

Selective action of laser radiation on matter

V. S. Letokhov

Institute of Spectroscopy, Academy of Sciences of the USSR, Troitsk, Moscow Province
Usp. Fiz. Nauk **125**, 57-96 (May 1978)

The review deals with the problem of selective interaction of laser radiation with atoms and molecules. Objects of selective interaction (chemical elements and compounds, isotopes, molecular bonds, etc.) are considered first. Next, possible elementary selective processes (photoionization of atoms and molecules, photodissociation and photoisomerization of molecules, photodeflection of particles, photochemical reactivity, etc.) are discussed and the available techniques are classified into photophysical and photochemical methods, atomic and molecular methods, and so on. The review is concerned mainly with the photophysical and photochemical methods of selective interaction in the specific case of laser isotope separation. The last sections of the review deal with other applications which are in the course of development, such as preparation of pure substances, selective laser biochemistry, selective detection of nuclei, atoms, and molecules, and spatial localization of molecular bonds.

PACS numbers: 28.60. + s, 82.50. - m, 32.80. - t, 33.80. - b

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1. INTRODUCTION

The development of tunable lasers has made it possible to excite selectively practically any quantum states of atoms and molecules with excitation energies in the range 0.1-10 eV. Throughout the wavelength range from 2000 Å to 20 μ we can now generate coherent radiation of power sufficient to excite a considerable proportion of atoms and molecules to a selected quantum state. This qualitative growth of quantum electronics has made it possible to start, from 1969-1970, systematic investigations of the selective action of laser radiation on matter. One of the most important and urgent tasks has undoubtedly been laser isotope separation. The exceptional role

played in nuclear technology and power applications by materials with isotopic composition other than natural and also the existing shortcomings of all the available isotope separation methods, on the one hand, together with the feasibility of developing new laser methods, on the other, have opened up a very attractive field of activity for scientists and engineers. This activity has combined the use of the latest data on the structure of atoms and molecules and of their interactions with coherent laser radiation and of the newest tunable lasers with one clear practical target of developing new isotope separation methods that will be cheaper, more efficient, more flexible, less labor-intensive, etc. than the existing methods. Many hundreds of scientists in tens of laboratories in a number of countries are

now working on laser isotope separation. The first few pioneering investigations, carried out in 1969–1972, have been followed by hundreds of papers on this very subject. Most of them have been discussed in the first brief reviews^{1–3} and in more detail later.^{4–8}

For the sake of brevity, we shall omit descriptions of tunable lasers which are essentially the primary experimental tools in all the laser isotope separation methods. We shall simply list the more important characteristics of laser radiation which make the laser an extremely valuable and effective instrument in this new branch of research:

1) *the tunability of the emission frequency*, which makes it possible to obtain radiation at any frequency in the infrared (IR), visible, ultraviolet (UV), and recently vacuum ultraviolet (VUV) parts of the spectrum;

2) *the high intensity*, sufficient to saturate the absorption in quantum transitions, i.e., to excite a considerable proportion of atoms or molecules;

3) *the short (and controllable) duration of radiation*, which can be made shorter than the lifetime of excited atomic and molecular states;

4) *the spatial coherence of the radiation*, providing an opportunity to produce directional laser beams as well as to illuminate extended objects;

5) *the monochromaticity and temporal coherence*, which ensure an unusually high degree of selectivity of the excitation in the case of a minute difference between the absorption frequencies of the elements being separated.

This combination of the valuable properties of practical optical radiation sources has provided the base for serious consideration and development of methods of selective interaction of optical radiation with matter at the atomic and molecular level.

2. OBJECTS OF SELECTIVE LASER PHOTOPHYSICS AND PHOTOCHEMISTRY

The term “selectivity” has two meanings in laser photochemistry and photophysics. Firstly, we may be speaking of selective photochemical conversion of molecules of one kind mixed with other molecules. This may be called the intermolecular selectivity. This selectivity is always implied in the photochemical methods for isotope separation. Secondly, we can speak, in principle, of selective photoexcitation of any one molecular bond. If a chemical reaction with such a molecule is ensured before the relaxation of the excitation between many molecular bonds, one may hope to control the photochemical reaction so that it occurs in the selected way. This selectivity may be called intramolecular. It can be realized only in a chemical reaction with an acceptor sensitive not only to the energy but also to the type of molecular excitation. Relatively little experimental work has been done on this type of selective laser photochemistry. Therefore, whenever we shall speak of selectivity we shall practically always mean the intermolecular selectivity.

The main processes of the selective interaction between laser radiation and matter, which are frequently called selective laser photophysics and photochemistry, are as follows:

I. selective separation of substances at the atomic and molecular levels;

II. selective chemical reactions with atoms or molecules of the desired kind (for chemical separation) or in the desired direction (photochemical synthesis);

III. selective detection of atoms, molecules, or molecular bonds.

The underlying basis of the selective interaction between laser radiation and matter is the difference between the absorption spectra of atoms and molecules, which makes it possible to excite selectively atoms, molecules, or molecular bonds of the desired kind. The differences between the absorption spectra are usually due to the differences between any of the following characteristics of atoms or molecules:

- 1) chemical composition;
- 2) spatial structure;
- 3) isotopic composition;
- 4) isometric composition of the nuclei;
- 5) relative orientation of the nuclear spins.

Therefore, in principle, we can use laser radiation to perform processes I–III (separation, chemical reactions, and detection) at the atomic-molecular level selectively on various chemical elements, molecular bonds, isotopes, nuclear isomers, molecular stereoisomers, ortho- and para-molecules, etc.

Although attention is concentrated now on isotopically selective chemical reactions and isotope separation, the processes being developed are, in principle, applicable to all the above objects of selective laser photophysics and photochemistry. Moreover, in addition to selective chemical reactions and selective separation of matter at the atomic and molecular level, there is also a very important aspect of selective detection of atoms, molecules, or molecular bonds. All this multitude of selective laser photophysics and photochemistry processes is presented in a highly formal manner in Fig. 1, where the types of selective processes are given horizontally and the

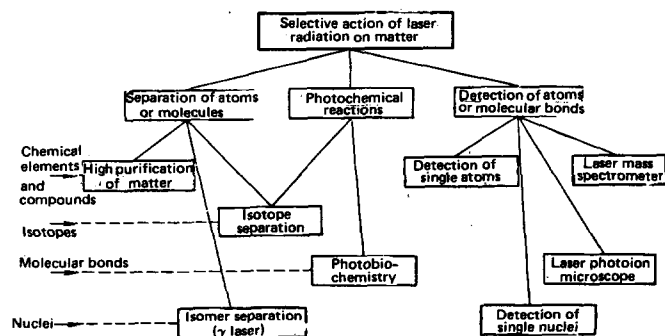


FIG. 1. Types and areas of application of processes in selective laser photophysics and photochemistry.

objects are shown vertically. One must stress that such a classification is largely arbitrary. For example, in the case of photochemical reactions the selectivity may be understood to be the selective participation in the reaction of selected atoms or molecules or the selective participation in the reaction of any particular bond of a molecule intended for desired chemical synthesis. Equally arbitrary but still useful is the division of the objects of selective processes into molecules and molecular bonds. For example, fragments of macromolecules can be regarded as molecular bonds.

Isotopically selective photophysical and photochemical processes are now being investigated quite intensively. Papers presented at recent international conferences on lasers and their applications demonstrate clearly the continuing rapid progress. It is unlikely that there is anyone who has doubts about the enormous promise of these processes in science and technology. The present review will attempt to outline not only the existing but also future, less obvious, applications of selective laser photophysics and photochemistry. Attention will also be given to some non-isotopic selective photoprocesses listed in boxes in Fig. 1. We shall review only the selective photoprocesses whose realization, in the author's opinion, opens up completely new possibilities in some related disciplines, such as nuclear physics, spectroscopy, molecular biology, chemical technology, and biochemistry. Some of the processes discussed below, such as laser identification of the sequence of nucleotides in DNA and laser-selective biochemical processes, are as important as laser isotope separation.^{7,11,12}

3. ELEMENTARY SELECTIVE PHOTOPROCESSES

Recent years have seen the proposals, discoveries, and successful demonstrations of a fairly large number of elementary processes of selective interaction of laser radiation with matter with the aim of isotope separation in various aggregate states: 1. atomic and molecular gases; 2. condensed media; 3. heterogeneous media (interfaces between gaseous and condensed media). However, most of the experiments have been carried out on gases.

The excitation of the quantum states of atoms and molecules may alter the following of their characteristics (Fig. 2):

1. the excitation of an atom or a molecule may reduce the height of the energy barrier (activation energy E_{act}) or a chemical reaction and, consequently, increase the *reactivity* (process 1 in Fig. 2);

2. an excited atom or molecule may have an *ioniza-*

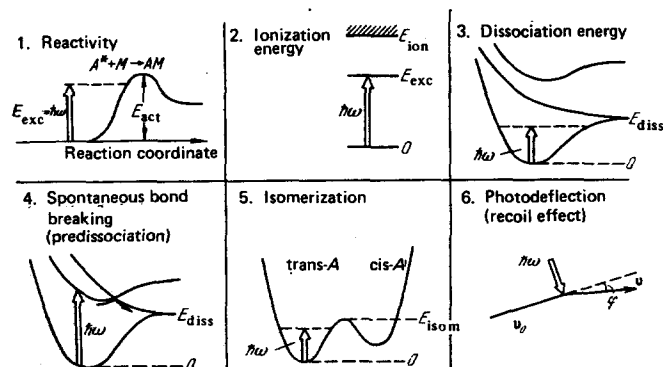


FIG. 2. Properties of atoms and molecules altered by excitation with laser radiation: 1) increase of reactivity; 2) reduction in ionization energy; 3) reduction in dissociation energy; 4) predissociation; 5) isomerization; 6) change in trajectory of motion.

tion energy lower than that of the unexcited species (process 2 in Fig. 2);

3. an excited molecule may have a *dissociation energy* lower than that of an unexcited one (process 3 in Fig. 2);

4. a molecule excited to a stable state may make a transition to a state unstable with respect to dissociation: this is known as *predissociation* (process 4 in Fig. 2);

5. the excitation of a molecule may modify it spatially and this is known as *isomerization*, the result being a molecule with different chemical properties (process 5 in Fig. 2);

6. the absorption of a photon by an atom or a molecule may result, because of the recoil effect, in a minute but entirely observable change in the direction of motion of the absorbing particle, i.e., *particle photodeflection* may take place (process 6 in Fig. 2);

7. an excited atom or molecule may have a higher *polarizability*, different *wave-function symmetry*, etc., which—in principle—should manifest itself as a change in the scattering cross sections of an excited particle by other particles, a change in the nature of its motion in external fields, etc.

Numerous possible photochemical and photophysical laser separation methods follow immediately from the above classification.

In the case of an atomic gas we can use three basically different processes (Fig. 3a): 1. photochemical reaction; 2. ionization; 3. change in the velocity or deflection of a trajectory of selectively excited atoms. In the case of a molecular gas (Fig. 3b) we can use not

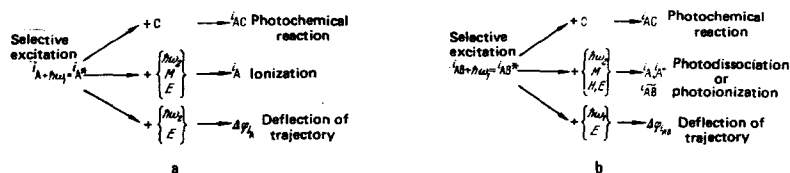


FIG. 3. Main methods of selective interaction of laser radiation with atoms (a) and molecules (b).

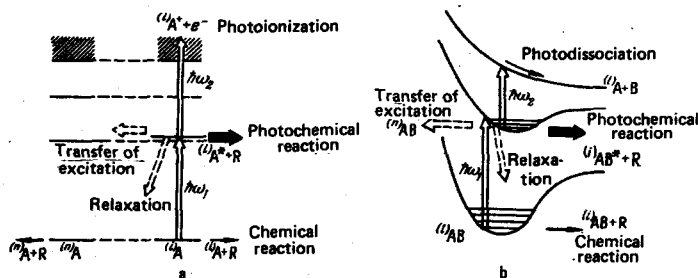


FIG. 4. Universal processes of two-step selective interaction of laser radiation with matter: a) selective two-step photoionization of atoms; b) selective two-step photodissociation of molecules and comparison with photochemical processes.

only these atomic methods, but also two other methods: selective photodissociation of molecules and photoisomerization.

Beginning from 1970¹⁰ our work at the Institute of Spectroscopy of the USSR Academy of Sciences has been concentrated mainly on the photophysical approach in selective action of laser radiation on matter, particularly in isotope separation. The photophysical approach differs greatly from the photochemical methods. This is explained in Fig. 4.

