Polyatomic molecules in a strong infrared field

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Usp. Fiz. Nauk 134, 45–92 (May 1981)

A review is given of the physical phenomena observed when polyatomic molecules interact with intense infrared radiation pulses. A brief historical account is given of earlier investigations and the main processes are classified. Then, the following topics are considered: 1) multiphoton infrared absorption and transition of molecules through lower vibrational levels; 2) dynamics of molecular excitation in a vibrational quasicontinuum and distribution of the vibrational energy between the modes and levels; 3) dissociation of highly excited molecules. The main experimental and theoretical results, and possible future trends are discussed. The review concludes with a brief list and illustrations of typical applications of the phenomena described in molecular spectroscopy, chemical physics, nuclear chemistry, and chemical synthesis.

PACS numbers: 33.20.Ea, 33.80.Kn, 33.10.Gx, 82.80.Di

CONTENTS

1. INTRODUCTION

Interaction of light with molecules is a subtle physical process whose complexity ranges from the relatively simple case of the interaction with diatomic molecules in the gaseous phase to the interaction of light with complex biomolecules in condensed media, which have hardly been investigated by direct physical methods. Studies of the latter interaction should be carried out not only to satisfy our natural curiosity and the need to understand the surrounding world, but also because of the great importance of molecular photoprocesses in the appearance of life and man. It is sufficient to mention the relatively simple photoprocesses occurring in the ozone layer in the upper atmosphere of the earth and photoprocesses in complex biomolecules, responsible for the photosynthesis in plants and for the vision of animals and man.

The absorption of light by a molecule imparts an excess internal energy and this may be manifested by many processes which are collectively called photochemical. They include particularly the change in the rate of chemical reaction as a result of illumination with light of wavelength absorbed in a given substance. This was discovered back at the beginning of the nineteenth century (see the monograph of Calvert and Pitts[1]): an electronically excited molecule may participate in reactions which do not occur or occur very slowly in the unexcited state. Another important photo-

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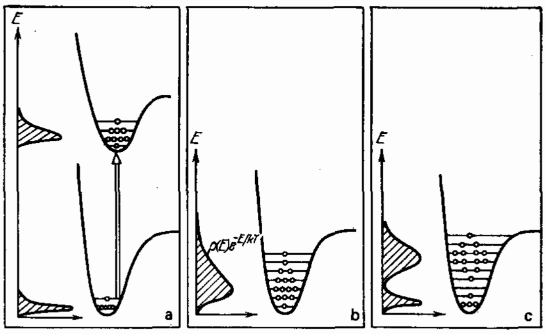

FIG. 1. Molecular excitations resulting in acceleration of chemical reactions: a) nonequilibrium electronic excitation, underlying photochemistry in excited electronic states (electronic photochemistry); b) equilibrium thermal excitation, underlying thermal reactions; c) nonequilibirum vibrational excitation, underlying photochemistry of the ground electronic state (vibrational photochemistry).

process is the splitting of simple molecules under the action of ultraviolet light, discovered and investigated in detail by Academician A. N. Terenin back in the nineteen twenties and thirties.[2] At present this branch of science, which overlaps molecular physics, chemistry, and biology, is known as photochemistry. Many monographs[1-6] and thousands of papers have been written on the subject of photochemistry.

All the photochemical processes investigated until recently have been associated with the excitation only of electronic states of atoms or molecules (Fig. 1a) and, therefore, photochemistry should, strictly speaking, be called photochemistry of excited electronic states or electronic photochemistry. On the other hand, in most cases in chemistry we deal with processes in which electronically unexcited molecules participate. In the ground electronic state an assembly of molecules is distributed between vibrational, rotational, and translational degrees of freedom. If the energy in these degrees of freedom exceeds a certain minimum value, the chemical reactions are again possible. These reactions with molecules in the ground electronic state play a dominant role in chemical technology and, in contrast to photochemical reactions, they are called thermal, because they occur under conditions of equilibrium thermal excitation of molecules in which the role of thermal radiation is negligible.1)

In principle, there is another way of accelerating chemical reactions. Sufficiently strong infrared radiation can create nonequilibrium vibrational excitation of molecules when the temperature of the medium is relatively low, by analogy with the excitation of electronic states of molecules by ultraviolet light. In this case a translationally cold molecule will have a considerable internal energy and, consequently, can participate in new chemical processes (Fig. 1c). Before the appearance of infrared-emitting lasers this potentiality could not have been readily implemented. Nevertheless, direct observations have been reported[9] of an increase in the rate of cis-trans isomerization of vibrationally excited HNO_2 molecules in a matrix by a noncoherent source of infrared radiation. The possibility of using this effect in photochemical separation of isotopes has also been discussed.[10] However, only after the development of high-power pulsed infrared lasers and the discovery of strong excitation of polyatomic molecules by high-power resonant infrared laser radiation a basis has been provided for a rapid development of a new branch of research, which is *the photochemistry of highly excited molecules in the ground electronic state or multiphoton vibrational photochemistry.*

