rate constant of vibrational relaxation. This engenders the need for performing relaxation measurements on the molecular gases of interest for isotope separation that haven't yet been subjected to the pertinent analysis.

The existing experimental data show that the probability p generally does not differ strongly from the probability of pairwise interaction and that it is small. Moreover, for a number of systems such as the hydrogen halides relaxing on atoms of the heavy noble gases, the probability of relaxation in a pairwise interaction amounts to 0.1–0.01,^[34] while the probability of relaxation in collision with a wall can be as much as 1–0.1. The value of γ in the series HI–HF can range from 1.2 to 3.0. Yet the use of halogen molecules instead of hydrogen halides with the same adsorbents leads to infinitesimally small separation coefficients per collision. This indicates the need of careful selection of the adsorbent-adsorbate pairs.

Evidently an increase in the degree of vibrational excitation of the adsorbate molecules facilitates an increase in the separation coefficient in adsorption.

Thus in principle, vibrational excitation of the molecules of the sought isotopic composition substantially increases the coefficient of adsorptive separation, which is especially important for heavy molecules. The separation efficiency is determined by the probability of vibrational relaxation in the field of the adsorptive forces. Therefore the choice of the adsorbent-adsorbate system is of great importance.

Increase in the affinity of the adsorbate molecules and the adsorbent atoms increases the relaxation probability. It seems expedient to perform a more careful

analysis of the adsorption of vibrationally excited polyatomic molecules that possess a rather rich spectrum of normal vibrations, as well as to devise the appropriate experimental studies.

Thus qualitative considerations, the results of experiments, and analysis of relaxation of vibrational energy in physical adsorption lead to the conclusion that selective heterogeneous methods of laser isotope separation are realizable and promising.

3. SELECTIVE DIFFUSION STIMULATED BY LASER RADIATION

The preceding chapter has treated the selectivity of the elementary event upon laser excitation of the adsorbate in physical adsorption. The latter can serve as the major way of carrying out many heterogeneous molecular-kinetic methods of laser isotope separation. The traditional molecular-kinetic methods of isotope separation are based on the difference in the mean statistical properties of isotopically substituted molecules caused by mass difference (see, e.g., Ref. 11). As is well known, these methods show high mass throughput but a small unit separation coefficient. Therefore a possible increase in their efficiency involving selective one-step processes upon laser stimulation is of great interest.

An example is gas diffusion through porous membranes. Thus far nuclear power in the United States has been based on gas-diffusion plants for separating the isotopes of uranium (diffusion of UF_6 molecules).^[35] In gas diffusion the free flight path of the molecules of the gas substantially exceeds the mean dimensions of the pores of the membrane. Here one gets free molecular flow of the gas (Knudsen diffusion or effusion) in which the individual isotopic components diffuse through the membrane independently under their own concentration gradients. The velocity of motion of the gas through the membrane is proportional to the thermal velocity of motion of the molecules. That is, it is proportional to $(T/M)^{1/2}$. Consequently the gas at the output of the diffusion filter is enriched in the lighter isotope. In efflux into a vacuum, the maximum attainable separation coefficient η equals $(M_2/M_1)^{1/2}$, i.e., it is very small. Increasing the pressure in order to increase the throughput reduces η .

The gas-diffusion method is well known and has been carefully developed. This is just why Ref. 14 is of great interest, in which the authors propose using the difference in filtration penetration of selectively excited and unexcited molecules diffusing through porous structures transparent to laser radiation for laser separation of isotopes. In^[14] we report an experimental achievement of the proposed method as applied to molecules of boron trichloride BCl_3 vibrationally excited by CO_2 -laser radiation ($\lambda = 10.6 \mu m$). It is not ruled out that one can apply this method not only to vibrational, but also to electronic excitation, and not only to molecules, but also to atoms.

Apparently the most essential point in the experimental achievement was the use of a fine-pored filter made of a material transparent to CO_2 -laser radiation.

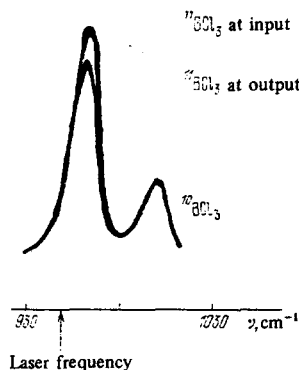


FIG. 1. Infrared absorption spectrum of the ν_3 vibration of $^{10}\text{BCl}_3$ and $^{11}\text{BCl}_3$ molecules after filtration in a laser radiation field.

The experiment was performed with BCl_3 molecules having the natural composition of boron isotopes using a continuous-wave CO_2 laser of 60 W power. The laser generation line P-20 of the 001-010 band is in resonance with the ν_3 vibration of the $^{11}\text{BCl}_3$ molecule. The gas was passed through a pressed diffusion filter made of finely disperse common salt NaCl that had been annealed and dried as carefully as possible. Scattering of the laser radiation in a finely disperse NaCl tablet led to an attenuation described by Bouguer's law with an attenuation coefficient of 10 cm^{-1} . The gas passed by the filter was analyzed with a mass spectrometer and by infrared spectra.

The gas passed by the laser-irradiated filtration cuvette was enriched in $^{10}\text{BCl}_3$. Figure 1 shows typical absorption curves in the ν_3 vibrational band of the $^{10}\text{BCl}_3$ and $^{11}\text{BCl}_3$ molecules for the enriched and the original gases. Figure 2 shows the results of mass-spectroscopic analysis in terms of elemental boron for the BCl_3 at the input a and the output b of the cuvette. Figure 3 shows the relationship of the separation coefficient determined by mass spectroscopy to the pressure of the gas at the output of the filter.