Let us consider an atom (ⁱA) which has ground and excited energy states, as well as a continuum corresponding to the detachment of an outer electron from the atom, i.e., to the ionization of the atom (Fig. 4a). An atom of the same element but different isotope (ⁿA) has slightly displaced energy levels, so that monochromatic radiation can be used to excite the atoms of the selected isotope. Successful experiments involving optical photochemical separation of mercury atoms, based on an increase in the rate of reaction of the excited mercury atoms (A*) with oxygen (acceptor R), were carried out before the last war (in 1933) in Germany.⁹ However, the case of the mercury atoms is exceptional because of the existence of metastable triplet states and high-intensity mercury lamps. Unfortunately, this photochemical approach cannot be applied widely to other elements. In 1970 we suggested a different method based on the ability of laser radiation to transfer a considerable proportion of atoms to a given excited state. We proposed¹⁰ photoionization of selectively excited atoms by an additional laser source before they return to the ground state or lose their excitation energy by collisions with atoms of different isotopic composition. In principle, this can always be done because the probability of photoionization is proportional to the intensity of the additional radiation. Thus, in contrast to the photochemical reaction, the process of selective photoionization does not require collisions with other particles and, consequently, it is fully controlled by laser radiation.

This applies also to molecules. Let us consider a molecule with ground and excited electronic states (stable or unstable), shown in Fig. 4b. In the photochemical approach a selectively excited (ⁱAB*) molecule should, in principle, react chemically—on collision with another particle (acceptor R)—at a rate exceeding the rate of reaction for unexcited molecules. The photochemical reaction process is in competition with the relaxation of the excitation energy and mixing of excitations due to collisions of molecules of different isotopic compositions. We suggested in 1970¹⁰

that selectively excited molecules be photodissociated by additional laser radiation at a rate exceeding the rate of all the undesirable competing processes, to be followed by chemical binding of the radicals formed by photodissociation. Again, in this approach, we have complete control over the selective interaction between laser radiation and matter.

Selective processes in *condensed media* have been studied much less and seem to be less promising because of the broadening of the spectral lines at normal temperatures and fast relaxation of the vibrational excitation. This imposes stringent conditions on the selective interaction experiments, which require: 1) deexcitation of electronic states relaxing much more slowly than the vibrational state; 2) the use of low temperatures at which the broadening of the spectral lines is much less and the vibrational-translational (VT) relaxation is much slower; 3) the use of ultra-short pulses. There are only a few examples of isotopically selective photoprocesses in condensed media^{11,12} and the most important applications to such media are those involving selective photobiochemical processes.

In the case of *heterogeneous media* one can interact selectively with particles in the gaseous phase and with atoms or molecules on the surface of a condensed medium. In the first approach one can employ such processes as photochemical reactions, photoadsorption,¹³ and condensation of excited atoms or molecules.¹⁴ The excitation of atoms or molecules on the surface of a condensed medium may result in selective detachment, photodesorption, and evaporation. The selective detachment of atoms and molecules of a given kind which are absorbed on a surface^{15,16} is a very important but, in practice, difficult to achieve and little-investigated process. The selective detachment of an electron or a proton from particular sections of a macromolecule may be very important in the direct interpretation of the spatial chemical structure of biological molecules.¹⁷

4. CLASSIFICATION OF METHODS

a) Type of photoexcitation

Various types of selective photoexcitation of molecules are shown in very simplified form in Fig. 5. The classical (prelaser) photochemical method is based on one-step excitation of an electronic state of an atom or a molecule. This type of excitation suffers from the following serious shortcoming when applied in selective photochemistry. The majority of molecules, particu-

larly of the polyatomic kind, have relatively wide structure-free electronic absorption bands at normal temperature. Therefore, the majority of such molecules cannot be subjected to isotopically selective excitation. Only a limited number of simple (mainly diatomic and triatomic) molecules has narrow electronic absorption lines suitable for selective excitation. On the other hand, the excitation of an electronic state is convenient because of the high quantum efficiency (yield) of photochemical reactions.

The one-step excitation of a vibrational state of a molecule (photochemistry in the ground electronic state) is characterized by a relatively high selectivity of the excitation of both simple and complex molecules. The main shortcoming of the method is the fast relaxation of the vibrational excitation into heat and the consequently low quantum efficiency of the subsequent photochemical process. Moreover, this method can be used only in the case of photochemical reactions with a low activation energy.

The two-step excitation of an electronic state of a molecule via an intermediate vibrational state by the combined action of IR and UV radiation (Fig. 5b) combines the advantages of the one-step IR and UV processes and eliminates their shortcomings.¹⁸ In the two-step photoexcitation by a two-frequency (IR + UV) laser field we separate the selective excitation function, when a molecule receives relatively small energy (an IR photon), from the absorption of a much higher energy (a UV photon) by a selectively excited molecule. This type of two-step photoexcitation has simultaneously a sufficiently high selectivity and the high quantum efficiency of the photochemical process. These advantages of the two-step (IR + UV) excitation should be manifested particularly clearly in condensed media where it is impossible to resolve the conflict between the high selectivity and high quantum efficiency at normal temperatures.

The two-step excitation of molecules via an intermediate electronic state (Fig. 5b) is not of such universal application as the IR + UV excitation. Its only advantage over the one-step excitation of electronic states is the possibility of exciting states having specific properties and high-lying states without the use of VUV radiation.

In the case of polyatomic molecules one can selectively excite higher vibrational and even excited electronic states simply by sufficiently powerful IR radiation.¹⁹ Multiple absorption of IR photons of the same frequency may result in a molecule acquiring an energy comparable with a typical electronic excitation energy (Fig. 5c). Therefore, it is possible to realize simultaneously the excitation selectivity sufficient even for isotope separation and a relatively high quantum efficiency of the subsequent photochemical process. Here one can also separate the functions of selective excitation and subsequent acquisition of a large amount of energy by an excited molecule in a two-frequency IR field,²⁰ which ensures an increase in the selectivity. A shortcoming of the method of multiple absorption of IR radiation is its applicability solely to polyatomic mole-

cules with a very high density of excited vibrational levels in the ground electronic state.

The last two approaches in selective photochemistry, illustrated in Figs. 5b and 5c, are feasible only in the case of laser radiation because one has to reach a high population of the intermediate quantum levels. This is basically impossible to achieve to any significant degree by means of conventional noncoherent light sources because the radiation temperature is then too low. Conventional light sources are useful only in one-step processes and even then they are much more effective in the case of electronic rather than vibrational states.

Table I summarizes the advantages and shortcomings of each of the above selective photoexcitation methods. Of course one can also use selective excitation techniques which are intermediate compared with those described above. For example, a multifrequency IR field can be used, by multistep excitation, to reach high vibrational levels of even a simple molecule. Alternatively, two-frequency visible laser radiation can be used to excite vibrational levels by a Raman-type process. Therefore, in some cases there may be no sharp divisions between the various methods and the proposed classification of these methods and of their advantages and shortcomings is to some extent arbitrary.

b) Type of photoprocess

An excited molecule may participate in the subsequent photochemical process in accordance with one of several mechanisms. In the most general and simplified form these mechanisms can be classified as follows: 1) photochemical reaction of an electronically or vibrationally excited molecule with a suitable acceptor; 2) photodissociation (or photopredissociation) of an excited molecule; 3) photoisomerization, i.e., a change in the spatial structure of an excited

TABLE I. Comparison of Various Methods for Selective Photoexcitation of Molecules.

Method	Advantages	Disadvantages
1. One-step excitation:		
a) of an electronic state	1) High excitation energy 2) Weak thermal effects	1) Low selectivity for polyatomic molecules
b) of a vibrational state	1) High selectivity	1) Low excitation energy 2) Loss of selectivity due to thermal heating
2. Two-step excitation of an electronic state via an intermediate:		
a) vibrational state	1) High excitation energy 2) High selectivity 3) Weak thermal effects	
b) electronic state	1) High excitation energy 2) Weak thermal effects 3) Flexibility in excitation of high-energy states	1) Low selectivity for polyatomic molecules
3. Multiphoton excitation of high vibrational levels	1) High excitation energy 2) High selectivity 3) Weak thermal effects	1) Unsuitability for simple molecules

molecule. All these photochemical transformations are well known in photochemistry (see, for example,²¹). However, they are not of equal value from the point of view of high selectivity of the photochemical process and its universality. Each of them has its advantages and shortcomings in selective photochemistry.

The first process (participation of excited molecules in reactions) is potentially the most universal. In fact, any molecule can have an excited electronic state with a higher reactivity, which—by means of a suitable scheme (Fig. 5)—may be excited selectively by laser radiation. However, this process requires selection of a suitable acceptor which then reacts faster with the excited than with unexcited molecules. The rate of reaction of the excited molecules with acceptors should be considerably greater than the rate of transfer of the excitation energy by collisions with molecules of the undesired kind, and also higher than the rate of relaxation of the excitation energy. Another fundamental requirement is the retention of the selectivity of the photochemical reaction in the unavoidable subsequent secondary photochemical reactions. These are fairly stringent requirements which are usually very difficult to satisfy. It is sufficient to say that only quite recently has it been possible to demonstrate a high degree of isotopic selectivity of a photochemical reaction²² (an electronically excited IC1 molecule reacted with a $C_2H_2Br_2$ acceptor molecule). All these requirements are particularly difficult to satisfy in the case of vibrationally excited molecules when the difference between the rates of reaction of the excited and unexcited molecules is relatively small.

The photodissociation of the molecules is as universal as the photochemical reactions of an excited molecule. The photodissociation can be achieved either by the excitation of an unstable electronic state (repulsive term) of a molecule or—within the ground electronic state—by strong vibrational excitation. Until very recently the only known photodissociation has been via an excited electronic state and only the availability of high-power IR pulsed lasers has made it possible to realize the second possibility. These two methods of the selective photodissociation of molecules differ very considerably.

Each molecule has excited unstable electronic states suitable for photodissociation. Since the dissociation of a molecule in a suitable electronic term is a very

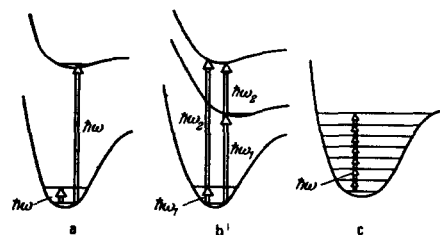


FIG. 5. Types of selective photoexcitation of molecules: a) one-step excitation of an electronic or vibrational state; b) two-step excitation of an electronic state via an intermediate vibrational or electronic state; c) multiphoton excitation by infrared radiation.

fast process ($10^{-13} - 10^{-14}$ sec), it is clear that during such a short time the relaxation and transfer of excitation are unimportant. Since an electronic absorption band representing a transition to a dissociated state is wide the excitation selectivity can be ensured only by a two-step (or multistep) process (Fig. 5b). Therefore, the requirements of the low losses of the excitation because of the relaxation and transfer of the excitation energy apply to an intermediate excited state. A suitable selection of the intensity and duration of UV radiation pulses during the second step can always satisfy these requirements.¹⁸ Since the dissociation products are usually radicals, it is necessary to use radical-collecting molecules which bind them chemically without affecting the original molecules. The selection of such collectors of the dissociation products which do not result in a serious loss of selectivity in the secondary photochemical processes is a simpler task than in the case of chemical reactions of excited molecules.

Sometimes an electronically excited molecule dissociates not because of the repulsive nature of the relevant electronic term but because of the crossing of a stable term with a repulsive one. In this case the dissociation, known as the photopredissociation process, is much slower and takes $10^{-6} - 10^{-12}$ sec depending on the molecule and excited rovibronic states. In view of the narrowness of the absorption lines representing transitions to the predissociation state, a high selectivity of the excitation can be ensured by a one-step photodissociation process.^{23,24} This is an additional advantage of the photodissociation method but it is realized at the expense of the universality because of the limited number of molecules exhibiting the photopredissociation effect.

The photodissociation in the ground electronic state (Fig. 5c) even has potential advantages over the photodissociation via excited electronic states. First of all, it requires less energy; secondly, it yields less energetic radicals. However, it is practically impossible to realize this process with its advantages because of the absence of a suitable method for the photoexcitation of a molecule. One can consider only the vibrational transitions of a molecule but, because of the non-equidistant nature of the subsequent vibrational-rotational transitions in the photoexcitation up to the dissociation limit, one would have to use multifrequency IR laser radiation. This is, in principle, possible but the technology of tunable lasers is not yet sufficiently developed for practical realization of this approach. The situation has become much simpler since the discovery^{25,26} of collisionless dissociation of polyatomic molecules in a strong IR laser field. A rich structure of vibrational-rotational transitions of a polyatomic molecule makes it possible to absorb a fairly large number of IR photons if the laser field is sufficiently strong. Moreover, such a photodissociation process in a single-frequency strong IR field is characterized by a selectivity sufficient for isotope separation.^{19,27} Thus, the photodissociation in the ground electronic state subjected to a strong IR field is a much simpler process but once again at the ex-

pense of some loss of universality (it is inapplicable to simple diatomic and triatomic molecules). The other advantages and disadvantages are common to all the photodissociation methods.

