

Laser-induced processes in spectroscopy, isotope separation, and photochemistry

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The use of stimulated quantum transitions in atoms and molecules for their resonant excitation is reviewed. The applications of this approach in laser spectroscopy, laser isotope separation, and laser photochemistry are briefly discussed.

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In his famous 1916 paper, "Emission and absorption of radiation according to the quantum theory,"¹ Einstein introduced two types of transitions of an atom or molecule between quantum states. The first type of quantum transition is a spontaneous radiative transition of an excited particle from a state 2 to a state 1 of lower energy. The probability for a spontaneous transition is determined by the Einstein coefficient A_{21} . The probability for a quantum transition of the second type, called "induced" or "stimulated emission," is proportional to the radiation intensity I (in photons per square centimeter per second) incident in the spectral interval $\Delta\omega$ of the quantum transition, which is described by the cross section for the radiative transition, $\sigma_{21}(\omega)$:

$$W_{21} = \int \sigma_{21}(\omega) J(\omega) d\omega = \sigma_{21} I, \quad (1)$$

where $J(\omega)$ is the spectral intensity of the radiation. The transition cross section σ_{21} is related to the Einstein coefficients for stimulated (B_{21}) and spontaneous (A_{21}) emission:

$$\int \sigma_{21}(\omega) d\omega = \frac{\hbar\omega}{c} B_{21} = \frac{\pi^2 c^2}{\omega^2} A_{21}. \quad (2)$$

Dirac later derived a quantum theory of radiation² in which a rigorous proof was offered for Einstein's conclusions, and the two types of emission were described by a common formula for the probability for the emission of a photon by a quantum system on the 2–1 transition to the vibrational mode (quantum state or oscillator) of the field, in which there are n photons:

$$P_{21} = (1 + n) a_{21}, \quad (3)$$

where a_{21} is the probability for the spontaneous emission of the photon into one oscillation mode under consideration. When the probability for spontaneous emission is summed over all the vibrational modes with $n = 0$, we find the total probability for spontaneous emission, which is described by the Einstein coefficient $A_{21} = \sum a_{21}$. The probability for spontaneous emission is thus described by the first term in (3), while that for stimulated emission is described by the

second term. The first term in (3) is sometimes interpreted as a manifestation of zero-point vibrations in spontaneous emission, but this interpretation is incorrect (see the discussion in Ref. 3). An important point is that the probability for the induced emission of a photon into a definite vibrational mode is proportional to the number of photons already there. It might be said that here we are seeing a tendency of photons, as Bose particles, toward bunching.

The probabilities for stimulated transitions downward (accompanied by the emission of a photon) and upward (accompanied by the absorption of a photon) are

$$B_{21} = B_{12} \quad \text{or} \quad B_{21} = \frac{g_1}{g_2} B_{12}, \quad (4)$$

where the degeneracy of the levels, g_1 and g_2 , has been taken into account.

Relations (1)–(4) underlie the operation of a laser. If some system, in particular, a resonator,^{4,5} keeps the photons preferentially in one or two vibrational modes, there will be a buildup in the number of excited particles in precisely these vibrational modes through stimulated transitions, by virtue of (3). In other words, a coherent light field will be established. The same relations describe many laser applications that are based on the resonant effect of laser light on matter, in which the laser light stimulates quantum transitions in the matter. This is precisely the nature of those stimulated processes which are the essence of the new methods of laser spectroscopy, laser isotope separation, and laser chemistry—the subject of the present paper.

1. LASER SPECTROSCOPY

Table I gives an idea of the progress which has been achieved in optical spectroscopy by virtue of the use of new laser techniques. This is a list of the basic problems in optical spectroscopy from the standpoint of the attainment of its limiting characteristics⁶: spectral resolution, time resolution, sensitivity, and selectivity.

We see from this table that exceptional progress has been achieved, but there remains some very complicated

TABLE I. Progress in the characteristics of optical spectroscopy.

Parameter	Prelaser limit	Laser technique	Possibilities	
			Today	Future
1. Spectral resolution	10^{-2} – 10^{-3} cm^{-1}	Nonlinear spectroscopy without Doppler broadening	1 kHz = $3 \cdot 10^{-8}$ cm^{-1}	To 1 Hz
2. Sensitivity	$> 10^{10}$ particles	Resonant multi-step photoionization	1 atom or 10 – 10^2 molecules in observation volume	1 atom or molecule in sample
3. Time resolution	10^{-8} s	Spectroscopy with ultra-short-pulse lasers	$2 \cdot 10^{-14}$ s, 10 optical periods	~ 1 optical period
4. Selectivity	Very poor	Combination of highly sensitive techniques with separation techniques	Moderate	1 rare isotope or molecule in mixture

problems, whose solution will probably provide some extremely interesting results. Let us briefly examine the present status of each of these problems.

1.1. Spectral resolution

The very narrow spectral width of laser light, combined with frequency tuning, has furnished a natural solution for the problem of measuring atomic and molecular spectra without any sort of instrumental distortion. In practice, we are, admittedly, still experiencing some difficulties in the use of tunable lasers, since certain spectral ranges (UV, VUV, and IR) still require further effort.

The point of fundamental importance is that laser light is capable of stimulating quantum transitions in matter that reveal the structure of spectral lines and a hidden inhomogeneous broadening of these lines due to a random motion, position, or orientation of the particles. This laser "interference" in the disorder in the system of interest is used successfully in both gaseous and condensed media.

1.1.1. Doppler broadening in a gas

There are several extremely effective methods for eliminating this broadening.^{7,8} First, a coherent directed light wave which is tuned to resonance with a Doppler-broadened transition excites particles with a definite velocity projection onto the direction of the wave. As a result, at saturation of the transition there is a change in the velocity distribution of the particles in both levels. By scanning the frequency of an oppositely directed probing wave, one can detect a narrow dip which forms on the Doppler profile. When the frequencies of the oppositely directed waves are equal, the absorption (or amplification) of each wave decreases in a resonant manner exactly at the center of the Doppler profile (a Lamb dip⁹). The width of the resonant dip is equal to the homogeneous width. Many different versions of absorption saturation

spectroscopy with Doppler broadening have been developed and are being used successfully.^{7,8}

Second, during the simultaneous absorption of two photons from oppositely directed light waves, the Doppler shifts of a moving particle cancel out, since we have $(\omega + \Delta\omega_D) + (\omega - \Delta\omega_D) = 2\omega$. As a result, the two-photon absorption line in a standing wave has a narrow resonance, without any Doppler broadening, exactly at the center of the two-photon transition.¹⁰ A point of importance for spectroscopy is that *all the particles*, regardless of their velocity, interact with the laser field in this method in the case of the exact two-photon resonance ($2\omega = \omega_0$).