At present work is proceeding on this topic in tens of laboratories around the world. The international efforts of physicists and chemists have created in the last five years a new branch of science, which is at the confluence of quantum electronics, spectroscopy, and chemistry and represents the major part of laser photochemistry. The place occupied by multiphoton vibrational photochemistry in the wide front of research on selective interaction of laser radiation with matter can be established from an earlier review in the present journal.[11] Here, we shall consider only multiphoton infrared photophysics and photochemistry of polyatomic molecules. Several special review papers[12-14] and a monograph[15] have already been devoted to this subject. The monograph[15] reviews over 400 investigations carried out in a fairly short period. The aim of the present review is to give the reader an idea of the physical nature of the behavior of polyatomic molecules in an intense infrared field on the basis of only the key investigations without attempting to provide a complete picture of all that had been published. A complete review can be found in the monograph mentioned earlier.[15] We shall begin with a brief review of the history of multiphoton infrared vibrational photophysics and photochemistry in order to give credit where it is due. This will allow us to mention earlier studies representing bold persistent but not always successful attempts. To some extent, this historical review reflects the personal involvement of the authors.

2. HISTORY OF EARLIER WORK

Very soon after the appearance of lasers, when many nonlinear effects of the interaction between high-power optical fields and matter have been observed, Askar'yan[16] and Bunkin *et al.*[17] analyzed theoretically—in 1964 and later—multiphoton excitation of vibrations of diatomic anharmonic molecules. They discussed the buildup of molecular vibrations by high-power radiation of frequency $\omega \approx \omega_{vib}$ and its multiples. Dissociation of a diatomic molecule (regarded as an anharmonic Morse oscillator) requires, as calculated by these authors, an intensity of the order of 10^{11}–10^{12} W/cm^2. Even now,

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1) It should be noted that back in 1919 the famous French physicist Perrin explained an increase in the rate of some chemical reactions of complex molecules due to heating of a reaction vessel by putting forward a hypothesis[7] according to which infrared radiation from the heated walls of the vessel excites the vibrational levels of a molecule and this increases the rate of reaction. However, Langmuir[8] showed that the intensity of thermal infrared radiation would be too low to account for the observed effect.

when focusing of high-power infrared laser pulses makes these intensities fully attainable, multiphoton excitation of vibrations of diatomic molecules (Fig. 2a) is not observed.

After the construction of the first sufficiently powerful cw infrared laser (utilizing CO_2 molecules in the 10 μ range) the first experiments were carried out on the interaction between laser radiation and molecular gases. Borde *et al.*[18] observed visible radiation from gaseous ammonia and products of its dissociation caused by CO_2 laser radiation, whose frequency coincided with the vibrational-rotational absorption line of NH_3. The effect was attributed[16,19] to thermal heating of NH_3 to a high temperature by the incident laser radiation. Similar experiments were subsequently carried out using a CO_2 laser and BCl_3 molecules.[20] It became quite clear that in all these experiments the main role in the excitation of vibrational levels was played by collisions, which not only deexcited vibrations but also transferred vibrational energy to the molecules. Khokhlov *et al.*[21] considered the possibility of collisional-radiative excitation of vibrations of molecules by infrared radiation. In the model adopted the collisional excitation of high molecular levels is possible on condition that the rate of exchange of the vibrational excitation (VV exchange) described by $1/\tau_{VV}$ is considerably greater than the rate of relaxation $1/\tau_{VT}$ of vibrational excitation into heat (VT relaxation). Khokhlov *et al.*[21] found conditions under which we can expect acceleration of a photochemical reaction by infrared radiation which excites directly only the first vibrational level, followed by collisional transfer of excitation to higher levels (Fig. 2b). The required intensities are relatively low ($10-10^3$ W/cm^2) but selection of the molecules satisfying the condition $\tau_{VV} \ll \tau_{VT}$ plays a key role. Beginning from Refs. 22 and 23, many experiments have been carried out on the interaction of cw infrared radiation with molecular mixtures in order to accelerate chemical reactions. Since in none of these experiments on polyatomic molecules was the condition $\tau_{VV} \ll \tau_{VT}$ satisfied reliably, there is no agreed view on the results of these experiments. Many investigators are of the opinion that they can be explained by a purely thermal effect (see, for example, Refs. 24-26). We shall in this review consider the behavior of isolated molecules in a strong infrared field when the role of collisions is negligible and, naturally, the above method will not be discussed here. The interested reader is advised to turn to Refs. 22-29.