The photoisomerization of a molecule, like the photodissociation, is a monomolecular photochemical process which does not require collisions with other particles. This is an advantage of both these methods compared with chemical reactions of excited molecules, when we have to use collisions with all the resultant disadvantages (loss of excitation energy and of selectivity). But, in contrast to the first two methods, photoisomerization does not require any acceptors and, therefore, there is no loss of selectivity in the secondary photochemical processes. The only shortcoming of the method is the fairly limited number of the molecules which are susceptible to photoisomerization. Since the final state of a phototransition of a molecule in this process is stable, it follows that selective photoisomerization in the case of a narrow absorption line can be achieved by one-step photoexcitation.²⁸ Otherwise, one has to use two-step photoexcitation.

Table II summarizes the advantages and disadvantages of the photochemical process under consideration. This table is incomplete because it ignores such molecular processes as the photoionization and dissociative photoionization which produce charged particles (electrons, positive and negative ions). Although there have been suggestions of selective photoionization of molecules by two-step photoexcitation²⁹ and the first successful experiment has recently been performed,³⁰ these processes can hardly have any advantages in selective photochemistry over photodissociation. Their use is more likely to be limited to selective detection of complex molecules and of molecular bonds when, after selective interaction with laser radiation, it is of basic importance to obtain charged particles.¹⁷

We shall consider in greater detail the main selective photophysical and photochemical processes in the

TABLE II. Comparison of Different Photochemical Molecular Processes.

Process	Advantages	Disadvantages
1. Chemical reaction of molecules in an excited state	1) Universality	1) Special selection of suitable acceptor 2) Loss of selectivity in secondary photochemical processes 3) Loss of excitation due to relaxation 4) Loss of selectivity due to excitation transfer
2. Photodissociation (photopredissociation)	1) Universality (does not apply to photopredissociation) 2) Low excitation losses due to relaxation 3) Absence of selectivity losses due to excitation transfer	1) Need for two-step or multistep photoexcitation (may not apply to photopredissociation) 2) Special selection of acceptor for radical collection 3) Loss of selectivity in secondary photochemical processes
3. Photoisomerization	1) Low selectivity losses due to excitation transfer 2) No need to use acceptor 3) Absence of selectivity losses in secondary photochemical processes	1) Lack of universality

specific application to isotope separation. Naturally, the range of their applications is much wider than just isotope separation. Some of these applications will be considered in later sections of this review.

5. PHOTOPHYSICAL ISOTOPE SEPARATION METHODS

The main photophysical methods which are of practical interest and are being investigated actively in many laboratories, are as follows: 1) selective multi-step ionization of atoms; 2) selective multistep photodissociation of molecules by IR + UV radiation; 3) photopredissociation of molecules; 4) multiphoton dissociation of molecules in a strong IR field. Each of these methods has been demonstrated successfully under laboratory conditions, each has its own advantages and shortcomings, and is either in the stage of being tested under pilot industrial conditions (methods 2 and 3) or is already being used under such conditions (methods 1 and 4).

a) Selective multistep photoionization

The selective photoionization of atoms is the most universal photophysical method for selective separation of matter, particularly of isotopes, at the atomic level. A common feature of all the selective ionization schemes is the following sequence of processes: 1) selective excitation; 2) ionization of the excited atoms. Figure 6 shows some schemes of the selective ionization of atoms which are of interest in laser isotope separation. The two-step scheme is the simplest.^{10,18,31} The three-step scheme can be used, for example, in the case of atoms with a high ionization potential. The photoionization cross section may be increased by tuning the radiation frequency during the last stage to a transition to an autoionizing state (spontaneous³² or induced by an electric field³³), as shown in Fig. 6c. Finally, highly excited Rydberg states of atoms can be ionized either by IR radiation³⁴ or by electric field pulses³³ (see Figs. 6d and 6e).

The first successful selective two-step ionization of atoms (of rubidium) was carried out early in 1971 at the Institute of Spectroscopy of the USSR Academy of Sciences.^{18,31}

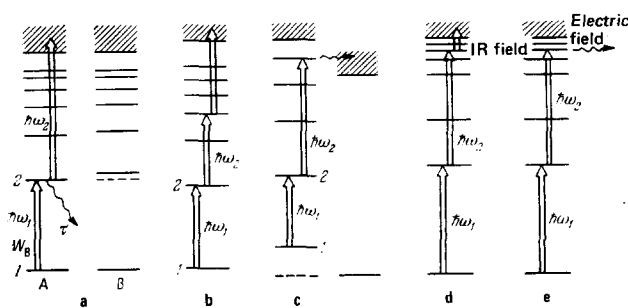


FIG. 6. Methods of selective multistep photoionization of atoms by laser radiation: a) two-step photoionization; b) three-step photoionization; c) two-step photoionization via an autoionizing state; d) two-step selective excitation of a Rydberg state and its photoionization by IR radiation; e) two-step selective excitation of a Rydberg state and its ionization by an electric field.

All the above schemes have been tested experimentally for their suitability in isotopically selective ionization. A detailed discussion of these schemes, their advantages and disadvantages, is outside the scope of the present paper. The interested reader is directed to a special review³⁵ or to corresponding, more compact sections of other reviews.⁴⁻⁷ By way of example, we shall simply list the general requirements which a selective ionization scheme must satisfy in a practical isotope separation system.

1) All the atoms in an unexcited beam should be in the ground state and there should be no ions in the beam. If atoms of the isotope being selected are distributed over several levels or sublevels, it is necessary to use multifrequency radiation to excite atoms from all these sublevels so as to extract completely the required isotope from the mixture. Any thermal ions existing in an atomic vapor should be removed before laser excitation.

2) The laser radiation should cause selective photoionization of each selected isotope. This imposes certain requirements on the power of the exciting and ionizing radiation, which depend strongly on the excitation and ionization cross sections.

3) The intensity of the laser radiation should be utilized practically completely for the excitation and photoionization of the selected isotope. This imposes some requirements on the geometry of the atomic and laser beams, and on the density of atoms in the beam.

4) There should be no transfer of the excitation or charge between the isotopes being separated. This condition limits greatly the permissible density of atoms.

At present the separation of uranium isotopes is attracting the greatest attention. The results of investigations at the Avco Research Laboratory at Everett and the Lawrence Livermore Laboratory have already been published. The first experiments at the Livermore Laboratory were reported at the Eighth International Conference on Quantum Electronics.³⁶ In these experiments the atoms of ^{235}U were excited by a cw dye laser and UV radiation from a mercury lamp was used to photoionize the excited atoms. The enrichment coefficient was 10^2 . In 1975 the same Laboratory reported experiments on two-step ionization of uranium atoms by xenon and krypton ion laser lines.³⁷ The yield of the $^{235}\text{U}^+$ ions in this experiment was at the rate of $2 \times 10^{-3}\text{g/h}$, which was 10^7 times greater than the rate in the first experiment.

A program of research and development on an industrial scale is being pursued in cooperation by the Avco Everett Laboratory and Exxon Nuclear Co. Some results obtained, according to the authors, during the earlier state of their work in 1971 were reported³⁸ in 1975. An experiment, in which the frequency of an exciting pulsed dye laser was varied over a fairly wide range of the transitions in ^{235}U and ^{238}U and a pulsed N_2 laser photoionized the excited uranium atoms in a natural mixture, gave an enrichment coefficient $K(235/238) \approx 140$.

In addition to the uranium isotope separation, which is subject to the fairly stringent conditions formulated above, the methods of selective ionization of other isotopes such as K, Ca, Rb, rare-earth, and trans-uranium elements with a much lower potential yield are being investigated in various laboratories. In such cases a serious problem is presented by the effective ionization of the excited atoms at a moderate average power of the ionizing radiation. The ionization schemes shown in Figs. 6a-6c are inconvenient in these cases and the greatest attention is now being given to the ionization schemes for highly excited atoms shown in Figs. 6d and 6e (these are discussed in a separate review³⁵).

Highly excited atoms are of the greatest interest in isotope separation because of the ease of ionization.^{33,35} The first successful experiment in which the photoionization cross section was increased by an electric-field-induced autoionization of a Rydberg state was carried out on sodium atoms.³⁹ Detailed investigations of the autoionization of highly excited states of Na were also reported elsewhere.⁴⁰⁻⁴² The quantum state with the principal quantum number n lies in the continuum if the electric field is (in atomic units)

$$E_{\text{cr}} \geq (16n^4)^{-1} \quad (1)$$

(1 atomic unit = 5×10^9 V/cm). Figure 7 shows the experimental dependence of the yield of ions on the electric field intensity for the Na atoms excited selectively in the 17^2S state. For electric field pulses of just a few kilovolts per centimeter it is possible to achieve complete ionization of the highly excited atoms.⁴¹ Thus, the use of an electric field provides an effective and simple means for the ionization of highly excited atoms.

b) Selective two-step (IR + UV) photodissociation

The process of selective two-step photodissociation of molecules is practical if the excitation of a mole-

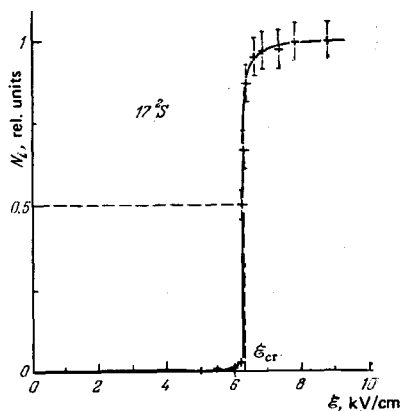


FIG. 7. Dependence of the ion signal on the intensity of a static electric field pulse ionizing an Na atom from the 17^2S state.⁴²

¹⁾ It should be noted that investigation of highly excited atoms is a very active part of research in atomic physics⁴³ but it is outside the scope of the present review.

cule shifts the continuous photoabsorption band which gives rise to the photodissociation. Then, selecting the frequency ω_2 of the additional laser radiation in the region of the shift, where the ratio of the absorption coefficients of the excited and unexcited molecules is largest, one can achieve photodissociation of the molecules excited selectively by laser radiation of frequency ω_1 via an unstable electronic state. In practice, the most interesting is the method of selective two-step photodissociation via an intermediate vibrational state under the action of IR and UV radiation (Fig. 8a).

The two-step photodissociation of molecules is more complex than the two-step photoionization of atoms because of the following effects which influence the selectivity and rate of the process:¹⁸ 1) the thermal nonselective excitation of vibrational levels; 2) the smearing out of the edge of the electronic photoabsorption band of molecules; 3) the bottleneck effect due to the rotational structure of vibrational levels. The first two effects restrict the dissociation selectivity and the third sets an upper limit to the rate of absorption of IR radiation by a molecule⁴⁴ and, consequently, to the rate of the two-step photodissociation of molecules in a gas. A detailed discussion of these effects can be found in reviews^{4,7} and original papers. Here, we shall simply mention that the influence of the first two effects can be reduced considerably by selective excitation of higher vibrational levels (Fig. 8b). This can be done in several ways: 1) direct excitation of high levels by laser radiation at the frequencies of the overtone transitions as was done, for example, for the HCl molecule⁴⁵; 2) successive multistep excitation of high-lying levels by multifrequency IR radiation; 3) resonant excitation of high-lying levels of a polyatomic molecule by IR field pulses involving multiple absorption of IR photons by the molecule, as has been demonstrated for the SF₆,^{20,27} OsO₄,⁴⁶ and many other molecules.

The first successful isotope separation by the method of two-step selective photodissociation was described by Ambartsumyan *et al.*^{47,48} These experiments were carried out on the ¹⁴NH₃ and ¹⁵NH₃ molecules because, firstly, they could be excited selectively by the CO₂

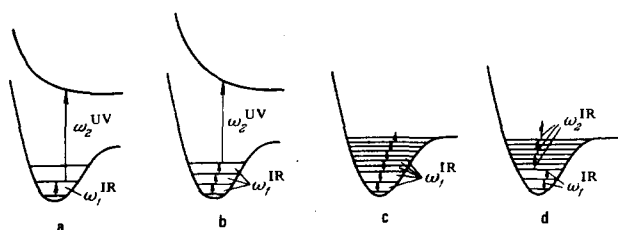


FIG. 8. Methods of selective multistep photodissociation of molecules by laser radiation via an excited electronic state (a, b) and ground electronic state (c, d): a) two-step IR + UV photodissociation; b) multistep selective excitation of high vibrational levels and their photodissociation by UV radiation; c) multiphoton selective excitation and dissociation by a single-frequency intense IR field; d) multiphoton selective excitation of vibrational levels by a resonant IR field and multiphoton dissociation of these levels by nonresonant intense IR radiation.

laser radiation and, secondly, the IR and UV absorption spectra and photochemical decomposition of ammonia had been thoroughly investigated. The enrichment coefficient of the final product in the form of N₂ varied from 2.5 to 6. These results were later confirmed by Japanese investigators.⁴⁹ Separation of the ¹⁰B and ¹¹B isotopes by two-step selective photodissociation of the BCl₃ molecule was carried out by Rockwood and Rabideau⁵⁰ using similar apparatus (a CO₂ laser and a coherent UV radiation source in the 2000 Å range). These experiments resulted in only 10% enrichment of the mixture with the light boron isotope, which was comparable with a typical kinetic isotopic effect.