With a diameter of the filtration cuvette of 3.2 cm and 50 W laser radiation power filling the entire aperture of the cuvette, and pressures of 0.3 Torr at the input and

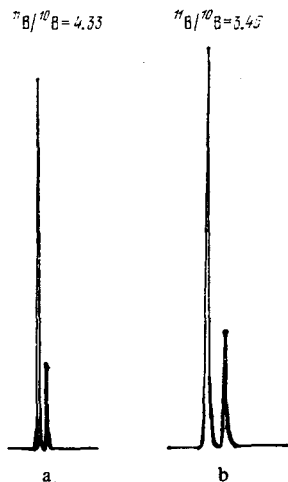


FIG. 2. Mass-spectroscopic analysis of BCl_3 gas for ^{10}B and ^{11}B at the input (a) and the output (b) of the diffusion filter. The recording scales for masses differ by a factor of 2.

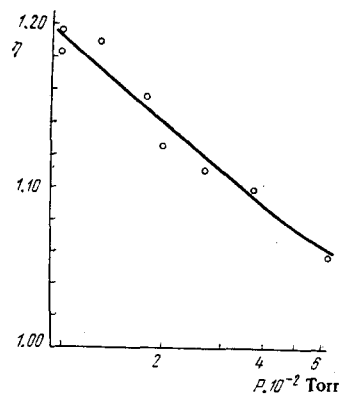


FIG. 3. Relationship of the separation coefficient to the gas pressure at the output of the filter.

0.03 Torr at the output of the filter, they collected in 30 min 8.3 mg of BCl_3 that was enriched in $^{10}\text{BCl}_3$ with a separation coefficient of 1.23 ± 0.005 . This corresponds to an expenditure of 10^3 quanta of laser radiation per molecule of enriched BCl_3 , or 7×10^3 quanta per molecule of $^{10}\text{BCl}_3$ in excess of the natural content. Apparently this is explained by the nonoptimal way of introducing the laser radiation into the filter and the departure of the parameters of the filter itself from optimal. Microscopic study of the pressed NaCl tablets showed a large scatter in dimensions and irregularity of the pores of the filter.

Control experiments without laser radiation and with the filtration cuvette cooled by running water, yielded an enrichment of 1.03 ± 0.01 , and when the cuvette was heated to 150°C , of 1.05 ± 0.02 . Replacement of the pressed NaCl tablet with a single crystal of zinc selenide ZnSe 10 mm thick that possessed randomly arranged straight, thin channels that penetrated the ZnSe plate led to an even greater enrichment. In contrast to NaCl, the ZnSe was not heated by the laser radiation.

The fact that an enrichment of BCl_3 was obtained by laser action on $^{11}\text{BCl}_3$ still indicates a laser stimulation and acceleration of the molecular-kinetic process of diffusional separation rather than its reversal. Yet this acceleration is substantial.

The difference in the filtering penetration of excited and unexcited atoms and molecules in porous media can arise from various physicochemical processes that occur at the phase boundary of the two media. Among these, physical adsorption or chemisorption on the walls of the pores can play a substantial role. The sparse existing experimental material does not allow us to choose for or against selective adsorption in the case at hand. It is not ruled out that the isotope separation arises under conditions involving strong VV-exchange between the molecules of $^{10}\text{BCl}_3$ and $^{11}\text{BCl}_3$ in the volume of the pores of the pressed NaCl. Then, in line with the results of Ref. 13, selective adsorption must enrich the gas mixture in the molecules whose vibrational levels lie higher, i. e., the lighter molecules, as is indeed observed.

Yet we must not rule out the effect of dipole nature of the surface of the adsorbent and its interaction with the

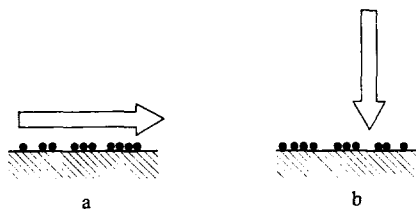


FIG. 4. Possible realizations of selective heterogeneous processes: a) action on the gas near the phase-boundary surface, and (b) direct action on the phase-boundary surface.

dipole moments of the adsorbate molecules that arise upon excitation. For ionic crystals, apparently the dominant role might be played by trapping of vibrationally excited molecules in the potential wells of the interaction of the molecules with the walls of narrow pores. Indeed, as we know,^[36] relatively small stretching of intramolecular bonds in some molecules causes the corresponding dipole moments to increase substantially. Symmetric molecules such as those of the XY_4 type having T_d symmetry have no dipole moment in the vibrational ground state, but excitation of degenerate vibrations confers an appreciable constant dipole moment.^[37(a)] As the dipole moment of the molecule increases, the ionic character of its outer chemical bonds rises, and the strength of its binding to a charged center of the pore wall increases. Then in very fine pores whose dimensions rule out VV-exchange within the volume of the pore, molecules will be preferentially captured that are in resonance with the laser radiation. The diffusion of the non-resonance molecules is relatively facilitated.

Yet situations can arise in which a boundary potential barrier exists at the surface of the walls of the pores of the diffusion filter that can be surmounted only by excited molecules.^[37(b)] Then they are captured by the material of the filter, while the unexcited molecules pass through the entire filter as a whole relatively more freely.

The evident promise of laser stimulation of the gas-diffusion separation process makes it expedient to perform thorough experimental studies on both the process as a whole and on its elementary events, together with developing the pertinent theoretical concepts. In analyzing gas filtration in transparent porous materials in the presence of a laser radiation field, we should also take into account the forces exerted by the walls of the porous material on the diffusion paths of the molecules when the dimensions of the pores become comparable with the dimensions of the molecules.

On the whole, the problem of filtration diffusion in finely porous media stimulated by laser radiation apparently fits the generalized statistical model of a porous medium and a filtration flux.^[38(a)]

Thus laser radiation substantially changes the character of the diffusion of gases through porous structures

by stimulating selective processes in these essentially heterophase systems. The elementary events of these processes require special study.