The minimum width of a narrow resonance in either of these methods is set by the finite duration of the interaction of a moving particle with the laser field; i.e., we have $\Delta\nu_{\min} \gtrsim v_0/a$, where v_0 is the average velocity of the particles, and a is the diameter of the laser beam. At $v_0 \approx 3 \cdot 10^4$ cm/s and at the comparatively large laser beam diameter $a \approx 30$ cm, the width of the resonance is limited by the value $\Delta\nu_{\min} \gtrsim 10^3$ Hz. Although this value is 10^5 – 10^6 times smaller than the Doppler width, this limit has already been achieved experimentally.^{11,12} Chebotayev and his colleagues have developed effective methods for overcoming this limitation in the optical range, by modifying Ramsey's method of spaced fields¹³ for the case of single-photon transitions (three spaced fields¹⁴) and two-photon transitions (two spaced fields¹⁵). In this method, the width of the narrow resonance is determined by the transit time not through one beam but through both beams, as well as the empty distance between them b : $\Delta\nu_{\min} \gtrsim v_0/(2a + b)$ (Ref. 16).

Finally, yet another approach, a fourth approach, to the production of narrow resonances is based on the change in the velocity distribution of atoms caused by resonant radiation pressure, which cools the translational degrees of freedom of an atom¹⁷ or of an ion localized in a confinement region.¹⁸ The first successful experiments on the laser cool-

ing of atoms were carried out in 1979 at the Institute of Spectroscopy, Troitsk (see the review by Balykin *et al.*²⁰). There is a need for a study of the possible production of very narrow resonances by means of cooled atoms in combination with the methods listed above. A particularly attractive possibility is that of carrying out experiments with localized, ultracold atoms. Although the idea dates back a long way,²¹ obstacles remain in the path of its realization. So far, it has been found possible to carry out experiments only with cooled ions in a confinement region.^{22,23} At any rate, it is not clear that it is definitely possible to produce ultranarrow optical resonances with a relative width $\Delta\nu/\nu \ll 10^{-11}$ through the use of laser cooling of atoms.

1.1.2. Inhomogeneous broadening in a condensed medium

The spectral lines of impurity ions and molecules in a condensed medium are broadened inhomogeneously at low temperatures by their random arrangement and orientation. Laser light makes it possible to excite molecules in a low-temperature matrix exclusively at frequencies corresponding to a resonance with the laser light. If the laser frequency is tuned to resonance with a zero-phonon "0-0" electron transition, narrow resonances appear in the fluorescence²⁴ with a width as low as the natural radiation width. Such narrow zero-phonon electron lines are sometimes called an optical analog of the Mössbauer effect.²⁵ An important point is that in many cases the resonantly excited molecules undergo a change in frequency because of photophysical and photochemical processes, so that a narrow hole is "burnt out" of their absorption spectrum at the frequency of the laser light.^{26,27} This circumstance significantly extends the possibilities of high-resolution spectroscopy of complex molecules in condensed media.

Another interesting direction in spectroscopy within an inhomogeneously broadened line involves the excitation of a coherent state of impurity ions in an extremely narrow spectral interval determined by the homogeneous width. The observation of the coherent emission from such an ensemble of coherently excited particles (usually on the basis of their beats with another laser beam at a close frequency) makes it possible to study subtle processes which are hidden by inhomogeneous broadening,²⁸ but this type of spectroscopy is based on measurements along a time scale, rather than along the customary spectral scale. For example, for impurity Pr^{3+} ions in a LaF_3 crystal, resonances with the width of only 10^3 Hz have been obtained; this width is 10^7 times smaller than the inhomogeneous width.²⁹

1.2. Sensitivity

The theoretical limit on the sensitivity of spectroscopy is one particle (one atoms or molecule). In the actual experiments that have been possible so far, however, it has been possible to measure spectra only under the assumption of a rather large number of particles in the sample (ranging from 10^{10} to 10^{20} for various methods and objects). The problem of increasing the sensitivity of spectroscopic methods has thus remained extremely important over the entire century

of the development of optical spectroscopy. A wide variety of methods can be used to record the spectra of a substance: absorption, fluorescence, Raman, etc. When ordinary light sources are used, the sensitivity of any of these methods is low, but even the use of laser sources for excitation does not make these methods capable of measuring spectra with a sensitivity at the level of individual atoms and molecules. The only exceptional case is the fluorescence method, which can detect single atoms in the case of the repeated reemission of many photons by a single atom (see the review in Ref. 30).

Lasers have made it possible to develop some fundamentally new, highly sensitive methods of laser spectroscopy which have no analog in ordinary spectroscopy. The *method of coherent anti-Stokes Raman scattering (CARS)* has been developed for vibrational spectroscopy of molecules. This method makes use of the coherence of laser light.³¹ In a two-frequency laser field with a frequency difference $\omega_1 - \omega_2 = \Omega$ equal to the frequency of molecular vibrations, a polarizability at the frequency Ω is produced in the sample, and this polarizability is coherent over volume. When a probing beam interacts with such a medium, it undergoes a Raman scattering by coherent molecule vibrations into the anti-Stokes region, $\omega_{\text{as}} = \omega_l + \Omega$. A huge improvement in sensitivity is achieved because the coherent-scattering signal is proportional to the square (N^2) of the number of scattering molecules in the volume and also by virtue of the directional nature of the coherent scattering. This method has improved the sensitivity of molecular spectroscopy by many orders of magnitude and has converted Raman scattering into a method that combines high sensitivity with a good spectral resolution.³¹

Another new and versatile spectroscopic method is based on the ability of laser light to cause a rapid resonant excitation of an atom or molecule through stimulated transitions, as several laser pulses with appropriate frequency are applied to high-lying states. The atoms or molecules are ionized from these states whether by the laser light or by some other effective method (an electric field or collisions). The atomic or molecular ions which result can be detected reliably by the methods available. This ionization method is quite versatile, since it does not require a special level diagram, special types of levels, or special level decay rates. It can be used for any atoms or molecules.