The universality of the two-step photodissociation of molecules by the combined action of IR and UV radiation is limited to species with an unstable excited electronic state of energy less than 4–5 eV, which can be excited by radiation in the available ultraviolet range ($\lambda_2 > 2000$ Å). From this point of view, a more universal method is provided by multiphoton dissociation of polyatomic molecules in a strong IR field, which occurs because of vibrational transitions within the limits of the ground electronic state. However, since the two-step IR + UV dissociation method is, in principle, applicable to various molecules with heavy isotopic atoms of practical interest, this method is being investigated actively in several laboratories.^{3,5,7}

c) One-step selective photopredissociation

Isotopes can be separated by photopredissociation if a molecule is in an excited state characterized by a resolvable isotopic shift and if it decays mainly by dissociation in such a way that the dissociation products can be removed from the original substance by some simple method. This approach is not as universal as the two-step photoprocesses. Moreover, for the majority of the molecules the spectroscopic and photochemical data are insufficiently comprehensive to determine *a priori* whether these requirements are satisfied.

The process of photopredissociation has been investigated in greatest detail for the formaldehyde molecule mainly by C. B. Moore and his associates. Near the edge of the first excited singlet state, the dissociation of H₂CO into H₂ and CO is characterized by a high quantum efficiency, i.e., the absorption of just one photon produces chemically stable dissociation products. The separation of hydrogen and deuterium in mixtures with equal amounts of H₂CO and D₂CO was demonstrated by Moore *et al.*^{23,51–53} They obtained enrichment coefficients $K(D/H)$ of the order of 9, limited by the laser excitation selectivity.⁵² An experiment was carried out⁵⁴ in which the hydrogen isotopes were separated from a natural mixture of H₂CO and HDCO and the enrichment coefficients $K(D/H)$ was 14 when formaldehyde was illuminated with radiation from a cw He–Cd laser at 325.03 nm. Illumination of the H₂¹²CO:H₂¹³CO = 1:10 mixture ensured 80-fold enrichment of CO with the ¹²CO isotopic molecule.⁵⁵ Current spectroscopic and photochemical investiga-

tions⁵⁸ should give us a fuller understanding of the photoprocesses in formaldehyde and result in practical systems for the separation of the ¹³C, ¹⁸O, and ¹⁷O isotopes.

A number of experiments has also been carried out on selective photopredissociation of other molecules. Leone and Moore⁵⁷ excited Br₂ to the predissociation ³Π_{0,+} state and avoided many potential mixing processes by the fact that they observed IR chemiluminescence of the HBr molecules formed in vibrationally excited states in the course of the reaction of Br with HCl. The enrichment coefficient $K(^{81}\text{Br}/^{79}\text{Br})$ was about five. Bazhutin *et al.*^{58,59} converted ortho-iodine molecules into para-iodine by selective predissociation of ortho-I₂ excited with the 514.5 nm line of an argon laser and reported that the enrichment coefficient $K(\text{para}/\text{ortho})$ was of the order of 2-4. This process can be used to separate the iodine isotopes. Hochstrasser and King¹¹ and Karl and Innes⁶⁰ obtained independently high enrichment coefficients of the nitrogen and carbon isotopes by irradiation of *s*-tetrazine molecules with natural proportions of the isotopes in a low-temperature condensed medium¹¹ and in the gaseous phase.⁶⁰ They demonstrated that predissociation was due to the reaction *s*-tetrazine - N₂ + 2HCN.

Photopredissociation promises to become a practical isotope separation method. The work done on H₂CO and, possibly, on *s*-tetrazine may lead to economically viable methods for the enrichment with the ¹³C, ¹⁴C, ¹⁷O, and ¹⁸O isotopes. Although this method is not as universal as the two-step techniques, it may be more practical in those situations in which it is applicable.⁷

In spite of the great simplicity of the photopredissociation approach, it has not yet reached the stage of pilot installations for any one of the isotopes mentioned above. This may be due to the limited output energies of narrow-band UV tunable lasers. The discovery of high-efficiency excimer lasers may greatly accelerate the practical implementation of this method.

d) Multiphonon dissociation of molecules

All the above laser isotope separation methods are based on the excitation of the electronic states of atoms and molecules with visible or ultraviolet radiation. The method described below is quite different because it utilizes only high-power IR laser radiation for the direct excitation of very high vibrational levels in the ground electronic state (Figs. 8c-8d). The method is based on the isotopically selective dissociation of polyatomic molecules (BCl₃,¹⁹ SF₆,²⁷ OsO₄,⁴⁶ and others) by high-intensity CO₂ laser pulses. This effect was discovered in 1974 at the Institute of Spectroscopy of the USSR Academy of Sciences.¹⁹ Its discovery was a logical and natural result of our systematic work on the isotopically selective dissociation of molecules by laser radiation. This discovery was preceded by several investigations^{25,26,61-63} of the interaction of high-power IR radiation pulses with molecular gases. This early work was reviewed in detail by

Ambartsumyan and Letokhov⁸ and was briefly mentioned elsewhere.⁶⁴

One should recall here also the work of Askar'yan⁶⁵ and of Bunkin *et al.*⁶⁶ who considered theoretically the build up of vibrations and dissociation of a diatomic molecule in a strong laser field. Although multiphoton dissociation of a diatomic molecule requires exceptionally high intensities (10¹¹-10¹² W/cm²) and has not yet been realized experimentally, the early studies^{65,66} put forward the idea of a strong vibrational excitation and dissociation of a molecule within the ground electronic state. There is some similarity here with the phenomenon of strong excitation and dissociation of polyatomic molecules in a resonant IR field of moderate intensity (10⁵-10⁷ W/cm²) discussed earlier.

The essence of this effect is as follows. When the frequency of the CO₂ laser radiation is tuned to a vibrational band of a molecule whose isotopic shift is comparable with or even greater than the width of the Q branch of the vibrational band, irreversible dissociation of isotopic molecules occurs at intensities of the order of 10⁷-10⁹ W/cm². This is reflected by a change in the isotopic composition (enrichment) of undissociated molecules and of molecules formed as a result of dissociation. In the first experiments²⁷ the enrichment coefficient of the residual SF₆ gas with the ³⁴S isotope reached values in excess of 3000.

The chemical composition of some pure gases (BCl₃, OsO₄, etc.) remains unchanged under the action of even strong radiation which produces visible luminescence, i.e., which definitely dissociates these molecules. Investigations have shown that this is due to the reverse reaction, i.e., due to the recombination of the dissociation products to form the original molecules again. If acceptor molecules are added to the gas and these react with the dissociation products before their recombination, an irreversible isotopically selective dissociation of the original molecules takes place when high-power IR radiation acts on a gas mixture (BCl₃ + O₂,^{19,67} OsO₄ + C₂H₂,⁴⁶ etc.). In this more general sense the dissociation under the action of high-power IR radiation is typical of all polyatomic molecules and is not limited to some of them.

Much information has now been gathered on the separation of isotopes by dissociation as a result of multiphoton IR absorption in a large number of polyatomic molecules (⁽ⁱ⁾BCl₃,^{19,67,68} ⁽ⁱ⁾SF₆,^{27,69,79} ⁽ⁱ⁾OsO₄,⁴⁶ ⁽ⁱ⁾C^(j)Cl₄,^{71,72} ⁽ⁱ⁾SiF₄,⁶⁸ ⁽ⁱ⁾C₂F₂Cl₂,⁶⁸ CH₃⁽ⁱ⁾NO₂,⁷³ ⁽ⁱ⁾MoF₆,⁷⁴ ⁽ⁱ⁾H₂Cl₂C₂,⁷⁵ ⁽ⁱ⁾H₂CO,⁷⁶ etc.). The most thorough and comprehensive investigations were made of the dissociation of the SF₆ molecules.^{69,77} These investigations made it possible to understand the nature and principal characteristics of the process of selective dissociation itself and of the isotope separation by this process. A detailed description of the method of multiphoton IR laser photochemistry was given in a special review.⁸ Here, we shall discuss briefly only some of the most important features of this method.

A polyatomic molecule can absorb a large amount of

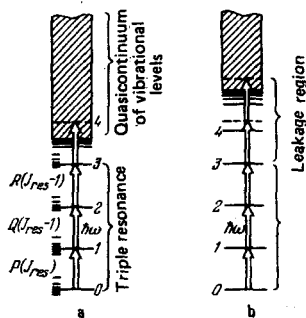


FIG. 9. Explanation of the mechanism of dissociation of a polyatomic molecule in a strong IR field: a) selective multi-step excitation by triple vibrational-rotational resonance and subsequent excitation of molecules in "vibrational quasicontinuum"; b) selective excitation due to triple resonance followed by "leakage" to the vibrational quasicontinuum.

energy (3-5 IR photons) from an IR field of relatively moderate intensity (about 10^5 - 10^6 W/cm²) because of "soft" compensation of the vibrational anharmonicity in lower transitions. The threshold intensity (or, more precisely, the threshold energy density of laser pulses of less than 10^{-6} sec duration) needed for dissociation is clearly related to the saturation of vibrational transitions lying in the vibrational quasicontinuum, which is characteristic of polyatomic molecules. Figure 9 gives a very simplified explanation of the dissociation of polyatomic molecules by a resonant IR field. The existence of the mechanism of soft compensation of the anharmonicity in the case of lower vibrational transitions was proved by successful experiments²⁰ on the dissociation of the SF₆ molecule in a two-frequency IR field (Fig. 8d). The IR field of relatively low intensity and frequency ω_1 excites molecules selectively and transfers them to states at the lower edge of the vibrational quasicontinuum. The frequency ω_1 is in resonance with a molecular vibration ν_3 . The infrared field at the second frequency ω_2 is detuned relative to ω_1 and serves to excite the molecules by transitions in the vibrational quasicontinuum right up to the dissociation limit.

The soft compensation of the anharmonicity may be ensured by a change in the rotational energy of a molecule in vibrational transitions in the P and R branches⁷⁸ or by anharmonic splitting of degenerate vibrational levels of a symmetric polyatomic molecule.^{79,80} The dissociation in a two-frequency IR field makes it possible to separate the functions of selective excitation and dissociation between two fields of different frequencies. This increases the dissociation selectivity because the nonresonant strong field does not broaden the lower resonant transitions as a result of the dynamic Stark effect and, on the other hand, in the case of dissociation of selectively excited molecules one can use a strong field with a fairly coarse frequency tuning. In the very first experiments on the dissociation of the SF₆ molecule in a two-frequency IR field²⁰ it was found that the rate of dissociation depended on the frequency ω_2 of the dissociating radiation. This dependence was much broader compared with the sharp dependence on the frequency ω_1 of the ex-

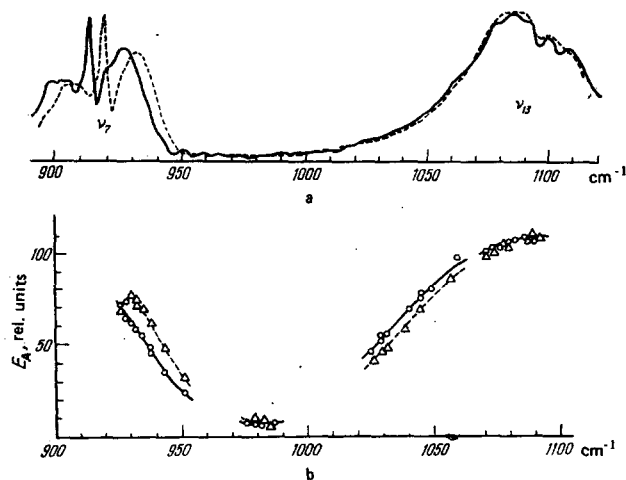


FIG. 10. Isotopic effect in the ν_7 and ν_{13} bands of nitromethane: a) linear absorption spectrum at 20 Torr; b) spectrum of multiphoton absorption of 10^9 W/cm² radiation at 2 Torr.⁷³ The continuous curves refer to CH₃¹⁵NO₂ and the dashed curves refer to CH₃¹⁴NO₂.

citing field. This indicated that the absorption by transitions in the vibrational quasicontinuum had broad red-shifted (for SF₆) maxima near the frequencies of the fundamental vibrations. Thus, fine tuning of the frequency ω_1 to a value corresponding to the maximum dissociation selectivity and coarse tuning of the frequency ω_2 to a value corresponding to the minimum threshold dissociation intensity ensures optimal conditions for isotopically selective dissociation of a polyatomic molecule in unfocused beams of two-frequency IR radiation.⁸¹

This method is now the most promising one for the separation of the isotopes of heavy elements by IR radiation.⁸ Recent investigations^{81,82} carried out using this two-frequency method resulted in the enrichment of the Os isotope by dissociation of the OsO₄ molecules of natural isotopic composition. The enrichment coefficient obtained was $K \approx 1.6$, whereas in the case of dissociation of the same molecule by a single-frequency strong IR field there was no enrichment at all.