It seems possible in principle to apply the method of laser control of diffusion for filtering not only gases but also liquids. An interesting topic, though lying outside the framework of this review, is laser stimulation of processes of thermodiffusion, mass-diffusion, and diffusion in supersonic flows.

4. RESONANT CONTROL OF PROCESSES AT A SURFACE BY LASER RADIATION

In the treatment above we have examined heterogeneous processes whose selective course stems from resonant laser excitation of molecules in the gas phase directly over the surface of a solid and from the differing interactions of excited and unexcited molecules with this surface. Yet the direct effect on the boundary of two phases is of undoubted interest. Figure 4 illustrates the difference between these two varieties of selective heterogeneous processes. The effect on the boundary between two phases can involve either the surface of a solid or a liquid. Evidently, in studying the possibility of resonant control of processes occurring at a surface, we should consider not only desorption of atoms and molecules adsorbed at the surface and the effect on diffusion of the adsorbate over the surface and into the interior of the adsorbent or a change in the catalytic properties of the adsorbent and the adsorbate, but also a selective effect directly on the liquid or solid. Therefore the recently found effect^[15] of selective evaporation of frozen gases by laser radiation is of great interest.

Gaseous boron trichloride having the natural isotope composition was frozen in the form of a thin film on a substrate transparent to infrared held at liquid-nitrogen temperature. Here it turned out that the isotopic structure of the ν_3 vibrational band in the solid BCl_3 film did not differ substantially from the structure of the spectrum of gaseous boron trichloride. Freezing only involved an identical displacement of the ν_3 bands of the $^{10}BCl_3$ and $^{11}BCl_3$ molecules toward lower frequencies by about 20 cm^{-1} without substantial change in their width. The thickness of the film corresponded to 100–500 molecular layers. The conservation of the structure of the spectrum upon freezing allowed the authors^[15] to treat the molecules selectively with the radiation of a CO_2 laser that was in resonance with the ν_3 vibrations of the $^{11}BCl_3$ molecule. Unfortunately, the shift of the ν_3 isotopic doublet of the BCl_3 molecule to lower frequencies did not allow them to carry out a resonance treatment on the $^{10}BCl_3$ molecules.

In the laser irradiation of the film they found a preferential evaporation of the resonance-excited $^{11}BCl_3$ molecules provided that the irradiation was relatively brief and of low intensity.

Figure 5 shows simultaneously for convenient comparison: (a) the increase in spectral absorption as freezing on the ZnSe substrate progressed, and (b) the gradual enrichment of the film in $^{10}BCl_3$ molecules with

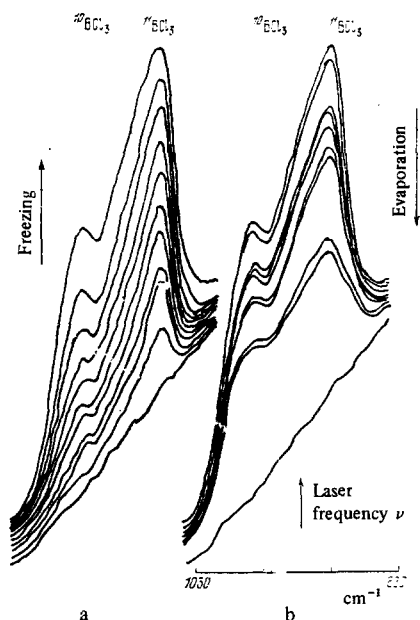


FIG. 5. Absorption spectra of the ν_3 vibration in a solid film of $^{10}\text{BCl}_3$. a) Increase in absorption as freezing progresses. The film thickness increases from bottom to top. b) Decrease in thickness and change in spectrum during laser thawing. The number of laser irradiation events increases from top to bottom.

increasing number of irradiation events. The irradiation was performed with pulses of duration 1–3 min at an intensity of 1 W/cm^2 , i. e., practically in a continuous regime. However, it was important not to overheat the film as a whole. Figure 6 shows the relationship of the separation coefficients of BCl_3 in the gas and solid phases to the intensity of the radiation transmitted through the film. As usual, the separation coefficient η equals the ratio of concentrations $^{11}\text{BCl}_3/^{10}\text{BCl}_3$ after irradiation divided by the concentration ratio in the original gas. The separation coefficient thus defined characterizes the isotopic enrichment caused by irradiation for the particular period. Figure 6 pertains to the case of continuous irradiation for 20 sec.

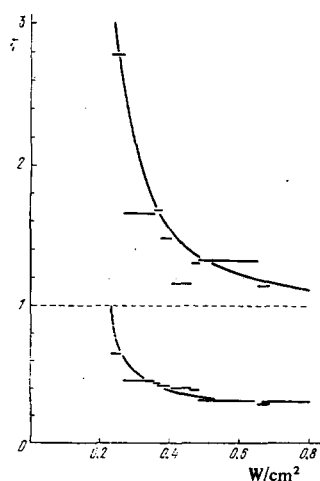


FIG. 6. Relationship of the separation coefficient in the gas phase (upper curve) and in the solid film (lower curve) to the intensity of laser radiation transmitted through the film.

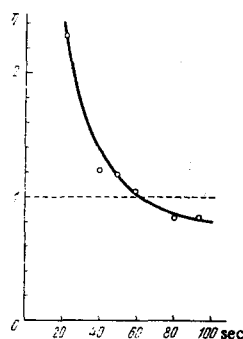


FIG. 7. Relationship of the separation coefficient in the gas phase to the irradiation time.