The *method of resonant photoionization spectroscopy* was proposed in the course of the development of new methods for selectively acting on atoms and molecules with laser beams; these methods are discussed below. The two-step resonant ionization of an atom was proposed for separation of isotopic atoms and for detecting trace elements.³² The first experiments on resonant two-step photoionization were carried out in the Institute of Spectroscopy as early as 1971 for the rubidium atom.³³ At the same time, it was suggested that the selective stepwise photoionization of molecules might be used in the beam of a mass spectrometer to improve the sensitivity and selectivity of mass spectrometry of molecules.³⁴ It was clear from the outset that stepwise resonant photoionization of atoms and molecules would make it possible to

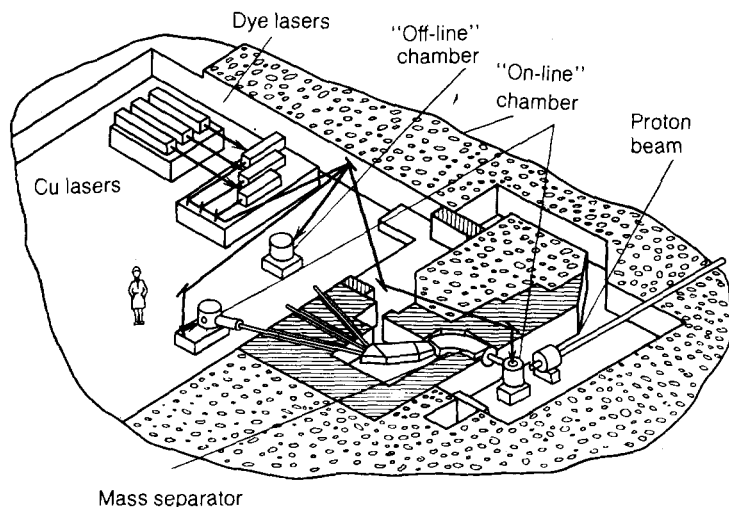


FIG. 1. General view of the laser-nuclear complex at the Leningrad Institute of Nuclear Physics and the Institute of Spectroscopy, Troitsk, installed at the proton accelerator at Gatchina. The proton beam bombards a target in which short-lived isotopes are produced in nuclear reactions. These isotopes are evaporated from the hot target, ionized, and separated in a mass separator. In "off-line" operation, the isotopic atoms of interest are accumulated in the sample and then transferred to a chamber in which, during heating, they pass into vacuum in the form of neutral atoms with a radioactive nucleus. The atoms are bombarded by the laser pulses in this chamber. For a study of short-lived isotopes and of nuclear isomers with a lifetime ranging from a few hours to a few seconds, "on-line" operation is used. In this case a stream of radioactive nuclei is continuously accumulated in the sample and evaporated from it in the form of neutral atoms. In this case, because of the low concentration of atoms with a short-lived nucleus that are formed, it is necessary to maximize the sensitivity of the detection while also providing a high spectral resolution. The resonant photoionization of the atoms occurs in a three-step scheme during the simultaneous application of three laser pulses from three independent tunable dye lasers.

develop a laser detector of single atoms and molecules.^{35,36} The first successful experiments on the detection of single atoms were carried out in 1977 at Oak Ridge National Laboratory (Cs atoms in a buffer gas³⁷) and at the Institute of Spectroscopy, Troitsk (Na atoms in a beam³⁸; see the review in Ref. 30).

At the same time, there has been a successful development of methods of multistep and multiphonon resonant ionization of molecules, especially in combination with mass spectrometry of the resulting ions. In this direction there has been a successful experiment on the photoionization detection of single molecules in the chamber of a mass spectrometer.³⁹ Laser photoionization spectroscopy of molecules is presently a rapidly developing field of research (see the review by Antonov *et al.*⁴⁰).

Photoionization spectroscopy, based on a multistep resonant excitation and subsequent ionization of excited atoms and molecules, is a unique method, in which all of the limiting characteristics can be achieved: 1) a sensitivity at the level of individual atoms and molecules; 2) a spectral resolution determined in the limit by the homogeneous width $\Delta\nu_{\text{homo}}$; 3) a time resolution limited by the inverse spectra width of the transition and lying in the range 10^{-6} – 10^{-13} ; and 4) a selectivity determined by the product of the selectivities in each step of the excitation $S = S_1 \dots S_n$, which can in principle reach values of 10^{15} – 10^{20} .

The unique characteristics of photoionization spectroscopy open up a broad field of applications, ranging from nuclear physics to medical diagnostics. We shall discuss one of these applications here in nuclear physics.

The high resolution of the photoionization method, combined with the limiting possible sensitivity, is particularly useful for studying the hyperfine and isotropic structure of the spectral lines of atoms with short-lived nuclei, which are accessible to measurements in very small numbers (10^3 – 10^{10} atoms). This method is being used successfully to measure the radii of the nuclei of short-lived isotopes which are produced on the proton accelerator at the B. P. Konstantinov Leningrad Institute of Nuclear Physics, Academy of Sciences of the USSR. In work carried out there, in collabora-

tion with the Institute of Spectroscopy, Troitsk, a laser-nuclear measurement complex has been developed in which a method of three-step photoionization of atoms is used to detect radioactive nuclei in an "off-line" approach and an "on-line" approach.⁴¹ A distinctive feature of the apparatus, shown in Fig. 1, is the use of specially developed tunable dye lasers with a high pulse repetition frequency (10 kHz) to cause the photoionization. These lasers are pumped by the beams from periodic-pulse cesium vapor lasers. Such high repetition frequencies of the laser pulses are required to maximize the "interception" of the rare atoms, which are moving rapidly through the region of laser illumination. At a resolution of about 100 MHz, determined by the width of the spectral line of the atomic beam, the sensitivity of the photoionization method is at a record high level, since it is possible to measure the spectra of isotopes that are produced in the target at a rate of $3 \cdot 10^3$ nuclei per second. At a nuclear lifetime of 10 s, this production rate corresponds to an equilibrium number of $3 \cdot 10^4$ nuclei in the target. The results of measurements of the isotopic shifts can be used to calculate

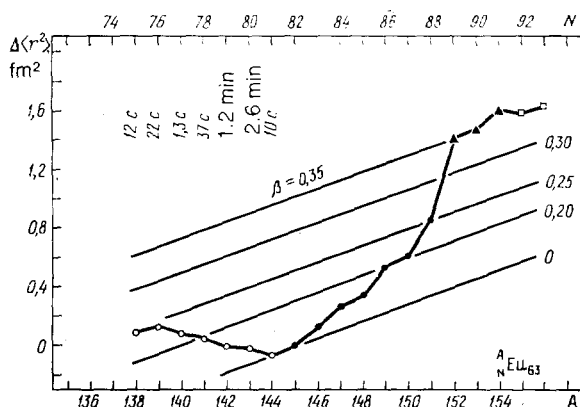


FIG. 2. Variations in the rms charge radii of europium nuclei with various neutron numbers according to measurements in the laser-nuclear complex of the Leningrad Institute of Nuclear Physics and the Institute of Spectroscopy, Troitsk.⁴² The nuclear lifetimes and the deformation parameters β of the nuclei are shown.

an extremely important characteristic of a nucleus—its rms charge radius—and the variation of this radius upon a change in neutron number. Figure 2 shows the results of such measurements for a chain of Eu isotopes.⁴²

This method is used with equal success to analyze traces of rare elements, e.g., for an analysis of the ruthenium content in oceanic objects.⁴³ This content has remained unknown because of the low abundance of this element and the absence of methods sensitive enough to determine it. Analytic spectroscopy has been enriched by this powerful new method for analyzing traces of atoms at concentrations out of reach by conventional analysis methods.