Multiphoton excitation of the vibrational levels opens up a new possibility for isotopically selective excitation in the absence of an isotopic shift in linear IR absorption.⁷³ Figure 10a shows the spectrum of linear absorption by the CH₃¹⁴NO₂ and CH₃¹⁵NO₂ molecules in the 900-1100 cm⁻¹ range (ν_7 and ν_{13} bands), obtained with a resolution of 0.5 cm⁻¹. Within the limits of experimental error, there is no isotopic shift of the ν_{13} band. In a strong IR field (of intensity in excess of 10^7 W/cm²) the absorption spectrum of both molecules changes in different ways, which is equivalent to the appearance of an isotopic shift at ν_{13} of the order of 5 cm⁻¹ (Fig. 10b). This effect has been used to separate nitrogen isotopes in an isotopic mixture of nitromethane molecules.

Only a small proportion of the laser methods of isotope separation demonstrated successfully in the laboratory to yield a trace or even a weighable amount is promising for isotope separation on an industrial

scale. A method potentially suitable for industrial application should have at least the following two features:

- 1) the availability of laser radiation with an average power between 1 kW and 1 MW (depending on the required yield rate);
- 2) simplicity and relatively low cost of the laser equipment in the installation and operation stages.

These two requirements limit greatly the number of methods suitable for exploitation on an industrial scale if the currently available lasers are to be used.

The ready availability and the relatively low cost of generating high-power IR radiation in molecular lasers and the relative simplicity of the multiphoton dissociation by IR fields makes this method the most suitable for implementation in pilot units. The first experiments⁸³ on isotope separation in the field of a pulsed CO₂ laser with a high average power (up to 500 W) and a high pulse repetition frequency have shown that even under these conditions a relatively high isotopic selectivity of the dissociation process is retained. Figure 11 shows the experimental dependence of the isotopic selectivity of the dissociation of the SF₆ molecule (deduced by mass analysis of the dissociation product SOF₂) on the repetition frequency of the CO₂ laser pulses for the same total number of pulses. These results demonstrate clearly the possibility of constructing a sufficiently efficient unit for the separation of isotopes by the CO₂ laser radiation.

The simplicity and technological feasibility of this laser isotope separation method should make it possible to use it on an industrial scale in the near future.⁸³ If we use the parameters of the process already achieved under laboratory conditions, we find that for an average CO₂ laser pulse power of 1 kW (pulses of 10 J energy and 100 Hz repetition frequency) and for 10% utilization of the laser radiation we may expect about 0.3 g/h of the ³⁴S isotope enriched to 80%. The expected cost of the enriched stable isotopes ¹³C, ¹⁵N, ¹⁷O, ¹⁸O, and ³⁴S applicable to the prototype apparatus should be tens of times lower than the current cost.

We shall conclude by drawing attention to the possibility of using the method in large-scale isotope manufacture. We have in mind the separation of isotopes required in atomic industry, such as monoisotopic construction materials, enrichment of nuclear fuel, and

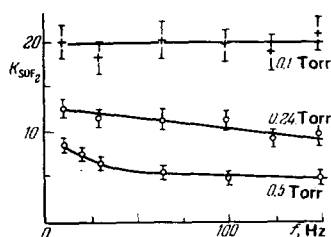


FIG. 11. Dependences of the isotope enrichment coefficient of the product (SOF₂) of the dissociation of the SF₆K molecule (³²S/³⁴S) on the repetition frequency *f* of pulses from a TEA CO₂ laser at various pressures (0.1, 0.24, and 0.5 Torr) for a fixed total number of pulses *N* = 1000.⁸³

manufacture of heavy water for reactors.^{3,4}

By way of example, we shall consider the possibility of preparing monoisotopic materials with a low neutron capture cross section, in particular, the separation of the titanium isotopes.³ The ⁵⁰Ti isotope (natural abundance 5.3%) has an exceptionally low capture cross section for slow neutrons (0.14 b). Its various alloys have excellent mechanical properties at high temperatures and are highly resistant to corrosion. Titanium might be used instead of zirconium for jackets of nuclear reactor elements. It is already possible to predict with high probability that an efficient and economic process will be developed for the separation of the titanium isotopes by the use of the CO₂ laser radiation on TiCl₄ molecules, which have an overtone vibrational band in the stimulated emission region of the CO₂ laser and which have a large isotopic shift. The dissociation of one TiCl₄ molecule requires about 10 eV of the CO₂ laser radiation and if the efficiency of utilization of this radiation is 10% and the laser efficiency is also 10%, about 1 keV of electrical energy is required to extract one ⁵⁰Ti atom, which corresponds to about 500 kWh per 1 kg of ⁵⁰Ti. Since TiCl₄ is the intermediate product in nonferrous metallurgy, and its vapor pressure will permit the occurrence of the process at room temperature, we may expect the cost of enrichment with the titanium isotopes to be lower than, or of the same order as, the cost of the preparation of the original product.³

6. PHOTOCHEMICAL ISOTOPE SEPARATION METHODS

The possibility of photochemical separation of isotopes by excitation of the electronic states of atoms and molecules and of the vibrational levels of molecules has now been demonstrated successfully. However, in spite of the considerable optimism of the early investigations, the actual progress has been much less remarkable²² than that achieved by the photophysical methods described above.

a) Electronic photochemistry

Chemical reactions of electronically excited atoms and molecules have been the subject of active research for many years, mainly before the appearance of the first lasers. Photochemical separation of the mercury isotopes by excitation with the 253.7 nm resonance line using a large number of various reagents has been demonstrated successfully.^{9,84,85} For example, Pertel and Gunning⁸⁴ increased the amount of ²⁰²Hg from 30% of its natural abundance to 85% in mixtures with Hg, H₂O, and butadiene. The kinetics of the photochemical reactions of Hg has been found to be so complex that even the intensive work of Gunning *et al.* (see the relevant review⁸⁶) has failed to give the full picture of the process. Harteck *et al.*^{87,88} separated successfully the following isotopes by excitation with atomic resonance lamps: the (¹)NO molecules by a lamp based on the Br atoms and (¹)CO by a lamp based on the I atoms. The enrichment coefficient was of the order of 4–6.

Clearly, laser sources have many advantages over

noncoherent radiation in the optical separation of isotopes. The wide tuning range and the high resolution limit make it possible to select relatively freely the absorption lines in the visible, ultraviolet, and possibly vacuum ultraviolet regions and to ensure the highest selectivity.

Several successful photochemical laser separation schemes have been reported recently mainly by Zare *et al.* The most interesting results were obtained in photochemical separation of the ^{35}Cl and ^{37}Cl isotopes by selective excitation of the I^{37}Cl molecules with radiation of a cw dye laser.⁸⁹ The laser radiation excited only the I^{37}Cl molecules to a state below the predissociation limit. These excited molecules participated in two types of reaction. In one case the I^{37}Cl molecules reacted with trans-ClHC=CHCl , forming cis-ClHC=CHCl , enriched by 10% with the ^{37}Cl isotope. In the other case they reacted with 1,2-dibromoethylene, forming trans-IClC=CHCl , enriched by 50% with the ^{37}Cl isotope. The highest enrichment in this scheme at a pressure of 7.5 Torr in the mixture was reported by Zare in the summer of 1976.⁹⁰ Using a dye laser with a high average output power, Stuke and Schafer were able to improve greatly on these results.⁹¹ At present these are the most promising results in isotopically selective electronic photochemistry.

Another successful experiment on a diatomic halogen was described by Balykin *et al.*^{59,92} Molecules of ortho- I_2 mixed with 2-hexene were excited with the 514.5 nm line of a cw argon laser. The excited molecules of ortho- I_2 reacted with 2-hexene and the unexcited molecules of para- I_2 did not react. Selective photochemical reaction of the ortho- I_2 molecules investigated in these experiments^{59,92} was a repetition, under new circumstances, of an experiment in pre-laser selective photochemistry⁹³ and could be used directly to separate the stable and radioactive iodine isotopes.

Lamotte *et al.*⁹⁴ excited selectively a mixture of Cl_2CS molecules with diethoxyethylene and achieved enrichment of the Cl isotopes. A mass-spectroscopic analysis of the residual Cl_2CS molecules obtained after irradiation with an argon or a dye laser indicated that the concentration of ^{35}Cl changed from the natural value (75%) to 64% or 80%, depending on the isotopic molecule selected for irradiation.

The considerable potentialities of the electronic photochemistry have not been demonstrated to the extent expected of such an old classical approach. This may be due to a number of factors. Firstly, as pointed out in the Introduction, the problem of the loss of selectivity in secondary processes is much more serious in photochemical than in photophysical methods. For example, even in such an ideal case as the reaction of selectively excited metastable mercury atoms, the enrichment coefficient (because of the secondary processes) does not exceed 14 in spite of the large number of experiments.⁸⁶ Secondly, the electronic photochemistry method⁴⁻⁷ is not suitable for separating the uranium isotopes and probably the majority of investi-

gations are attempting this separation. Thirdly, it is still expensive to generate visible and UV laser radiation and high-power lasers for this range are still few and far between.

b) Vibrational photochemistry

The rate of a chemical reaction may be increased considerably by vibrational excitation of the reacting molecules. Gibert⁹⁵ suggested this method for laser isotope separation back in 1963. However, the first successful experiment was carried out by this method over a decade later.⁹⁶

Vibrational levels may be excited in a great variety of ways (Fig. 12). The fundamental vibration active in absorption may be excited by just one photon (Fig. 12a). The excitation of a composite or overtone band creates two or more vibrational excitation quanta in a molecule after the absorption of one photon of higher energy (Fig. 12b). High vibrational levels may also be reached by multistep excitation via one or more intermediate vibrational levels using multifrequency laser radiation (Fig. 12c). One can also use a Raman-type process (Fig. 12d). This is the only method for the excitation of vibrations with zero dipole moment of the transition (for example, in the case of homonuclear diatomic molecules). Selective excitation of high vibrational levels by multiphoton absorption of IR radiation of relatively moderate power (10^6 – 10^7 W/cm²) gives one additional and probably the only effective method for direct excitation of vibrational levels of energies amounting to a few electron-volts (Fig. 12e). All these excitation schemes were tested in experiments on laser isotope separation.^{4,5} Positive results were obtained by the last three schemes (Figs. 12c–12e). However, the number of the experiments carried out was very small and did not give any totally conclusive evidence. The success or failure of any given experiment was most probably governed by the selection of the experimental conditions and a suitable acceptor rather than by the excitation scheme. Naturally, the schemes involving the excitation of high vibrational levels are preferable because they potentially ensure a wider range of possible chemical reactions and a

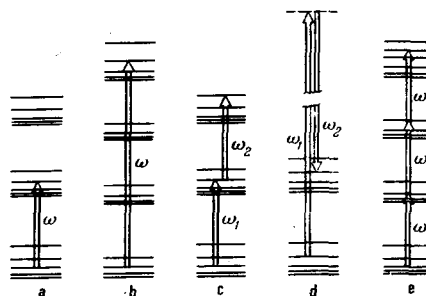


FIG. 12. Methods of selective excitation of vibrational levels of molecules by laser radiation: a) absorption of one photon in the fundamental band; b) absorption of one photon in the second overtone; c) two-step excitation in a two-frequency IR field; d) Raman excitation of a vibration inactive in infrared absorption giving rise to two-frequency visible laser radiation; e) multiphoton excitation of high vibrational levels by single-frequency intense IR radiation.

weaker influence of the thermal mechanism of reduction of the separation selectivity.

Arnoldi *et al.*⁹⁶ reported enrichment with the ³⁵Cl isotope because of an increase in the rate of the reaction of Br atoms with HCl molecules. They used a pulsed chemical HCl laser for successive excitation of the HCl molecule from the $\nu = 0$ state to the $\nu = 1$ state and then to $\nu = 2$ (Fig. 12c). Selective excitation of HCl accelerated the $\text{Br} + \text{H}^{35}\text{Cl}(\nu = 2) \rightarrow \text{HBr} + {}^{35}\text{Cl}$ reaction by about eleven orders of magnitude compared with the rate of the reaction between Br and $\text{HCl}(\nu = 0)$. The isotopic enrichment was measured by mass-spectroscopic analysis with a time resolution of the BrCl molecules formed in the secondary $\text{Cl} + \text{Br}_2 \rightarrow \text{BrCl} + \text{Br}$ process. For equal pressures of Br and HCl the enrichment factor was 2.

Recently Panfilov *et al.* were able to observe enrichment of the carbon isotopes in the reaction of selectively excited (¹)CH₃F molecules with bromine atoms.⁹⁷ Although the enrichment coefficient was small, this experiment was interesting from the point of view of using a cw IR laser.