Thus the authors of Ref. 15 have distinctly observed selective evaporation of $^{11}\text{BCl}_3$ with a high separation coefficient. An essential point was that the selectivity of evaporation declined as the film and substrate became heated. Figure 7 shows the time-dependence of the separation coefficient in the gas phase as measured mass-spectrometrically in terms of elemental ^{11}B and ^{10}B . The loss of selectivity of evaporation of resonance-excited $^{11}\text{BCl}_3$ molecules leads to preferential evaporation of $^{10}\text{BCl}_3$. As it turned out, the separation coefficient in the evaporated gas is inversely proportional to the intensity of the radiation transmitted through the film (Fig. 6), or in other words, to the intensity of the radiation heating the film.

As we have said, the critical interaction energy is small in heterogeneous selective processes. Therefore the absorption of a single infrared quantum by a molecule substantially changes the character of the interaction. When selective vibrational excitation is maintained, the molecule in resonance is excited. Yet efficient vibrational exchange between the molecules of differing isotopic composition causes the molecules to become activated that possess the greater vibrational energy. The experiment on selective evaporation of frozen gases having well resolved isotopic structure by resonance laser radiation qualitatively fits these rather general concepts.

More careful experiments must be performed to determine the time of migration of vibrational energy and to elucidate the role of the thickness of the film, its defect nature, and the spectrum of the phonons in it when selective evaporation is conserved or breaks down. In the resonance evaporation of molecules frozen in matrices, we should apparently expect increased selectivity of action at a great enough dilution.

Thus a recently published paper^[38(b)] on the vibrational spectra and ultraviolet photolysis of UF_6 molecules isolated in argon or xenon matrices at temperatures about 10°K and dilutions from 1:200 to 1:1000 gives values of the width of the fundamental infrared absorption lines from 0.3 to 0.7 cm^{-1} . Such a narrowing of the spectrum, which is especially important for the fundamental ν_3 vibration (619.3 cm^{-1}), is analogous to that observed in the gas-dynamic cooling of a molecular gas, and it is quite sufficient for isotopically selective laser effects. The problem of the advantages of freezing

in matrices as compared with gas-dynamic cooling requires special study.

Dissociation of SF_6 molecules isolated in an argon matrix by infrared laser radiation has been observed^[38(c)] simultaneously with the first successful experiments on selective evaporation of frozen BCl_3 molecules.^[15] A solid SF_6 :Ar matrix at dilutions from 1:500 to 1:2000 and at temperatures of 8–10 °K was irradiated with pulses of radiation of a frequency-tuned CO_2 laser. The intensity of irradiation was 5–30 MW/cm², the pulse duration was 90 nsec, and the width of the laser line was 0.035 cm⁻¹. When the laser was tuned to the absorption line of the ν_3 vibration of the $^{32}\text{SF}_6$ molecule, a change in the infrared absorption spectra of the matrix was observed as a result of 100–150 irradiations of the matrix. It corresponded to preferential loss of the resonance $^{32}\text{SF}_6$ molecules. Possible mechanisms of the selective effect observed by the authors of Ref. 38(c) might be not only selective dissociation in the matrix, but also, as we see it, selective dissociation of the nonselectively evaporated vapor of the molecules over the matrix or selective evaporation, as in Ref. 15. This problem requires further study.

In a recent report^[58] that was also given at the 6th International Conference on Applications and Developments of Lasers,^[59] boron trichloride frozen in a xenon matrix (1:100 dilution) was subjected to the action of the radiation of a low-power continuous-wave CO_2 laser. The author found an isotopically selective migration of excited $^{11}\text{BCl}_3$ molecules through the atoms of the matrix, while they froze out in the crystalline phase at the surface of the cold wall. These results agree well with those obtained earlier in Ref. 15. Just like Ref. 15, the treatment of the results of Refs. 58 and 59 requires further studies.

It would be interesting to perform some experiments on resonance evaporation of frozen molecules using a selective laser effect on the electronic spectra of the molecules using, e.g., dye lasers.

It is expedient to note that a dye laser has been applied for selective dissociation of tetrazine molecules frozen in a benzene matrix at temperatures of 1.6°, 4.2°, and 10 °K.^[38(d)] The products of dissociation were molecular nitrogen and hydrogen cyanide. The enrichment in ^{13}C and ^{15}N in the residual tetrazine was as much as a factor of 10^4 – 10^5 . They also observed an enrichment in deuterium, though not as significant. Apparently Ref. 38(d) is the first experimental realization of laser isotope separation in a solid.

Application of infrared laser radiation for enrichment in deuterium by resonance evaporation of vibrationally excited HDO molecules has been proposed rather recently.^[38(d)] This proposal corresponds to the experiment results of Ref. 15. The authors of Ref. 38(d) propose using the radiation of a chemical DF laser of wavelength 3.6 μm , which is in resonance with the stretching vibration of the O–D bond in the HDO molecule, for preferential evaporation of HDO molecules from water that has been adsorbed on a transparent or reflective substrate.

The fact that laser evaporation can be selective allows us to expect laser stimulation of selective chemical processes on the surface of a solid or a liquid. Thus, for example, it seems interesting to reproduce the experiment of Ref. 39 on photochemical isotope separation by the method of isotope trapping with laser excitation. The authors of Ref. 39 separated the isotopes of heavy and light hydrogen in mixtures of the acetaldehydes CH_3CHO and CH_3CDO frozen at liquid-nitrogen and liquid-helium temperatures by illuminating them with the light of a mercury lamp in quartz ampules. Owing to the difference in energies of electronic excitation of the molecules of differing isotopic composition and the appearance at low temperatures of isotope energy traps, the photolysis of the normal acetaldehyde ran much faster. Use of laser methods would not only allow one to determine all the structure-time characteristics of this process, but also perhaps might lead to large separation coefficients. The problem of laser stimulation of chemical processes in heterophase systems will be discussed in fuller detail in the following chapters of this review.