1.3. Time resolution

Before the appearance of ultrashort-pulse lasers, time resolution in spectroscopy had reached a few nanoseconds thanks to the use of the Kerr cell and fast flashlamps. This approach was used successfully in the effective method of flash photolysis, which made it possible to study the spectra of short-lived molecules and radicals.⁴⁴ Since 1965, five years after the invention of the laser, we have been observing the rapid development of methods for measuring subnanosecond intervals, thanks to the development of lasers which generate ultrashort light pulses.

Three effects underlie the operation of picosecond-pulse lasers. First, the rate of induced transitions is proportional to the light intensity, according to (1). If the intensity is sufficiently high, the rate at which the quantum system is excited from the ground state (or the rate at which it decays) can lie in the picosecond region. For example, the cross section for an allowed electron transition of a dye molecule in solutions is $\sigma_{12} \approx 10^{-16}$ cm², so that at a light intensity $I = 10^9$ W/cm² the rate of excitation of absorbing molecules (or the rate of decay of amplifying molecules) would be $W_{12} \approx 10^{12}$ s⁻¹.

Second, electronically excited molecules in solution can revert spontaneously to their initial electronic state through a rapid radiationless relaxation at a rate up to $W_{rel} \approx 10^{11}$ – 10^{12} s⁻¹. This rate is three or four orders of magnitude higher than the rate of radiative relaxation.

Third, the nonmonochromatic light, with a spectral width $\Delta\nu_{em}$, contains random fluctuations of the intensity with a duration $\tau_{fl} \approx 1/\Delta\nu_{em}$. For example, at a spectral width ~ 30 cm⁻¹ the fluctuation pulses have a length $\tau_{fl} \approx 10^{-12}$ s.

A multimode laser with a nonlinearly absorbing dye solution in its resonator emits ultrashort pulses,⁴⁵ since the most intense fluctuational ultrashort pulses can cause a predominant increase in the transmission of the absorber, be amplified, and ultimately stimulate emission in the active medium.⁴⁶ This phenomenon is called "mode self-locking," since the development of a single ultrashort pulse which is circulating in the resonator corresponds in spectral terms to a mutual phasing of many axial modes of the laser. The attainment of mode self-locking in a cw dye laser, with a gain band occupying a very broad interval, made it possible to generate subpicosecond pulses with a tunable frequency.⁴⁷ The optimization of this laser through the use of the method

of oppositely directed subpicosecond pulses in the dye has made it possible to sharpen greatly the output pulses and to cross the 100-fs boundary.⁴⁸

Especially short pulses can be achieved by expanding the spectrum in a nonlinear, transparent, dispersive medium and then compressing the pulse through a compensation for the dispersive spreading.⁴⁹ This method has not been used to produce the very shortest laser pulses, with a length of only⁵⁰ 16-fs, which amounts to only about 10 periods of the optical oscillation.

Ultrashort-pulse lasers are the essence of a variety of spectroscopic methods with a picosecond and, recently, femtosecond time resolution.^{51,52} While information on subnanosecond processes had been obtained previously in an indirect way, e.g., from the broadening of spectral lines, now an extremely wide variety of primary photophysical and photochemical processes have become accessible to direct measurement. We can illustrate the situation by listing briefly some processes that have been studied⁵¹: intraband relaxation of excitation in semiconductors and molecules, dephasing and relaxation of excitons in semiconductors, the dynamics of the solvation of an electron in a solution of molecules, the relaxation of phase and the population of vibrational levels of molecules in solutions, measurement of the rate of conformational conversions of a molecule, primary photoprocesses in visual pigments, bacteriorhodospin, chlorophyll, and many, many others.

1.4. Selectivity

This characteristic of spectroscopy is the least definite and the most difficult to attain. Optical spectroscopy is essentially based on resonant transitions in a substance, and in a sense it has a definite selectivity. In particular, any mixture of atoms can be identified precisely on the basis of the atomic spectral lines. This is a comparatively simple case, however, since the number of different atoms is no more than a hundred, and their spectral lines are narrow and overlap only rarely. If we attempt to observe rare atomic isotopes against the background of the most abundant isotope, this situation becomes more complicated, since the isotopic optical shifts are small.

When we turn to the problem of observing and identifying traces of molecules in a real molecular mixture, we run into real complications, since there are very many molecules, and their spectral lines are broad and overlap frequently. Laser spectroscopy thus has the task of detecting traces of isotopes and molecules and characterizing possible methods on the basis of their ability to solve this problem, i.e., on the basis of their selectivity.

An active effort is being made to develop methods for laser detection of rare isotopes.⁵³ The most promising method here is multistep laser photoionization, in which case there can be a multiplication of selectivities in each step of the excitation. Laser-spectral detectors of rare radioactive isotopes which do not make use of the radioactive decay to detect the isotopes will probably be developed in the near future.

Other approaches which have been suggested for

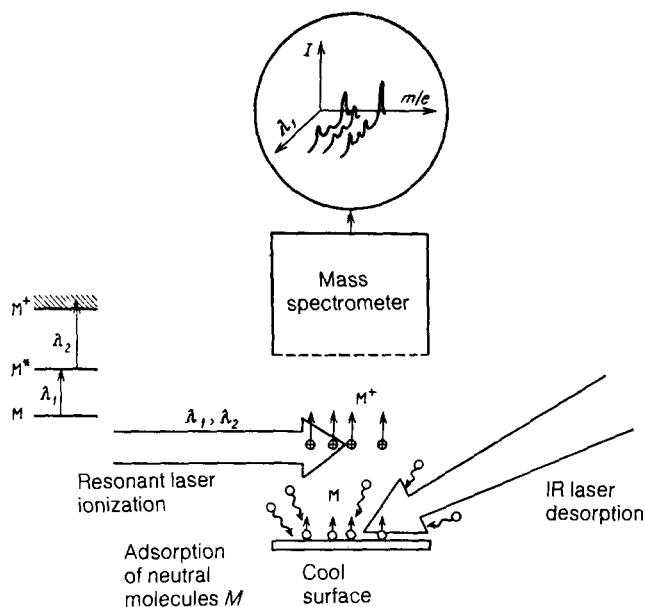


FIG. 3. Overall scheme for laser detection of traces of molecules through the accumulation of molecules on a cooled adsorbing substrate, pulsed laser desorption of these molecules, and a subsequent resonant photoionization and measurement of mass spectra.