Raman excitation of the N₂ molecules in air at 77 °K enables Basov *et al.*^{98,99} to obtain NO molecules enriched with the ¹⁵N isotope by a factor of 100. This could be due to the reaction $\text{N}_2^* + \text{O}_2 \rightarrow 2\text{NO}$. Basov *et al.* interpreted these results in terms of the mechanism^{100,101} based on the vibrational exchange of excitation between the N₂ molecules in the course of pumping of high levels by a mechanism considered by Treanor *et al.*¹⁰² (see the review by Basov *et al.*¹⁰³). The same separation method and the same interpretation were used by Basov *et al.* in the experiment on isotope separation in an electric discharge where the enrichment of NO with the ¹⁵N isotope reached 10. However, the results reported there were in conflict with those given by Manuccia and Clark.¹⁰⁴ Therefore, the interpretation of the results given by Basov *et al.*^{98,99} should not be regarded as final.

Pumping of the BCl₃ molecules in BCl₃ + H₂S and BCl₃ + D₂S mixtures by focused CO₂ laser pulses, which probably excited fairly high vibrational levels of BCl₃, resulted in separation of the boron isotopes.¹⁰⁵ Irradiation of a mixture with a natural proportion of the boron isotopes either with the P(16) or with the R(20) line of the 10 μ band of a CO₂ laser resulted in enrichment of the residual BCl₃ amounting to $K(10/11)$ of about 1.7 and $K(10/11) \approx 0.7$, respectively. Clearly, this experiment was intermediate between one-photon IR photochemistry in a weak field and multiphoton IR photochemistry in a strong field.

An attractive feature of the vibrational photochemistry in isotope separation is the possibility of using IR photons of low energy emitted from highly efficient molecular lasers so as to ensure a high efficiency of the process. However, in respect of the efficient utilization of IR photons, the IR photochemistry method has strong competitors in the methods of multiphoton excitation and dissociation of polyatomic molecules in a strong IR field. The multiphoton ap-

proach has a number of shortcomings compared with the vibrational photochemistry (in particular, the applicability to polyatomic molecules alone) but it is less critical in respect of many other conditions. Later experiments will undoubtedly demonstrate the range of conditions under which each of these approaches can be used with advantage.

7. PREPARATION OF PURE SUBSTANCES

The methods of selective photophysics and photochemistry developed for isotope separation enable a fresh approach to be made to the technology of preparation of substances at the atomic and molecular level because laser radiation makes it feasible to manipulate directly atoms and molecules of a given kind, i.e., to collect macroscopic amounts of matter, one atom or one molecule at a time. The most important process with universal atomic-molecular laser materials-science applications is undoubtedly the preparation of very pure substances in the atomic state and of alloys and molecular compounds. Very pure substances can be prepared or impurities can be removed by selective photoionization of atoms and by selective photodissociation of molecules. Their potentialities and ranges of application are naturally very different.

a) Selective photoionization of atoms

This approach to materials science is the most universal and flexible. An optimal selective photoionization scheme for atoms using two (or, in principle, a larger number) laser beams with suitably tuned frequencies and appropriate intensities makes it possible to ionize each atom in 10^{-5} – 10^{-7} sec. If we assume 20% utilization of the laser radiation energy of average power 10^3 W, we find that photoionization of atoms of $E_i \approx 7$ –8 eV ionization energy makes it possible to ionize selectively about 1 mole per hour. Consequently, a small-scale unit may, in principle, produce several tonnes of a pure substance per year. Therefore, the method of selective ionization of atoms by tunable lasers with an average output power of 100–1000 W can be regarded as a sufficiently productive method for fine separation of matter at the atomic level.¹⁰⁶

Laser purification by selective ionization¹⁰⁶ should have a number of important advantages compared with the existing methods for the purification of substances based on the difference between any chemical or physical properties of the substance being purified and impurities. We shall now review briefly these advantages.

1) *High selectivity or high degree of purification in a single-stage process.* The degree of purification in the process of separation of a given element from any impurities may reach values exceeding 10^3 . This value is governed by the process of charge exchange in collisions of ions of a given element with neutral impurity atoms. In principle, a reduction of the density of atoms in a beam should make it possible to achieve selectivity much higher than 10^3 at the expense of the rate of yield. In particular, if a material produced on a

mass scale of $10^{-7}\%$ purity is considered, then selective ionization of atoms may help to purify it to $10^{-100}\%$.

2) *Universality.* Selective ionization may be achieved by a suitable selection of laser frequencies for practically any element irrespective of its physical and chemical properties (melting and boiling points, reactivity, etc.). If one or several specific elements have to be removed, it may be possible to ionize selectively only the impurities and remove them from an atomic beam. This gives the maximum productivity and minimum loss of energy of the coherent light.

3) *Flexibility.* This makes it possible to use directly ion beams in preparation of pure films or for implantation of ions in a homogeneous substance (ion-implantation doping). An ion beam may be directed on the surface of a substrate to prepare a pure film of a given element. It may be possible to simultaneously and independently ionize selectively two or three elements in different beams and to deposit their ions on the same surface. In this way it may be possible to prepare films of complex atomic compounds, whose stoichiometric composition is controlled by the intensities of the laser and ionic beams. The whole process of selective ionization of atoms, extraction of ions from the beam, and their deposition on the substrate may take place in high vacuum. The process does not require any contact of the substance being purified with reagents or other materials apart from the substrate, and the latter can always be chosen to be free of undesirable impurities.

One should draw attention separately to the application of selectively formed photoions of boron, arsenic, phosphorus, and other elements in ion-implantation of semiconductors.³⁵ Electrode-free laser preparation of ions of a given kind, firstly, removes the need to use an electromagnetic mass separator and, secondly, makes it possible to construct separately a high-temperature source of atoms and an ionizer. This is quite important because it facilitates photoionization of atoms near a high-voltage electrode and, consequently, may simplify greatly the construction of electrostatic accelerators producing ions of energies of the order of a MeV or more.

The successful development of this photoionization method will depend, firstly, on the development of optimal multistep systems for selective ionization of various elements and, secondly, on the availability of sufficiently efficient tunable UV and visible lasers with a high average power and high performance characteristics. A universal and optimal ionization scheme ensuring a high degree of excitation and a high ionization yield is the multistep resonant excitation of states near the ionization limit and subsequent autoionization of highly excited atoms by electric field pulses, proposed by Ivanov and Letokhov.³³ The first experiments demonstrated the fruitfulness of this approach.^{39,40} As far as lasers are concerned, the existing main difficulty involving UV range lasers will be overcome by the use of excimer lasers.

b) Selective dissociation of molecules

This process can be used to purify substances in the gaseous phase by removal of molecular impurities which are difficult to remove by conventional means. The possibility of purification by the method of dissociation of impurity molecules is based on the difference between the physicochemical properties of the dissociation products and the original substance. This makes it possible to apply standard purification methods at the end of the process after irradiation of the mixture.

The feasibility of purification in the gaseous phase by the dissociation of impurity molecules in a high-power infrared radiation field was recently demonstrated experimentally¹⁰⁷ by purifying arsenic trichloride AsCl_3 from 1,2-dichloroethane ($\text{C}_2\text{H}_4\text{Cl}_2$) and carbon tetrachloride (CCl_4) impurities. The usual purification methods ensure that the minimum content of these impurities is of the order of 10^{-2} – $10^{-30}\%$. The absorption bands of the $\text{C}_2\text{H}_4\text{Cl}_2$ and CCl_4 impurity molecules lie in the CO_2 laser emission range, where there are no absorption bands of the main substance AsCl_3 (Fig. 13). Therefore, one can use the dissociation of polyatomic molecules in a strong CO_2 laser field. The final dissociation products are identified by the IR absorption spectra (in the case of $\text{C}_2\text{H}_4\text{Cl}_2$) and by the mass spectra (in the case of CCl_4). The reported experiments¹⁰⁷ demonstrated clearly selective dissociation of the $\text{C}_2\text{H}_4\text{Cl}_2$ and CCl_4 impurities in AsCl_3 when the pressure of the latter was of the order of 10 Torr. The initial content of the impurity molecules was relatively high, which was not due to the limitations of the method but due to the sensitivity of the recording procedure. In the case of 1,2-dichloroethane the products differed greatly in respect of their properties from AsCl_3 , so that it was possible to separate them easily and ensure purification of AsCl_3 . A recent experiment carried out in Los Alamos¹⁰⁸ demonstrated the possibility of selective dissociation of impurity molecules (PH_3 , AsH_3 , B_2H_6) by ultraviolet radiation from an ArF excimer laser illuminating SiH_4 molecules. The selectivity was based on the stronger absorption of the ultraviolet radiation of 193 nm wavelength by the impurity molecules. Laser purification of monosilane is of practical interest in connection with the technology of the preparation of pure silicon for semiconductor industry.¹⁰⁸

The method of selective dissociation of molecules is clearly applicable not only in the preparation of pure materials but also in the removal of toxic or

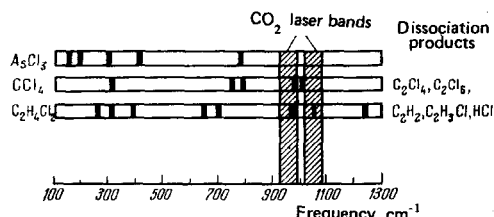


FIG. 13. Purification of AsCl_3 gas by selective dissociation of CCl_4 and $\text{C}_2\text{H}_4\text{Cl}_2$ impurity molecules by CO_2 laser radiation.

carcinogenic materials from gaseous impurities, i.e., in selective atmospheric photochemistry. If such impurities are transformed to their inactive forms, the method becomes quite simple and self-contained.

8. SELECTIVE LASER BIOCHEMISTRY

Selective action of laser radiation on complex molecules in condensed media is a possibility important because of its consequences in molecular biology, but which has been little investigated and is not self-evident. In the case of a condensed medium at normal temperatures, the conflict between the requirements imposed on selective excitation and the possibility of retention of the excitation selectivity is particularly acute. The electronic states of biomolecules are grouped in the ultraviolet range and it is difficult to expect a high selectivity of the excitation of selected molecules in a mixture. On the other hand, the electronic excitation is usually retained for a time ($\sim 10^{-9}$ sec) sufficient for photochemical reactions with a significant quantum efficiency.¹⁰⁹ Vibrational excitation of molecules is much more selective but the excitation energy relaxes quickly into heat (at 300°K the relaxation time is $T_{1}^{vib} \leq 10^{-11}$ sec). Since the energy of a single vibrational quantum differs only by a small factor from the thermal energy kT , it is difficult to expect a significant contribution to the biochemical reaction rate from short-lived vibrationally selective excitation compared with the continuously acting non-selective thermal excitation.

The successful experience in realizing isotopically selective photoprocesses in gaseous media suggests at least two possible ways of avoiding the conflict referred to above: 1) a combination of selective vibrational excitation with subsequent electronic excitation from vibrationally excited states, i.e., two-step IR + UV excitation; 2) multiphoton vibrational excitation in a strong IR field. Naturally, in contrast to gaseous media, in both cases one should use picosecond pulses to ensure that a molecule absorbs significant energy of a few electron-volts before thermal relaxation of the vibrational excitation. The most universal is the process of two-step IR + UV excitation which definitely combines only the distinguishing advantages of the vibrational and electronic excitation. Naturally, in each specific case it is necessary to prove from first principles the potential feasibility of two-step IR + UV selective photoexcitation of the selected molecule in a solution or a molecular bond in a macromolecule. Scarcity of spectroscopic data, particularly on the excited states of biomolecules, makes this selection far from a trivial process. We shall now consider some potential applications in the case of several molecules and bonds. However, in addition to this general problem, there are also other "tricky" problems, particularly: 1) heating of the medium in the process of selective photoexcitation; 2) absorption of infrared radiation by the solvent molecules. These problems are particularly serious in the case of *in vivo* experiments.

The estimates obtained¹¹⁰ suggest the possibility of avoiding heating at molar concentrations of molecules

in a solution below $10^{-3}M$ and with sufficiently weak absorption of infrared radiation by the solvent molecules. To weaken the IR absorption by molecules of a typical solvent (water) when experiments take place *in vivo*, one might attempt to excite overtones and combination vibrations in the near infrared, in spite of the consequent reduction in the selective absorption cross section. In some cases the absorption in the solvent can be reduced considerably by operating in the "induced self-transparency" regime for the solvent molecules. It is also possible to excite vibrational levels selectively by stimulated Raman scattering in the field of two-frequency visible laser radiation, to which the solvent is completely transparent, as has been done in the reported experiments.¹¹¹ Estimates indicate that the necessary intensities of IR and UV pulses of 10^{-11} – 10^{-12} sec duration are within the range 10^8 – 10^9 W/cm². Naturally, cooling of the molecules reduces the VT relaxation rate and, therefore, helps greatly to overcome the above difficulties.