Some theoretical studies^[20,21,40] have been devoted to the possible control of surface phenomena by laser radiation. References 20 and 40 have treated resonance pumping of atoms in an adsorption potential by using a choice of frequencies and ejecting the atom from the surface. The analysis of Ref. 21 was the fullest. Here the aim was to determine what new potentialities and effects involving the presence of a phase boundary might arise in the effect of laser radiation on heterogeneous systems. Here the authors of^[21] pay major attention to direct action on the surface. They examine selective effects on desorption of atoms and molecules, change in the catalytic properties of adsorbents, and the possible obtaining of information on the composition and distribution of active groups lying on the surface of the adsorbent.¹⁾

The authors of Ref. 21 distinguish two sharply differing cases in evaluating the action of laser radiation on an adsorbate. Infrared radiation can pump the particles lying in the given potential; while ultraviolet or visible radiation alters their interaction potential with the surface by exciting electronic transitions in the adsorbed particles.

In analyzing infrared pumping, one should first estimate the lifetime of the excited states and then the probabilities and excitation cross-sections of the vibrations in the adsorption potential. Using first-order perturbation theory and assuming that the lifetime is governed by the creation of acoustic phonons, the authors of Ref. 21 estimate a lifetime of the excited state of 10^{-11} sec for the temperature 100 °K and with other reasonable conditions. This generally coincides with the characteristic values for condensed media. This estimate seems realistic enough, though strictly speaking, the dissipation of the energy of the vibrations of the adsorbate atoms into the lattice of the adsorbent can be multiphonon in

¹⁾The latter topic is outside the scope of this review.

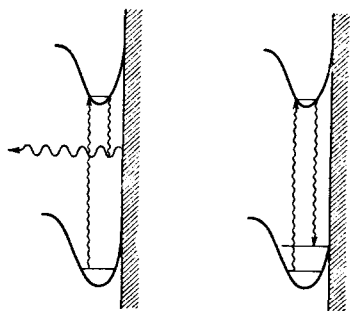


FIG. 8. Electronic transitions in adsorbate atoms. A transition to the ground electronic state accompanied by desorption is shown at the left.

type.^[41] In line with the estimate of the lifetime, the excitation cross-section of the vibrational levels by resonance quanta is of the order of magnitude of 10^{-15} – 10^{-16} , i. e., rather large.

If desorption from the excited level occurs more intensively than from the ground level, then selective excitation can substantially increase the probability of detaching the particles of the required type. The probability of such a stimulated desorption can be written in the form

$$P = \frac{\sigma}{\hbar\omega} I, \quad (18)$$

Here I is the flux density of the laser radiation, $\hbar\omega$ is the difference between the energy levels of the ground and excited states, and σ is a certain effective desorption cross-section, which the authors of Ref. 21 estimate under reasonable conditions to be 10^{-17} – 10^{-18} cm².

The performed estimates indicate that selective desorption with infrared laser pumping should be realizable in principle. The problem of whether the theory of^[21] can be applied to analyzing the selective evaporation of frozen gases by resonance radiation of infrared lasers^[15] requires a special examination.

Electronic transitions in the adsorbate atoms are transitions between vibrational states in the different adsorption potentials (Fig. 8). The cross-section of the transition calculated in the usual way amounts to 10^{-15} – 10^{-16} cm². The probability that an atom or molecule will be desorbed in a transition to the ground state is

$$P = 1 - \sum_j \left| \int \psi_1^* \psi_2 dv \right|^2. \quad (19)$$

Here the summation is performed over all possible wave functions of the discrete spectrum, while ψ_2 is the wave function of vibrational motion in the upper adsorption potential (see Fig. 8). If the adsorption potentials of the particles in the electronically excited and ground states differ sharply, then we can assume that $P \approx 1$ as a crude estimate. Then the selective-desorption cross-section proves to be approximately equal to the excitation cross section, i. e., 10^{-15} – 10^{-16} cm². This estimate makes it^[21] very interesting to seek objects for experimental

realization of selective desorption of particles by laser radiation in the ultraviolet or visible range.

Moreover, upon being selectively excited to higher energy levels, the adsorbate particles prove to migrate over the surface of the adsorbent. Here the coefficient of stimulated diffusion is proportional to the flux density of the laser radiation.

The possible effect of laser irradiation on heterogeneous catalysis processes seems interesting. Laser radiation can both alter the concentration of the reacting substances by selective desorption and alter the number of active centers on the surface of the adsorbent catalyst. An essential requirement is to keep the temperature of the catalyst low in order to avoid spontaneous desorption. The problem of selective activation of the catalyst surface proper is as yet open.

Thus the experimental results and theoretical treatment unambiguously indicate the possibility of selective laser control of processes that occur at the surfaces of condensed media. Further studies should lead to a more concrete understanding of the physical essence of these processes and determine their fields of application.

5. LASER CHEMISTRY AT THE INTERFACE OF TWO MEDIA

A direct consequence of the possibility of laser control of processes that can occur at the boundary of two phases is laser stimulation of heterogeneous chemical reactions. Evidently we should consider two substantially different situations in these cases. First, the bulk excitation of a gas consisting of some specific atoms or molecules can activate a chemical reaction of this gas with the surface of a condensed phase. Second, in line with the results of the experimental and theoretical studies discussed in the last chapter, direct laser action on a surface can alter its chemical activity.

Chemical reactions at a surface arising upon bulk excitation of the gas near the surface essentially differ from homogeneous laser chemical reactions in the gas phase^[3-8] in that the surface of the solid or liquid in the heterogeneous system is the specific acceptor that rapidly removes the particles excited by the laser radiation. This fact is essential in analyzing the problem of how to maintain selectivity of excitation and how the energy of the molecule is acquired in its excitation by infrared laser radiation.