achieving laser detection of traces of molecules combine different methods. Figure 3 is a simplified diagram of a laser detector of molecules, which might be called a "laser nose." The traces of molecules are adsorbed (a selective adsorption is possible in principle) and accumulate on a surface cooler than the surrounding medium. The adsorbent is then irradiated in a vacuum chamber, where the laser pulse causes a pulsed desorption of the molecules and then a multistep selective photoionization by laser pulses, with measurements of the mass spectrum of the resulting ions. This method has already achieved a detection sensitivity of only 10^4 – 10^6 molecules on a surface.⁵⁴ We are about to see the development of two-dimensional laser optical-mass spectrometers which use tunable IR and UV lasers and also methods of selective adsorption and desorption. Along this path it will probably be found possible to solve an interesting and difficult problem posed by Kapitsa⁵⁵: "Use physical instruments to achieve the sense of smell of a dog" (see also the review by Antonov *et al.*⁴⁰).

Finally, the development of highly selective methods of laser spectroscopy will be of major interest for the detection and identification of biological molecules, where the capabilities of the methods of optical spectroscopy are so far extremely limited.

2. LASER ISOTOPE SEPARATION

The basic ideas and suggestions in the field of the selective effects of laser light on atoms and molecules^{56,57} have been directed to a large extent toward the solution of a problem of practical importance: the separation of isotopes with laser light (see the reviews in Refs. 58 and 59). Although a wide variety of elementary processes for isotopically selective action of laser light on matter in various states of aggrega-

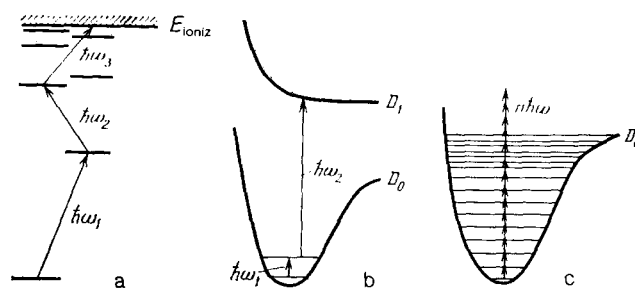


FIG. 4. Diagrams of those methods for applying laser light in an isotopically selective way to matter that are most effective for isotope separation and that have been brought to the stage of prototype apparatus. a—Three-step photoionization of an atom by visible laser light; b—two-step IR-UV photodissociation of molecules through excited vibrational states by the combined action of IR and UV laser light; c—multiphoton IR photodissociation of polyatomic molecules by an intense IR laser pulse.

tion (atomic and molecular gases and beams, condensed media, and heterogeneous media) were examined in the first few years of the effort, only a few processes have actually been developed so far. These processes are represented by the few diagrams in Fig. 4. All of these processes are essentially an isotopically selective multistep photoionization of atoms³² and photodissociation of molecules.⁶⁰

All of these schemes are based on the rapid selective transfer to an atom or molecule of radiant energy through stimulated transitions at a rate W_{exc} , which exceeds the relaxation rate τ_{rel}^{-1} and also the rate of transfer of excitation between isotopic atoms or molecules, Q_{ir} :

$$W_{\text{exc}} \gtrsim \frac{1}{\tau_{\text{rel}}}, Q_{\text{ir}}. \quad (5)$$

Since the rate of stimulated transitions is proportional to the intensity (I) of the resonant light, with given transition cross sections it is always possible to select an intensity I or an energy flux density $\Phi = I\tau_p$, of laser pulses with length $\tau_p < \tau_{\text{rel}}, Q_{\text{ir}}^{-1}$, to satisfy condition (5). In this case the laser light completely controls the photoionization for the atom or the photodissociation of the molecule. This approach is fundamentally different from the photochemical methods of isotope separation, where the relaxation rate is proportional to the rate of collisions of the reacting particles, and the collisions unavoidably result in not only the useful, selective, reaction but also a loss of excitation and selectivity.

The isotopically selective multistep photoionization of atoms, which is being used successfully for the spectroscopy of single atoms, as described above, underlies a practically feasible process for separating uranium and plutonium isotopes which has been implemented at the Lawrence Livermore Laboratory in the USA.⁶¹ This process is based on a three-step ionization of ^{235}U atoms by means of three pulses from dye lasers (the dye is rhodamine 6G) in the visible range (Fig. 4a), which are pumped by copper-vapor lasers with a high pulse repetition frequency. This program has become practically feasible thanks to the development of extremely sophisticated dye lasers with a high average power. The total average power of the laser light, with a spectral

width of 10^3 MHz and a stability of about 30 MHz, is 30 kW for the industrial facility which is to be constructed at Oak Ridge in the late 1980s. This facility will have a productivity of 10 000 metric tons of uranium per year enriched to 3% ^{235}U . The laser ionization process for separating uranium isotopes is distinguished from the gaseous diffusion and centrifuge processes currently being used by a low capital expenditure (which is ten times lower per unit of separation work per year), a low energy demand (24 times less than for gaseous diffusion or the centrifuge process), and low operating expenses.⁶¹

Another competitive isotope-separation process makes use of the isotopically selective vibrational excitation of a molecule by an IR laser beam, followed by a photodissociation of the excited molecules by an UV laser pulse⁶⁰ (Fig. 4b). This approach was first demonstrated experimentally at the Institute of Spectroscopy, Troitsk, in 1972 for the particular case of the NH_3 molecule and the ^{14}N and ^{15}N isotopes.⁶² The practical realization of this method becomes possible after the invention of excimer lasers (see the paper by N. G. Basov *et al.* in This Issue), which generate intense UV light with a high efficiency. Extensive work has been carried out at the Los Alamos National Laboratory in the USA on the use of this method to separate uranium isotopes through the use of the UF_6 molecule.⁶³ Significant progress has been made in methods of high-resolution laser IR spectroscopy of polyatomic molecules and in interpreting these spectra in the course of this research.⁶³

A method of gasdynamic cooling of molecules during expansion into vacuum at a supersonic velocity has been introduced in this research. This method greatly simplifies the IR absorption spectrum, making possible an isotopically selective vibrational excitation of $^{235}\text{UF}_6$ molecules by light in the $16\text{-}\mu\text{m}$ region, despite the small isotope shift involved here (less than 1 cm^{-1}). The method of IR-UF isotopically selective photodissociation of UF_6 molecules is real competi-

tion for the method of isotopically selective photoionization of uranium vapor.⁶⁴