We shall now consider several specific possibilities in selective laser biochemistry.¹¹² They look quite simple "on paper" but may be very difficult to implement experimentally.

a) Selective excitation of bases in DNA

The polynucleotide chain molecules DNA and RNA are important objects because of the possibility of selective laser-induced mutations and also because of the simplicity of their structure. In spite of their colossal size, both molecules contain five repeated nucleotide bases: guanine (G), cytosine (C), thymine (T), adenine (A), and uracil (U). All five bases are purine and pyrimidine rings, which have similar UV spectra with two maxima in the 4–6 eV range. Clearly, we can expect selective electronic excitation of the long-wavelength bands of the G and C bases, corresponding to the excitation of the π -electron system of the G–C base pair.¹¹³ On the other hand, it is not possible to excite the nucleotides A and T without exciting the other three bases.

The difference between the molecular structures of these nucleotides means that we can expect each of them to have a specific vibrational band manifested in the UV absorption spectrum. Figure 14 shows, by way of example, the UV and IR spectra of thymine. This figure also indicates a possible shift of the UV absorption because of the excitation of the IR band in the region of 1600 cm^{-1} due to vibrations of the C=C and C=O double bonds in a ring. The infrared spectra of DNA have not been investigated sufficiently thoroughly¹¹⁵ to identify the specific frequencies of all the nucleotides. It seems that the excitation of the vibrations of the DNA nucleotides by picosecond IR frequency-tunable pulses and simultaneous probing of the changes in the UV spectra may be a good method for investigating and interpreting the vibrational spectrum of DNA, and provide the necessary intermediate stage in investigating the possibility of selective action on the DNA bases.

The first experiments involving two-step IR + UV

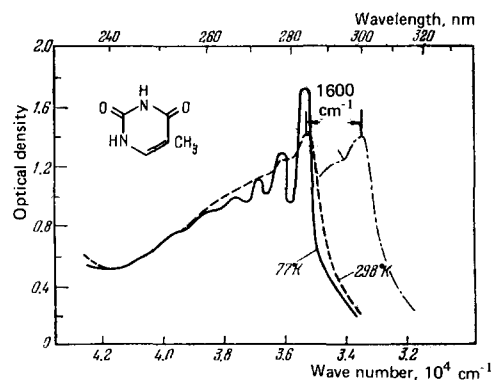


FIG. 14. Ultraviolet and infrared absorption spectra of thymine.^{103,114}

excitation of an electronic state of a complex molecule in a solution by picosecond IR and UV pulses were carried out recently on coumarin molecules in CCl_4 ¹¹⁶ and on rhodamine B molecules in D_2O .¹¹⁷ The latter experiment¹¹⁷ demonstrated the main difficulties encountered with the biomolecules and ways of overcoming them. Usually biomolecules are in an aqueous solution. The strong IR absorption in water may be overcome by excitation by means of overtones and also by the use of heavy water as a solvent because it has an IR absorption spectrum shifted toward longer wavelengths. In the experiment just mentioned the complex molecules were excited by the two-step method employing a two-channel parametric oscillator generating single ultrashort (10 psec) pulses whose frequency could be tuned continuously in the 0.26–4.0 μ range. The IR channel was designed for the excitation of the vibrational transitions (tuning range 1.5–4.0 μ) and the short-wavelength channel for the electronic states (tuning range 0.26–1.6 μ). The first overtones of the valence asymmetric vibrations of the methylene and methyl groups of rhodamine B in the 5800 cm^{-1} range were used as the intermediate vibrational states. These overtones were very weak and usually did not appear in the IR spectrum. The excitation of an electronic state was deduced from the appearance of fluorescence under the combined action of two ultrashort pulses. The selectivity of the excitation was checked by measuring the fluorescence intensity when the IR radiation frequency was tuned (Fig. 15). The resonant dependence found experimentally gave clear information on the spectrum of the weak overtone vibration of the methyl group CH_3 not observed by conventional spectroscopic methods.

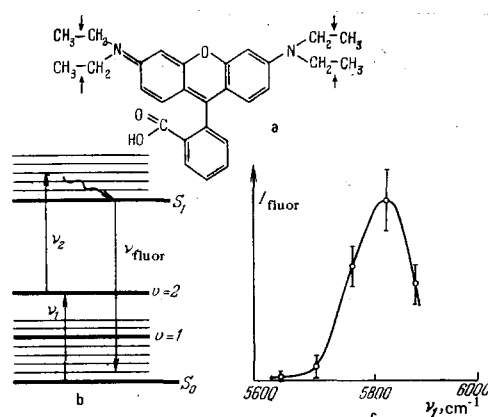


FIG. 15. Selective two-step excitation of an electronic state of a rhodamine B molecule in a D_2O solution by combined action of two ultrashort pulses of frequencies ν_1 and ν_2 : a) structure of the rhodamine B molecule with arrows identifying excited vibrations of the molecular groups; b) two-step excitation and generation of fluorescence; c) dependence of the fluorescence intensity on the frequency ν_1 of tunable IR radiation.¹¹⁷

b) Selective excitation and breaking of hydrogen bonds in DNA

The double helix of DNA is formed by hydrogen bonds between the guanine–cytosine and adenine–thymine bases. Breaking of these hydrogen bonds should split the double helix into two identical chains and result in subsequent replication of DNA. Clearly, selective excitation of the hydrogen bonds and their selective breaking provide an interesting laser method for control of the DNA replication process.¹¹² It seems to the author that this is important not only as a potential laser means of stimulation of the rate of biological processes but also as a basically new possibility of externally controlled “triggering” of the DNA replication process, whose details are not yet fully understood.

Two pairs of the DNA bases have slightly different hydrogen bonds. The A–T base pair is bound by two hydrogen bonds N–H...O and an energy of about 7.0 kcal/mole is required to break this pair of bases. The G–C base pair is bound by two hydrogen bonds N–H...O and one N–H...N bond, which require about 9.0 kcal/mole to break.¹¹³

The G–C bonds in natural DNA correspond to an infrared absorption band at about 1720 cm^{-1} and the A–T bonds to a band of about 1700 cm^{-1} . In denaturation of DNA, when the hydrogen bonds are broken, the two bands disappear.¹¹⁵ Therefore, it has been suggested¹¹⁰ to use high-power IR picosecond pulses at these frequencies (5.814 and 5.888 μ) to stimulate the breaking of these hydrogen bonds. Naturally, there are many more other possibilities, particularly from the point of view of choosing more suitable wavelengths which are not absorbed by solutions when experiments are carried out *in vivo*.

The potential function of a hydrogen bond has two characteristic minima, corresponding to two possible

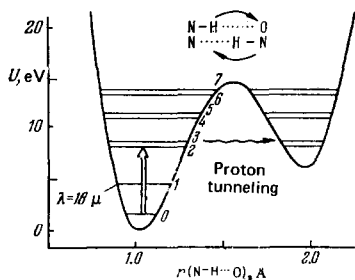


FIG. 16. Potential function of a hydrogen bound in DNA¹¹³ and possible method for excitation of levels by IR laser radiation to stimulate proton tunneling.

spatial and energy positions of the proton (Fig. 16). The energy levels of the proton in the hydrogen bonds N-H...O and N-H...N have been calculated¹¹³ but not yet observed experimentally. It is assumed that the transfer of a proton (or, more exactly, two protons in a pair of adjacent hydrogen bonds) to an energetically higher tautomeric state results in mutation (Löwdin mechanism¹¹⁸). Clearly, a laser emitting at a wavelength of 1.8 μ may be used to transfer a proton to an excited state and thus stimulate its tunneling to a higher energy minimum. This possibility has already been considered¹¹³ and, in view of the progress in the technology of tunable picosecond IR lasers, it should be investigated experimentally. The excitation of a proton should also be manifested in the electronic UV absorption spectrum and, consequently, can be used to achieve two-step selective process in accordance with the scheme: selective IR excitation of the proton vibrations + UV excitation of an electron.

9. SELECTIVE DETECTION OF NUCLEI, ATOMS, AND MOLECULES

The methods of selective laser photophysics solve fundamentally the problem of physical extraction of an atom or molecule of a strictly defined kind from a mixture of very similar (in respect of their chemical properties) other atoms and molecules. Naturally, the first and the simplest task is the selective detection of single atoms and molecules. The method of selective two-step or multistep photoionization of atoms and molecules is particularly suitable for this purpose. This possibility has been discussed on many occasions by the present author in a number of lectures and reviews on laser spectroscopy.^{112,119-122} A proposal to use the method of selective photoionization for the detection of atoms and molecules was made also in an earlier paper.¹⁹ We shall now consider some of the possibilities.

a) Detection of excited nuclei

Excited (metastable) nuclei are currently detected only on the basis of their radioactive decay. However, the individual features of an excited nucleus are manifested not only by its nuclear transitions, but also by the hyperfine structure of optical transitions in the electron shells surrounding the nucleus. Since the isomeric structure is usually much greater than the Doppler broadening of spectral lines, it is quite feasible to achieve selective photoionization not only of nuclei of specific isotopic composition but also of excited nuclei with a particular nuclear spin and

quadrupole moment. This possibility has already been discussed from the point of view of separation of isomeric nuclei and preparation of active media for future γ -ray lasers.¹²³ We shall stress here the possibility of selective detection of excited nuclei as a new approach to the study of and search for metastable nuclear levels. The electron "jacket" of a nucleus can be used to determine the quantum state of the nucleus without exciting the latter in the process of detection. After each selective detachment of an electron and its detection the ion can be recharged and the process can be repeated many times.

b) Detection of single atoms

A selectively excited atom may be ionized with a quantum efficiency close to unity if the energy density of the ionizing laser pulse exceeds the saturation energy density $\mathcal{E}_{\text{sat}}^{(i)}$ of an induced transition of the excited atom to the continuum, i.e.,

$$\mathcal{E}_{\text{ion}} \gg \frac{\hbar\omega_2}{\sigma_{ie}} = \mathcal{E}_{\text{sat}}^{(i)} \quad (2)$$

where σ_{ie} is the cross section for the photoionization from an excited state e , and the duration of the ionizing laser pulse is assumed to be less than the relaxation time of the excited state. For a typical photoionization cross section $\sigma_{ie} = 10^{-17} - 10^{-18} \text{ cm}^2$ at $\hbar\omega_2 = 2 \text{ eV}$ the energy density of the photoionizing laser pulse should be within the range $\mathcal{E}_{\text{ion}} = 0.03 - 0.3 \text{ J/cm}^2$. An experimental investigation of the dependence of the ionization yield on the energy of the ionizing pulses was carried out by Ambartsumyan *et al.*¹²⁴ for the Rb atoms. Figure 17 shows the experimental dependence of the total ion yield on the energy density \mathcal{E}_{ion} . The point of intersection of the linear part of the curve with the continuation of the plateau (point A) corresponds to the saturation energy density $\mathcal{E}_{\text{sat}}^{(i)}$ at which 63% of the excited atoms become ionized.

The first successful experiments involving detection of single atoms (for example, Cs) by the method of two-step photoionization were carried out by Hurst *et al.*,¹²⁵ in which an ionized atom in a proportional-counter chamber produced a signal quite sufficient for the detection of a single selective photoionization event. When the conditions for the saturation of the exciting and ionizing induced transitions are satisfied, so that

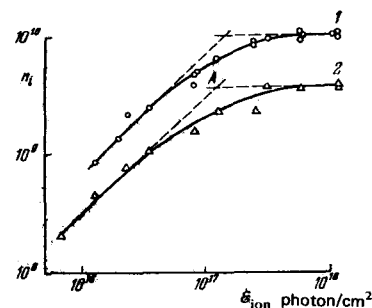


FIG. 17. Total photoion signal plotted as a function of the energy density \mathcal{E}_{ion} of a laser pulse ionizing an Rb atom excited to the 6^2P state in different electric fields (2.4 and 1 kV/cm for curves 1 and 2) extracting photoions.¹²⁴

the quantum efficiency of the ionization process is close to unity, the method described above can be used to detect selectively single atoms. The lowest laser energy in detection of single atoms is needed in a scheme of selective photoionization via highly excited (Rydberg) states. This method for detection of single atoms was first put into practice by Bekov *et al.*¹²⁶ The universality and flexibility of this method make it possible to use it widely both in scientific and in applied analytic problems. In particular, the method is fully applicable to the search for new heavy and superheavy elements¹²⁷ and for atoms with superdense nuclei.¹²⁸ The optical spectrum of an atom—the hyperfine structure of its lines—is its “passport” which guarantees that the detection is definite and makes it possible to identify a new element or a new nucleus. Therefore, the method of selective photoionization is of great interest in such experiments.¹²¹

c) Detection of complex molecules

It is known that selective detection of microscopic amounts of complex polyatomic molecules is an extremely difficult task, which has not yet been solved by physical methods. At present the standard method for the detection and identification of complex molecules is mass-spectroscopic analysis but its sensitivity is insufficiently high and it has hardly any selectivity in the detection of complex molecules differing only in respect of the spatial structure. Therefore, development of new methods for this task is extremely desirable and urgent.