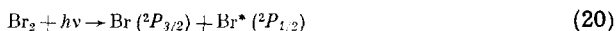
In the case of infrared laser photochemistry, in which the quantum energy of the laser radiation is considerably smaller than the activation energy of the reaction, the phase-boundary surface must apparently hinder the gain by collision of the energy essential for realization of laser reactions in the gas phase^[42] at relatively low laser power levels. The case seems clearer with pulsed infrared high-power lasers, in whose radiation field collisionless, purely radiational gain of the energy of the molecule can occur, up to the point of dissociation and even above the ordinary dissociation limits.^[43-45] In this case, owing to the high overexcitation of the molecule, the selectivity of dissociation of the molecule

persists even in the collisional phase directly following a short pulse of laser excitation.^[46] Hence, strongly excited molecules of a chosen composition and their fragments can actively interact with the boundary surface between the gas and the condensed phase if the gas has been excited near this surface.

The case is substantially simpler of activation of a surface reaction by laser radiation having large enough energy quanta. This eliminates the problem of gaining the energy by the molecule or atom, while the problem of competition of relaxation processes in the gas with the chemical reaction at the surface is solved by choosing an appropriate experimental geometry and gas pressure over the surface. In this sense, Ref. 19 is of interest, in which the authors initiated a surface chemical reaction of monocrystalline germanium with gaseous bromine by using a high-power argon laser at 4880 Å wavelength.

They chose an etching reaction involving photodissociation under the action of laser radiation. The specimen was irradiated with grazing light so as to eliminate heating owing to absorption of light by the specimen. The concentration of molecular bromine in the closed cuvette was measured with the 5145-Å absorption line of the same argon laser. Kinetic studies of the process of loss of Br₂ molecules as a function of the initial bromine pressure in the cuvette revealed an optimal pressure at which the reaction runs fastest. This indicates that the most favorable relationships between the rates of dissociation, recombination, and loss by chemical reaction of the elemental Br are established at this pressure at the given power of laser radiation.

Atomic bromine is generated by radiation at the wavelength 4880 Å in the elementary process



with a quantum efficiency of unity and a cross-section of 5×10^{-19} cm².

In the opinion of the authors of^[19], the primary process that consumes the bromine in the cuvette is the elementary surface reaction



where the complex $[\text{GeBr}]_{\text{ads}}$ describes the state of a bromine atom chemisorbed on the surface of the germanium. The energy of the adsorption complex is rather high. Therefore the bonds of the surface germanium atom with the atoms in the bulk of the crystal are broken to form bromides having the general formula GeBr_x, where $x < 4$.

With a laser power of 40 W at the wavelength 4880 Å, the laser effect accelerates the reaction by 3–4 orders of magnitude as compared with thermochemical etching.

It is expedient to stress the importance of analyzing the secondary reactions at the surface that follow the primary events of laser stimulation of heterogeneous processes.

Stimulation of chemical reactions at the phase boundary of two media by a resonance laser effect directly

on the surface of the condensed phase is a difficult problem. Some certain progress along this line has been achieved in an experimental study^[18] that was carried out in accord with the ideas of the theoretical paper^[21] that we discussed in the previous chapter of this review. The authors of Ref. 18 selectively desorbed compounds containing hydroxyl and amine groups chemically adsorbed on the surface of crystalline silicon oxide taken in the form of a pressed, highly-disperse powder. They used a continuous-wave CO₂ laser of relatively low power (flux density up to 10 W/cm²) retuned to the radiation frequencies 950 cm⁻¹ and 932 cm⁻¹ (resonance with the vibrations of OH and NH₂ groups adsorbed by the SiO₂ surface, respectively).

The kinetics of chemisorption in the absence of laser radiation is described in the first approximation by the Langmuir theory (see, e.g., Ref. 47). The fundamental equation of this theory is the rate equation

$$\frac{dN}{dt} = \alpha(N^* - N) - \beta N, \quad (22)$$

Here N and N^* are the surface densities of the adsorbed particles and the adsorption centers, respectively. The adhesion coefficient α determines the probability of attachment of a particle to the surface, which is proportional to the gas pressure and which depends on the molecular parameters, in particular the choice of adsorbent-adsorbate pair, and β is the desorption coefficient.

An essential point is that the temperature-dependence of the coefficients α and β and the number N^* is exponential over a broad range of the parameters^[47]:

$$\alpha = \alpha_0 e^{-E_1/kT}, \quad \beta = \beta_0 e^{-E_2/kT}, \quad N^* = N_0^* e^{-E_3/kT}. \quad (23)$$

Relationships like (23) allow us to assume the existence in the adhesion and desorption processes of certain potential barriers whose surmounting can be appreciably facilitated by resonance laser radiation. Any chemical reaction at a surface that is stimulated by heat or laser radiation involves highly excited vibrational states of groups of atoms on the surface. The surface mobility of these groups is much higher than that of unexcited groups. Two-dimensional collisions of excited groups of atoms lead to chemical reactions similarly to the three-dimensional case.^[7] The surface mobility of chosen groups of atoms can be selectively stimulated by resonance laser radiation, and thus selective control of surface chemical reactions can be effected. In order that one might actually alter selectively the kinetics of Eq. (22) in this way, the vibrational energy in the modes to be excited must substantially exceed the energy of thermal motion. In the case of the surface of a solid, this means that the vibrational temperature of the modes to be excited must exceed the temperature of the acoustic phonons. However, estimates of the relaxation time of the excited states from the line widths usually give values of the order of 10⁻¹¹ sec for solids. This time is too short to permit one to raise at all substantially the vibrational temperature above the phonon temperature at laser fluxes of 10 W·cm⁻². Under the conditions of the discussed experiment, the thermalization time of

the vibrations should not exceed 10^{-6} sec. Yet situations can happen in which the relaxation time of the required vibration in complicated molecular complexes is rather long (see the next chapter). Moreover, we know examples in which the relaxation time is long for very simple molecules adsorbed on a surface. Thus, the nitrogen molecule N_2 can last in the excited state on a surface up to 10^{-3} sec.^[48]

Two fundamental conclusions arise from the experimental study.^[18] First, different chemical-desorption reactions occur when different groups of adsorbates are subjected to resonance laser action. Second, the kinetics of laser desorption substantially differs from that of thermal desorption.