Yet another efficient method for isotopically selective photodissociation of molecules, through the absorption of a large number of IR photons by a polyatomic molecule on stimulated transitions along a ladder of vibrational levels up to the dissociation boundary, within the electronic ground state (Fig. 4c), was demonstrated⁶⁵ in 1974 at the Institute of Spectroscopy, Troitsk, for the particular case of the BCl_3 molecule and the isotopes ^{10}B and ^{11}B . Those experiments used high-power IR pulses from a CO_2 laser in the $10\text{-}\mu\text{m}$ region. This method quickly won wide popularity because of its simplicity and efficiency, and it is now the subject of many hundreds of papers (see the reviews^{66,67} and monographs⁶⁸⁻⁷⁰). The many studies led to an early understanding of the physics of the multiphoton isotopically selective excitation of molecular vibrations. The best schemes for multiphoton IR photodissociation were identified. The scaling of the separation process has been studied in prototype apparatus with a CO_2 laser of high average power.⁶⁹

The possibilities of the method of multiphoton excitation of vibrations and dissociation of molecules go far beyond the field of isotope separation. In the first place, this method makes it a comparatively simple matter to prepare molecules in highly excited vibrational states. It is essentially only as a result of research on the excitation of molecules in strong IR fields that information became available on the characteristics of polyatomic molecules in highly excited vibrational states (these characteristics pertain to intramode and intermode anharmonicity, the randomization of vibrational energy as a result of an interaction between modes, the boundary of the vibrational quasicontinuum, the absorption cross section, the intramolecular and intermolecular relaxation, etc.). Figure 5 illustrates, in a simplified way, the characteristics of a vibrationally excited polyatomic molecule which have come under study by the method of excitation in

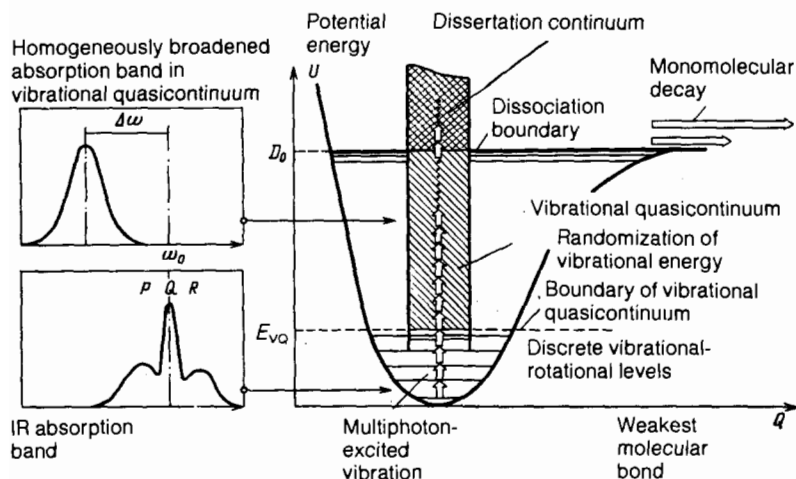


FIG. 5. Multiphoton excitation of a polyatomic in an intense IR laser field whose frequency is tuned to resonance with a vibrational absorption band. The vibrational levels can be grouped in a qualitative sense into three types on the basis of increasing energy. The lowest group consists of discrete vibrational levels of a certain type of vibration. Above a certain boundary, there is a relatively broad absorption band, which progressively shifts in the long-wave direction because of an anharmonicity which results from the interaction with many types of vibrations. Above the dissociation boundary, there are wide vibrational levels of a reexcited molecule. These vibrational levels rapidly decay into the real continuum.

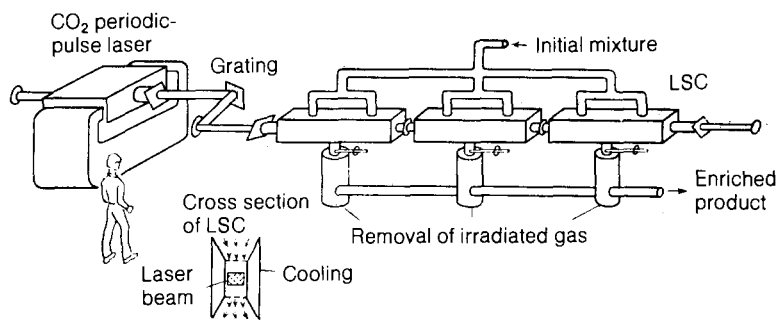


FIG. 6. General view of an apparatus for laser isotope separation which has been used to study the scaling of the method of IR isotopically selective photodissociation of molecules (CF_3I , CF_2HCl , etc.) by the beam from a high-power periodic-pulse CO_2 laser. The laser is at the left; the laser separation cell (LSC) is at the right. This cell is 5 m long. There is a transverse flow of the molecular mixture through the cell at a rate of 500 liter/s.

a strong IR field. Second, a photochemistry in the electronic ground state has become possible, along with the well-known photochemistry of molecules in excited electronic states. In particular, it has become possible to carry out a photochemical synthesis using radicals produced in the photodissociation of molecules in the electronic ground state, without a thermal heating of the gas mixture (more on this in Section 3 below).

Various schemes for the IR photodissociation of molecules have been developed on the basis of what has been learned about the behavior of the vibrational spectrum of polyatomic molecules with increasing excitation level. These schemes make it possible to achieve the highest degree of isotopic selectivity and the highest dissociation yield. Among these schemes we might mention the dissociation in a two-frequency IR field with separation of the functions of selective excitation and dissociation of the excited molecules⁷¹ and the recently implemented photodissociation in a multifrequency field of comparatively simple polyatomic molecules with a high boundary for the vibrational quasi-continuum.⁷²

The photodissociation of molecules by intense pulses from a CO_2 laser is being used successfully for isotope separation. In many laboratories in several countries, this process is being developed specifically for this purpose, in particular, for the separation of isotopes of light elements. Figure 6 shows the overall layout of a laser installation for separation of the isotopes ^{12}C and ^{13}C by this method which has been constructed in a collaboration among the I. V. Kurchatov Institute of Atomic Energy, Moscow, the Scientific-Research Institute of Stable Isotopes of the State Committee on the Use of Atomic Energy of the USSR, and the Institute of Spectroscopy, Troitsk. This apparatus consists of a periodic-pulse CO_2 laser with an average power up to 5 kW, with a wavelength tunable by means of a diffraction grating, and with a fast-flow laser separation cell. In this cell, polyatomic molecules containing the carbon ($^{12,13}\text{CF}_3\text{I}$ or $^{12,13}\text{CF}_2\text{HCl}$, etc.) are irradiated. Another part of the apparatus is a chemical separation column, where the products of the dissociation of the inertial molecules and the molecules containing ^{13}C are separated. The productivity of the laser separation module is about 100 kgf/yr of elemental ^{13}C enriched to 80% (the initial abundance is 1%), for a 10-kW beam from the CO_2 laser.