The method of selective photoionization of molecules by laser radiation can provide the basis of a laser mass spectrometer,¹⁸ whose general scheme was described by the present author.¹²¹ A laser emitting a tunable frequency ω_1 excites selectively a vibrational (for some molecules, an electronic) state (Fig. 18). This excitation shifts by a small amount the photoionization band edge of the investigated molecule, which usually lies in the VUV range. A second laser emitting in the VUV range photoionizes the molecule and the frequency of this laser ω_2 is selected to lie in the region of the maximum slope of the photoionization band edge. In this case a preliminary selective excitation of a molecule by a tunable laser providing a relatively small energy $E_{exc} \approx 0.1-0.5$ eV results in a detectable change ($10^{-1}-10^{-2}\%$, when allowance is made for the

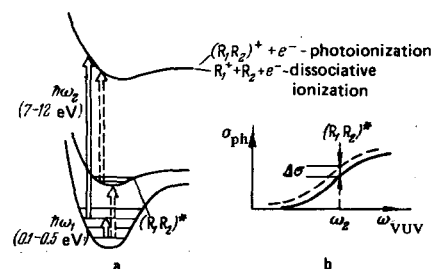


FIG. 18. Explanation of selective two-step photoionization of molecules by laser radiation: a) transition scheme; b) change in photoionization cross section of selectively excited molecules.

distribution of the molecules between the rotational states) of the photoionization cross section, i.e., it alters the photocurrent. The photoions are directed to a conventional mass spectrometer which then determines the mass spectrum, i.e., measures $i = f(M/e)$. This variant of a mass spectrometer can also be used to determine the photocurrent for a given value of M/e as a function of the tunable laser frequency ω_1 . This involves determination of the IR spectrum of a micro-amount of complex molecules because the coincidence of the tunable laser ω_1 with the absorption frequency of a molecule transfers the molecule to an excited state and, consequently, alters the ion photocurrent. A laser mass spectrometer with selective photoionization of molecules instead of the usual non-selective ionization by an electron beam (or continuous VUV radiation) gives simultaneously the optical (IR and visible) absorption spectra as well as the mass spectrum. Thus, it is possible to obtain information on the spatial structure of molecules with the same mass, etc.

Our team started a systematic investigation of this method of detection of molecules after the development of a simple VUV H_2 laser.¹²⁹ The first stage was one-step photoionization of dimethylaniline and methylaniline by H_2 laser radiation in the 1600 Å range¹³⁰ and also of the NO molecule by laser radiation in the 1200 Å range. Next,³⁰ we carried out two-step photoionization of the H_2CO molecule by the combined action of an N_2 laser pulse of $\lambda_1 = 3371$ Å wavelength, which excited the 1A_2 states, and by H_2 laser radiation of $\lambda_2 = 1600$ Å wavelength, which photoionized the excited molecules (Fig. 19a). The ionization potential of the H_2CO molecule was $E_i = 10.87$ eV and the total energy of the two laser photons $h\omega_1 + h\omega_2 = 3.7 + 7.7$ eV = 11.4 eV was fully sufficient for the photoionization of this molecule. The time delay of the H_2 laser pulse (of duration less than 1 nsec) was varied relative to the N_2 laser pulse (duration about 2 nsec), which made it possible to determine the dependence of the photoion yield on the delay time (Fig. 19b). The experimental curve was close to the exponential dependence with a decay time of 15 ± 2 nsec, which was equal to the lifetime of the H_2CO molecule in the excited 1A_2 state. The opposite sequence of the N_2 and H_2 laser pulses produced no N_2CO photoionization signal.

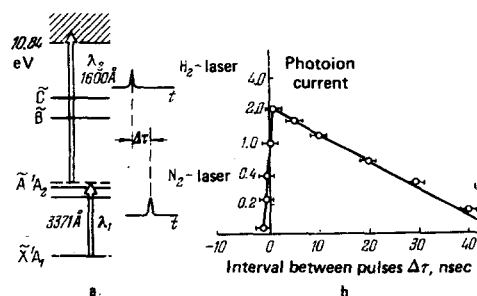


FIG. 19. Two-step photoionization of an H_2CO molecule by the combined action of N_2 and H_2 laser pulses: a) transition scheme; b) dependence of the photoion yield on the time interval between the pulses.³⁰

In a different series of experiments¹³¹ we investigated two-step photoionization of the NO₂ molecule by exciting an intermediate electronic state with radiation from a tunable dye laser (²A₂ - ²B₁ transition in the 4470-4970 Å range). The photoionization of the excited molecules was produced by a VUV H₂ laser pulse in the 1600 Å range. The ionization potential of NO₂ was 9.78 eV and the energy of two laser photons was 2.7 + 7.7 eV = 10.4 eV, so that the NO₂ molecule could be photoionized only because of the two-step process. Measurements of the dependence of the photoion current on the dye laser frequency gave the absorption spectrum of the NO₂ molecule at the electronic transition.

Finally, more recently we carried out successful experiments involving the photoionization of molecules by laser radiation in a molecular beam of a mass spectrometer.¹³² This laser-photoionization mass spectrometer was constructed at the Institute of Spectroscopy of the USSR Academy of Sciences with the cooperation of the L. Ya. Karpov Physicochemical Scientific-Research Institute (Fig. 20).

The first stage was one-step photoionization of dimethylaniline and other molecules in an H₂ laser beam, which increased the photoion current by several orders of magnitude. This was followed by two-step photoionization of diacetyl molecules by the combined action of UV (N₂) and VUV (H₂) lasers.¹³³ The simultaneous observation of the dependence of the yield of ions on their mass (determination of the mass spectrum), wavelength of the exciting radiation (determination of the optical spectrum), and time intervals between two laser pulses (determination of the decay time of the intermediate state) gave a large amount of information which was quite sufficient for the detection and identification of exceptionally small amounts of complex molecules. It should be understood that the identification of complex molecules requires investigation and practical implementation of two-step or multistep photoionization of molecules and excitation of intermediate vibrational states by the radiation of a tunable IR laser.

An infrared mass spectrometer promises to be a universal, highly selective, and very sensitive detector of complex molecules, which may prove useful

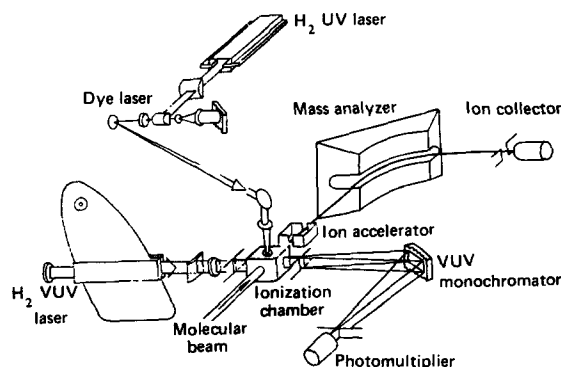


FIG. 20. Schematic diagram of a mass spectrometer with selective two-step photoionization of molecules in a beam by the combined action of a tunable dye laser pulse and an H₂ VUV laser pulse.¹³³

in many scientific and technical applications. In fact, since the detection of excited molecules by photoionization is highly sensitive, it should be possible to determine the IR spectra of extremely small amounts of matter, much smaller than those that can be tackled by the best existing classical and laser infrared spectrometers. One should add here the possibility of simultaneous attainment of an unusually high spectral resolution, which—in principle—is governed only by the residual Doppler broadening due to the angular divergence of the molecular beam involved. We are approaching here for the first time the solution of the fundamental problem of developing physical methods for the detection and identification of very small amounts of impurities of an organic substance with a degree of sensitivity that characterizes the smell organs of man and of animals.¹²¹

10. SPATIAL LOCALIZATION OF MOLECULAR BONDS

Selective interaction of laser radiation with molecular bonds opens up a new possibility of spatial localization of specific bonds, i.e., of mapping of macromolecules. The idea of this approach can be understood by considering the example of what is known as a photoelectron (photoion) laser microscope,¹⁷ shown schematically in Fig. 21. In contrast to a conventional field-electron or field-ion Müller projector,¹³⁴ an electron or an ion is detached from a molecule selectively by laser radiation and not by nonselective autoionization in a strong electric field. In the proposed microscope the function of the electric field is only to transfer electrons or ions along radial trajectories to the projector screen. The selective photoionization of specific molecular bonds in a macromolecule, which is located on the tip of the projector, can be performed in accordance with the multistep scheme using several picosecond laser pulses with specially selected frequencies.

In the case of selective detachment of an electron we can achieve a resolution of the order of 25 Å, which is limited by fundamental reasons: the presence of the tangential component of the velocity of the emitted electron and the indeterminacy relationship. In some cases a positive molecular ion formed after the photo-detachment of an electron is unstable and gives up a proton spontaneously.¹³⁵ A reversal of the polarity in the projector may send protons (instead of electrons) to the screen. The spatial localization of the point of emergence of a proton may be $(M/m)^{1/2} \approx 40$ times greater than in the case of a photoelectron. Such a

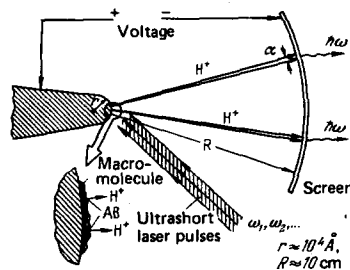


FIG. 21. Possible scheme of a laser ion microscope for spatial localization of molecular bonds.¹⁷

laser photoion microscope may have a resolution quite sufficient to distinguish atomic details of the molecular structure. A further improvement in the resolution of photoemission microscopy is possible by selective photoionization of a molecule to form heavy molecular ions.

The idea of the new approach to atomic-resolution microscopy is based on the combination of two important properties which are combined together from very different methods. The corpuscular (for example, electron) microscopy with a sufficiently high energy of a particle ensures a high spatial resolution. However, this automatically destroys the image "contrast" because a change in the particle energy due to its interaction with the investigated object is difficult to distinguish against the background of the high initial energy of the particle. Conversely, a reduction in the energy of the particle may increase the image contrast greatly and thus make possible the spectral selectivity in the observation of details of the image but it automatically reduces the spatial resolution. The method of selective photodissociation allows us to combine the high selectivity (or contrast) of the optical channel with the high spatial resolution of the corpuscular (ion) channel.¹⁷

One of the most important applications of a laser ion microscope is the determination of the sequence of nucleotides in the DNA molecule, which carries important information on each individual organism. The problem is to detach selectively a proton (or a heavier molecular ion) either from the A-T or from the G-C base pair. Naturally, we may attempt to realize the approach based on the two-step selective IR + UV excitation of an electronic state via an intermediate vibrational state of the selected nucleotide (see Sec. 8) and subsequent ionization of the electronically excited state. It is necessary to ensure that the selectivity of this process is sufficient for a clear distinction between the A-T and G-C pairs of bonds. One should particularly draw attention to the possibility of attaching, in principle, a preliminary chemical "label" to any one pair of bases so as to facilitate selective excitation and ionization. For example, it is known¹³⁶ that one of the DNA bases (cytosine) reacts selectively with hydroxylamine. This reaction is accompanied by a change in the UV absorption spectrum of cytosine by a greater amount than a typical difference between the spectra of the bases. In this case it may be sufficient to use selective two-step photoionization via an electronically excited state of the product of the reaction between cytosine and hydroxylamine. One can also attempt to "label" selectively one of the states with, for example, dye molecules which have absorption bands in the visible range. In this case it is sufficient to achieve ionization of selectively attached dye molecules.

For a magnification of a laser ion microscope $M = 3 \times 10^5$, a screen of $R = 10$ cm size can image a part of a linear DNA chain containing about 10^9 nucleotides (the distance between the neighboring nucleotides is 3.3 Å), i.e., a part of a chain about 3300 Å long!

Naturally, the recording of the sequence of nucleotides in long DNA chains would require successive projection and subsequent "matching" of the images of consecutive parts.

Successful implementation of the laser ion microscope for the observation of biological molecules first requires investigation of a number of fairly difficult problems: 1) selective excitation and ionization of macromolecules adsorbed on the tip of a point (the first experiments were described by Tsong *et al.*¹³⁸); 2) a search for schemes of selective dissociative ionization resulting in the detachment of a proton or a heavier molecular ion; 3) spatial scanning of the tip of a point in the microscope along a macromolecular chain, and so on. However, the solution of the problem of direct observation of a sequence of nucleotides in genes, including human genes, would provide extensive opportunities for controlling this sequence so that this branch of selective laser photophysics deserves most serious attention.

In conclusion, the author wishes to express his deep gratitude to his colleagues at the Laser Spectroscopy and Spectroscopy of Excited States Laboratories for their cooperation in the work on the problems of selective laser photophysics and photochemistry discussed above.

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Translated by A. Tybulewicz