While the second of these results can even be explained by the onset of temperature gradients upon heating by the laser and subsequent heat diffusion that accelerates desorption, the first of the results seems actually to indicate the successful realization of selective laser infrared photochemistry at the surface of a solid.

Thus the experiments show real potentialities of laser control of chemical processes at the boundary of a gaseous and a solid phase in heterophase systems with an effect either on the gas above the boundary surface or directly on the surface. We can expediently stress again the importance of this potentiality for catalytic chemistry.

6. LASER STIMULATION OF CHEMICAL REACTIONS AT THE INTERFACE OF TWO LIQUIDS

As we've said, practically the only object of experimental studies on selective laser effects has been a gaseous medium. Yet liquids are of great interest owing to their substantially greater density. A specific feature of liquids consists in their high rate of relaxation processes. The characteristic times of VT- and VV-processes arising from both binary collisions and collective processes amount respectively in a liquid to $\sim 10^{-9}$ sec and $\sim 10^{-11}$ sec.^[49] Under these conditions the energy of the laser radiation is rapidly converted into heat.

Owing to the speed of the relaxation processes in a liquid, we must take account of the reverse reaction as well as the forward one. That is, we must analyze the possibility of a shift in chemical equilibrium caused by the laser radiation.^[23] Here we must bear in mind that in liquids the possibilities for a shift in chemical equilibrium under the action of laser radiation are limited. Therefore, in order that the laser effect on a molecule in a liquid medium should be efficient and selective, in contrast to a gas, the direct excitation of any vibration must substantially alter a chemical reaction or the strength of chemical bonds so as to yield an appreciable shift in chemical equilibrium. This condition is satisfied by coordination (complex) compounds, with one of which it was first shown possible to get a nonthermal shift in chemical equilibrium in solutions under resonance action of infrared laser radiation.^[16]

The structure and reactivity of coordination compounds involves the mutual influence of the ligands of the complex. This influence has been studied experimentally by using chemical substitution of individual elements of the complexes, and it has proved to be quite substantial.^[50-52] It has been shown that weakening of the bond of the central atom of the complex with one of the ligands leads to angular deformations and to alteration of the strength of the bonds with the other ligands.^[51,52]

As we know,^[53] complex (coordination) compounds are compounds in which the number of closest neighbors of the central atom exceeds its valence. The valence of the central atom is determined by its unpaired electrons. The free orbitals or unshared pairs of electrons create additional donor-acceptor bonds. Complex compounds are easily formed by the atoms of the transition elements, the rare earths, and the actinides. The core of a complex compound is its central atom or complex-former, and the ligands coordinated with it. Complex compounds are characterized by the existence of inner and outer spheres of the complex, which are formed respectively by the primary and secondary ligands. The secondary donor-acceptor bonds about the main ligand compete with the bonds with the secondary ligands.^[52] Therefore excitation of vibrations of the main ligand with respect to the central atom weakens this bond and thus strengthens the bonds with the secondary ligands. This essentially intramolecular process occurs practically without lag. This allows us to expect a possible nonthermal laser stimulation of chemical reactions in liquids.

For example, for a quasioctahedral complex AXL_5 , the binding orbitals along the $X-A-L$ axis actually have the form^[51]

$$\begin{aligned}\psi_1 &\sim \chi_X + \chi_A^{(s)} + \delta\chi_A^{(as)} + \chi_L, \\ \psi_2 &\sim \chi_X + \delta\chi_A^{(s)} + \chi_A^{(as)} - \chi_L,\end{aligned}\tag{24}$$

Here χ_X , χ_T , and χ_A are respectively the orbitals of the ligands X and L and of the central atom A . Owing to the difference between the ligands X and L , the molecular orbitals ψ_1 and ψ_2 contain a mixture of the symmetric $\delta\chi_A^{(s)}$ and antisymmetric $\delta\chi_A^{(as)}$ orbitals. These mixtures always have opposite effects on the $A-X$ and $A-L$ bonds. One bond is strengthened as the other weakens. Here the internuclear distances vary in a self-consistent way and the equatorial bonds also become deformed. One observes an analogous pattern in the excitation of nonsymmetric stretching vibrations along the axially symmetric bond of the core of a complex compound possessing developed equatorial ligands.

The weakening of the axial bond leads to a corresponding change in the chemical equilibrium constant of the complex-formation reaction, which involves the formation of the equatorial bonds. When the equatorial ligands or the internal vibrations in the ligands of the core of the complex are excited, the variation in the equilibrium constant should apparently be considerably smaller than when the axial bonds of the central atom are excited.

A substantial shift in chemical equilibrium requires a high rate of pumping of the resonance transition. The intensity of laser radiation that yields a vibrational temperature T_{vib} in a given type of vibration is given by the relationship

$$I \approx \frac{h\nu}{\sigma\tau} e^{-h\nu/hT_{\text{vib}}}. \quad (25)$$

In the case of a CO₂ laser having characteristic values of the absorption cross-section $\sigma \approx 10^{-18}$ cm² and times of the VT- and VV-processes $\tau = 10^{-9}$ – 10^{-10} sec, the value of I required for appreciably shifting the chemical equilibrium amounts to 10^6 – 10^8 W·cm⁻². Here the equilibrium constant can change by an order of magnitude in the irradiated region.