IR multiphoton dissociation is of major interest for the

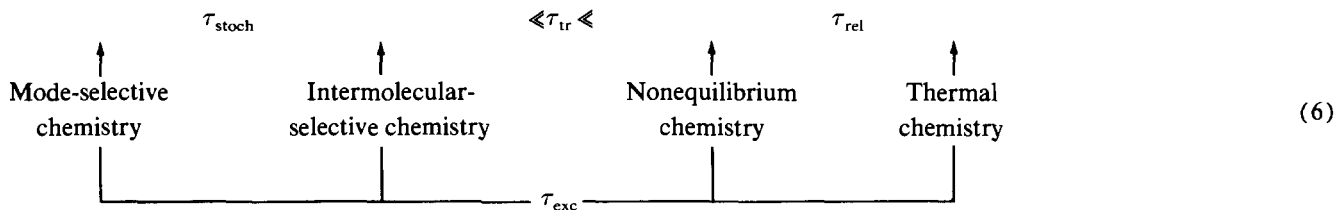
development of a process of practical importance: isolating the tritium that is generated in heavy-water reactors. Since tritium is produced in a liquid, rather than in the gas phase, the method of isotope exchange of a carrier gas with heavy water can be used in the photodissociation method. Successful experiments have been carried out on selective IR photodissociation of molecules containing tritium⁷³ (CTF_3). The development of an industrial process based on this method seems entirely realistic.

The three approaches to laser isotope separation described here (Fig. 4) use lasers of three completely different types, with a high pulse repetition frequency. These lasers may be called the basic lasers for each of the processes: dye lasers, UV excimer lasers, and IR CO_2 lasers, combined with various frequency-conversion methods. As these types of lasers are developed into highly reliable systems with average power levels above 1 kW, we shall approach the state of the industrial use of these methods for laser isotope separation.

3. LASER CHEMISTRY

The high intensity and short length of laser pulses result in the excitation of internal degrees of freedom of molecules that are at resonance with the field, up to a significant energy and at a high rate, e.g., up to 4-10 eV in 10^{-8} - 10^{-12} s. These results can be achieved with molecules in the gas phase, at or near a surface, or in solution. Some interesting and varied chemical processes that can be induced by laser light are based on this circumstance.⁷⁴

The excitation time τ_{exc} (or the excitation rate $W_{\text{exc}} = \tau_{\text{exc}}^{-1}$) should be compared with other molecular scale times: τ_{stoch} , the scale time for intramolecular redistribution of the absorbed energy among all the internal degrees of freedom of the molecule; τ_{tr} , the scale time for the transfer of excitation between different molecules; and τ_{rel} , the scale time for the relaxation of the excitation, e.g., into heat. These scale times typically conform to the hierarchy $\tau_{\text{stoch}} \ll \tau_{\text{tr}} \ll \tau_{\text{rel}}$. The numerical values of these times vary over broad ranges, depending on the gas pressure, the temperature of the condensed medium, etc. For example, reasonable estimates of τ_{stoch} are 10^{-11} - 10^{-13} s, while τ_{rel} can reach values of 10^{-3} s. Consequently, depending on the value of τ_{exc} , it would be possible in principle to arrange the following qualitatively different versions of laser chemistry:



The most fundamental questions here are the rate at which energy is distributed in an isolated molecule, τ_{stoch}^{-1} , and the possibilities of chemical processes that are selective in terms of the particular bond or the particular vibrational mode which is excited. This type of nonstatistical photochemistry, in which the photochemical conversion occurs *not in accordance with the weakest bond*, will probably be achieved through the excitation of vibrations by picosecond pulses in the case of rather large molecules.^{68,75} The situation is more favorable in the excitation of electronic states of molecules at low temperatures, for which photochemical conversions which are selective in terms of position have already been induced by laser light.^{26,27}

Laser chemistry with an intermolecular selectivity is of the greatest practical interest. In particular, it is this type of selective photochemistry that is realized in isotope separation by the methods of resonant laser photodissociation (Fig. 4, b and c). This approach is also being developed successfully for laser chemical synthesis. For example, molecules of a definite species can be dissociated in a molecular mixture by applying an intense IR pulse, a high concentration of radicals of interest can be produced without causing any heating of a mixture, and complex molecules can therefore be synthesized with a high yield.^{76,77} As an example we might cite the laser radical chemical synthesis of the $(\text{CF}_3)_3\text{CI}$ molecule through the selective IR photodissociation of the $(\text{CF}_3)_3\text{CBr}$ molecule near I_2 molecules.⁷⁸ The IR photodissociation produces $(\text{CF}_3)_3\text{C}^\cdot$ radicals; these react in an unheated molecular mixture with I_2 molecules, forming the compound $(\text{CF}_3)_3\text{CI}$, which is difficult to synthesize under the conditions prevailing in ordinary thermal chemis-

try. Under thermal-equilibrium conditions, a $(\text{CF}_3)_3\text{CI}$ molecule once formed should decompose rapidly, since its dissociation energy is lower than the dissociation energy of the original $(\text{CF}_3)_3\text{CBr}$ molecule. Laser light essentially makes it possible to achieve an efficient synthesis of compounds that are less stable than the compounds which are the starting point (energy-consuming chemical synthesis).

The laser opens up new possibilities for arranging chemical reactions on surfaces. One of the first studies in this direction was carried out by Khokhlov *et al.*⁷⁹ When laser light is applied to a surface and to molecules near it, it is a simple matter to arrange such processes of practical importance in technology (particularly in microelectronics) as the deposition of metals, etching, and the doping of surface layers.^{80,81} As a rule, such processes go by both photochemical and thermal reactions, but the elementary processes and their mechanisms have remained completely puzzling. Research on these processes is an interesting and important problem for the near future, which will probably be solved through the use of the powerful methods of laser selective excitation and laser spectroscopy, especially with the help of picosecond laser pulses.