Owing to the Arrhenius temperature-dependence of the equilibrium constant, heating diminishes the useful effect. The heat is released in a small volume, in line with the high value of σ and the correspondingly small depth of penetration. Depending on the concentration of the coordination compounds in solution, $\sigma = 5 \times 10^{-2}$ – 5×10^{-3} cm. With an energy release of 1–2 J, the temperature increase can amount to 10–100°.

The abovesaid implies that one must use pulsed irradiation, a through-flow regime, and fast removal of the reaction products.

The results of experimental study^[16] agree well with the ideas presented above.

The object of laser treatment was the complex compound that is formed upon extracting uranyl nitrate with tributyl phosphate.^[54] Extraction is generally a process of separation of a required substance in elevated concentration from a mixture by using selective solvents. In extraction the substance being removed diffuses from one liquid phase into another liquid phase upon mutual contact. Just like any other phase or chemical equilibrium, the condition for extraction equilibrium is that the chemical potentials of the substance being distributed should be equal in the two phases. The extraction equilibrium constant is determined exponentially by the change in free energy ΔF in going from one phase to the other:

$$K = e^{-\Delta F/RT}. \quad (26)$$

Usually the extractate-extractant interaction that governs extraction is rather weak, $\Delta F = 2$ – 10 kcal/mol = 10^{-20} – 5×10^{-20} J/molecule. We note that the quantum energy of the radiation of a CO₂ laser amounts to 2×10^{-20} J.

This energy relationship allows us to expect an increase in the extent of extraction upon selective laser activation of the component being extracted or of the functional groups of the extractant.

Uranyl nitrate when extracted with tributyl phosphate has an antisymmetric stretching vibration $\nu_3 = 945$ cm⁻¹, while the ester groups of tributyl phosphate (TBP) are characterized by intense absorption at the frequency 1040 cm⁻¹.^[50] As we know, the uranyl group is linear or almost linear and the axial (O = U = O) and equatorial bonds in uranyl complexes are interdependent.^[50,55] The

extraction is performed from an aqueous solution of uranyl nitrate, and the extractant is a solution of TBP in an organic solvent.

The experiment was performed with a pulsed CO₂ laser having an energy per pulse of 2–3 J, a pulse duration of 200 nsec, and wavelength of radiation 944 cm⁻¹. The laser was retuned to the wavelength 1040 cm⁻¹ practically without energy losses by putting a cuvette containing BCl₃ gas in the laser resonator. The frequency of repetition of the pulses was 1 Hz.^[56] The extraction was performed in a flow-through regime. A thin film of the extractant flowing over the surface of the aqueous solution was irradiated. The uranyl concentrations in the aqueous solution and in the extractant corresponded to equilibrium at the temperature of the experiment.

A twofold increase was obtained in the extractive power of TBP upon irradiating with laser radiation at $\nu = 944$ cm⁻¹ the layer of extractant flowing over the surface of the aqueous uranyl solution. The measured value of the increase in extraction power refers to the average over the time and over the whole volume of the flowing extractant. Evidently the local shift in chemical equilibrium is far more significant. Only a small variation (~8%) in the equilibrium constant was observed when the laser was retuned to $\nu = 1040$ cm⁻¹. No change in the extraction power was observed when a thin layer of the aqueous solution flowing over the extractant was irradiated. Rise in temperature impairs the extraction of uranium by TBP. All of this indicates that the observed effects are not thermal in type.

Thus an essential result of Ref. 16 is the observation of a shift in chemical equilibrium at the phase boundary of organic and aqueous solutions under the resonance effect of laser radiation on an axially symmetric bond of the core of the complex compound tributyl phosphate-uranyl nitrate.

Thus the experimental results and their theoretical analysis indicate that applying lasers for selective control of chemical reactions in a liquid phase shows promise for such an extensive class of reagents as the coordination compounds, since the intramolecular processes in them can occur practically without lag, while their strength changes under the action of laser radiation.

The coordination compounds include many biologically active substances, in particular hemoglobin, chlorophyll, and a number of enzymes. Hence laser control of chemical equilibrium in performing biological reactions is of interest, at least *in vitro*. An essential factor can also be the change in the spatial structure of the complexes when acted on by laser radiation.

All of this, together with the great role that coordination compounds play in chemical technology, including nuclear technology in the separation, purification, and accumulation of nuclear fuel and in the separation of products of nuclear reaction,^[57] make it important to continue the experimental and theoretical studies of laser control of chemical reactions in liquids.

7. CONCLUSION

We can apparently now consider that the resonance effect of laser radiation on matter and the selective course of the processes caused by this action are being realized in essentially heterophase systems. Owing to their high sensitivity to a change in the energy of the particles lying at the phase boundary of two media, selective heterogeneous processes have undoubted advantages. The development of laser methods based on them for separating isotopes and for selective laser photochemistry is in its very beginning stage. The first encouraging results have been obtained.

Yet selective heterogeneous processes are very difficult in experimental and especially in theoretical studies. Nevertheless studies of these processes, which are important in themselves, is of great value on the purely scientific level. This is because they give important information on the physical and chemical kinetics of essentially nonequilibrium processes at the phase boundary of two media in terms of the specifics of the broad spectrum of mechanisms of interaction of excited atoms and molecules in heterophase systems. This is precisely why the experimental realizability of selective heterogeneous processes that occur under the action of resonance laser irradiation is stimulating the growth of the pertinent studies.

Some of the selective heterogeneous methods, e.g., physical adsorption, have a general applicability, and some are especially efficient with some particular choice of the type of interaction and of interacting agents, e.g., extractive chemical adsorption. Undoubtedly we should expect the proposal and development of new selective heterogeneous processes that are efficient both in the general case and as applied to some particular type of interaction. It is expedient to add to those mentioned above, e.g., electrolytic processes and processes of ion migration in heterophase systems. The possibility seems interesting of carrying out selective processes under conditions of weightlessness.

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