There is the attractive possibility of arranging selective photochemical, especially photobiological, reactions with molecules in solutions.⁸² In a condensed medium, especially in solvents of molecules, the vibrational-excitation energy relaxes into heat in an unacceptably short time ($\tau_{\text{rel}} < 10^{-12}$ s), so that the most suitable states for photochemical reactions are electronic states, which usually have a lifetime $\tau_{\text{rel}} \approx 10^{-8} - 10^{-11}$ s. Ultrashort laser pulses can be used to excite these states efficiently.

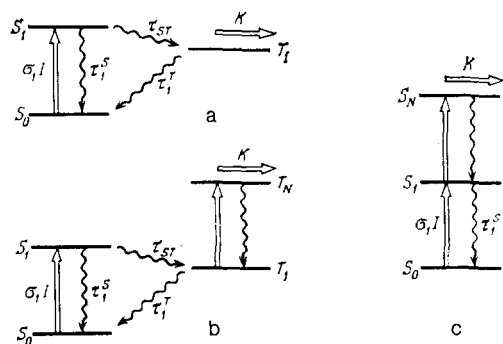


FIG. 7. Various pathways for a photochemical reaction of an electronically excited molecule. a—Well-known reactions in a long-lived triplet state; b—reaction from highly excited triplet states; c—reaction from highly excited singlet states.

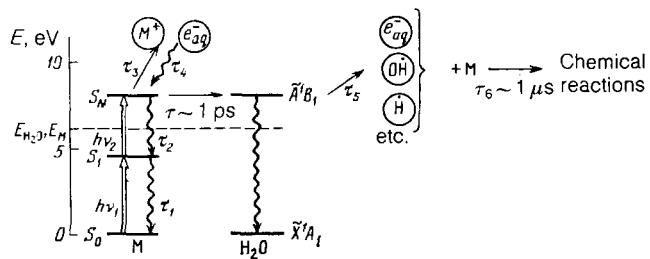
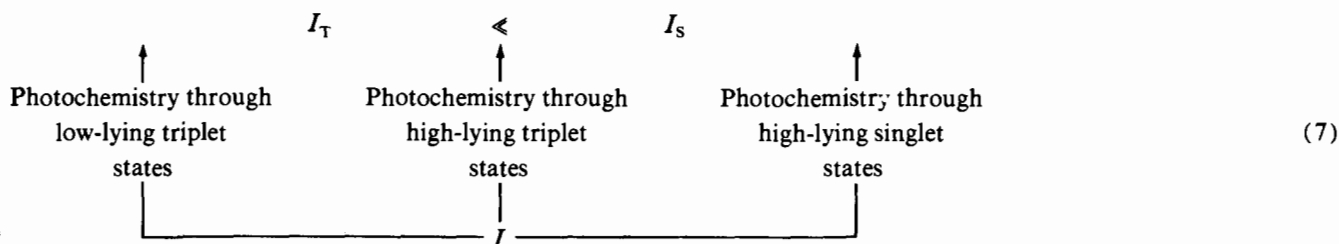


FIG. 8. Two-step excitation of high-lying singlet states (S_N) of molecules in aqueous solution.⁸⁶ The following primary processes are observed: ionization and geminal recombination of electron-cation pairs which are formed, the transfer of electronic energy to the solvent (water), and relaxation of the excitation. Chemical reactions with water radicals dominate the formation of the final products of the photodecomposition of the dissolved molecules.

By varying the parameters of the laser light, one can adjust the degree of electronic excitation of molecules in solutions and switch to different pathways for the photochemical reactions. Possible approaches here are shown in a simplified way in Fig. 7 for the typical case in which the lifetime (τ_T) of a molecule in a triplet state is longer than the lifetime (τ_S) in a singlet state, and the cross sections (σ_S and σ_T) for the electronic transitions are comparable in magnitude. We then have two characteristic parameters: 1) The intensity $I_T = \hbar\omega/\sigma_S\tau_T\varphi$ ISC, at which molecules accumulate in the triplet state, and the absorption of the second photon on a triplet-triplet transition at $\tau_p \gtrsim \tau_T$ becomes probable (φ ISC

is the intercombinational conversion yield); 2) the intensity $I_S = \hbar\omega/\sigma_S\tau_S$, at which molecules build up in the singlet excited state, and the absorption of a second photon on a second singlet-singlet transition becomes probable at a pulse length satisfying the condition $\tau_S \ll \tau_p \ll \tau_T$.

In all cases, the energy flux density (Φ) of the laser pulse which is tuned to resonance with an electronic absorption band, must satisfy the condition $\Phi \gtrsim \Phi_{\text{sat}} = \hbar\omega/\sigma_S$ in order to put a significant fraction of the molecules in the excited state. It is thus possible to use the length of a pulse with a given energy flux density $\Phi \approx \Phi_{\text{sat}}$ to switch between different pathways for the photochemical reaction:



At a high light intensity, i.e., during the excitation of molecules by ultrashort laser pulses, the absorption of two UV photons and a transition of the molecule to a highly excited electronic state become possible. The total energy of the two UV photons in $2\hbar\omega_{UV} \gtrsim 8-10$ eV; i.e., it corresponds to the energy of excitation by vacuum-UV radiation, which does not penetrate into the solvent.⁸³ This method of nonlinear excitation of molecules thus provides the experimentalist some new capabilities, which have already been reflected in several studies. First, photochemical conversions from highly excited electronic states become possible. These conversions have been observed for molecules of nucleic acids in water.^{84,85} This action on biological objects results in a photodamage of a new type. It is not observed during illumination with ordinary UV light, which excites only low-lying, primarily triplet, states. The basic elementary mechanism for photochemical conversions for nucleic acids was recently identified: the generation of OH radical in water as a result of the transfer of molecular excitation energy to the solvent (Fig. 8). The mechanism opens up the possibility of developing methods of laser phototherapy (to supplement the existing methods of radiotherapy which use ionizing radiations) through the excitation of electronic states of biological molecules which lie above the ionization boundary of water molecules.⁸⁶

Control of the pathways for photochemical reactions by varying the intensity of laser light has been observed in experiments on the photochemical synthesis of amino acids and hydroxy acids through the application of intense pulses of UV laser light of picosecond and nanosecond length.^{87,88}

In concluding this brief review of one of the most interesting applications of lasers, we can say that we have already seen demonstrations in very different fields (spectroscopy,

chemistry, and isotope separation) of new possibilities that have been opened up by the use of stimulated transitions during the absorption of several photons (from two to tens) in atoms, molecules, and biological molecules. In other words, the ideas regarding the use of light to stimulate transitions in matter expressed by Einstein back in 1916 have borne fruit not only in the laser itself but also in its applications.

I would like to express my deep gratitude to my colleagues and friends at the Institute of Spectroscopy with whom it has been my good fortune to develop the ideas discussed here over the past fifteen years.

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