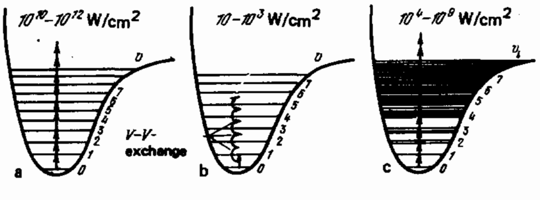

FIG. 2. Main methods for excitation of vibrational levels of molecules: a) multiphoton excitation of vibrations of a simple molecule requiring intensities of $10^{10}-10^{12}$ W/cm^2; b) collisional excitation of vibrations due to *VV* exchange with molecules excited resonantly by infrared radiation of $10-10^3$ W/cm^2 intensity; c) multiphoton excitation of vibrations of a polyatomic molecule requiring infrared radiation intensities 10^4-10^9 W/cm^2.

The development of high-power pulsed transversely excited atmospheric (TEA) CO_2 lasers has made it possible to study the interaction of intense (10^6-10^9 W/cm^2) infrared radiation pulses with molecules. Optical breakdown and visible fluorescence have been observed[30] in several molecular gases (NH_3, SiF_4, CCl_2F_2, etc.) as a result of focusing of CO_2 laser radiation pulses. It has been found that visible fluorescence appears at intensities much lower than the optical breakdown threshold at the focus. An investigation of the spectra has established that fluorescence is due to electronically excited molecular products of dissociation processes. More detailed quantitative studies of the kinetics and spectra of the fluorescence emitted by NH_3 and C_2F_3Cl molecules under the action of CO_2 laser pulses have been carried out.[31] A study of the kinetics showed that the fluorescence appeared without any noticeable delay relative to the leading edge of a laser pulse. Dissociation of the N_2F_4 molecules under the action of CO_2 laser pulses has also been investigated[32] but the rate of dissociation was deduced from the appearance of the NF_2 radicals in the ground electronic state (from the ultraviolet absorption and not the fluorescence spectra). A characteristic feature of the earlier investigations[31,32] has been the observation of dissociation of polyatomic molecules at a rate much higher than the rate of conversion (relaxation) of the absorbed energy into heat. However, in veiw of the relatively high pressures (tens of Torr), a few collisions accompanied by VT relaxation may have occurred during the observation time.

A discussion of the possible dissociation mechanism[31,32] demonstrated readily that it is not easy to interpret the experimental results. A more detailed calculation of the kinetics of radiative excitation of molecular vibrations by infrared laser pulses[33] showed that the participation of collisions in any one of the relevant processes (VT relaxation, VV exchange, and rotational relaxation) fails to account for the observed dissociation rate. On the other hand, direct radiative excitation of high vibrational levels without any participation of collisions may, in principle, account for the observed rate of dissociation but it meets with an obvious objection which is the anharmonicity of the vibrations. Anharmonic detuning of vibrations is the reason for the very high intensities (several orders of magnitude higher than those employed in the experiments described above) of infrared radiation required for direct multiphoton excitation.

The problem of accounting for the dissociation mechanism and, in particular, of demonstrating that it is possible in the case of interaction of an isolated molecule with infrared field was tackled at the Institute of Spectroscopy of the USSR Academy of Sciences in 1972: experimental studies were made with the aim of detecting isotopically selective dissociation of a mixture of $^{15}NH_3$ and $^{14}NH_3$ molecules by focused CO_2 laser radiation pulses of frequency tuned to resonance with the vibrations of the $^{15}NH_3$ molecules. The experiments gave a negative result, which is fully understandable only now when we know the conditions needed for isotopically selective infrared dissociation of molecules. At that time it was decided to carry out a detailed study of the fluorescence and dissociation employing another molecule, which was BCl_3. A similar series of experiments was carried out by Canadian researchers on SiF_4 molecules and their results were published[34] earlier than our work on BCl_3. Reduction of the pressure (to 0.03 Torr) made it possible to observe collisionless photodissociation of these molecules, as deduced from the instantaneous fluorescence peak, and the contribution of collisions was found from the delayed fluorescence. For all the similarity of the methods and results of these independent experiments,[34,35] there were also some significant differences. For example, in the Canadian experiments[34] on SiF_4 the CO_2 laser frequency was not in resonance with the fundamental vibration, whereas in our work[35] on BCl_3 the dissociation was clearly resonant. In the Canadian work[34] the nonresonant nature of the dissociation was explained by the idea of a vibrational quasicontinuum, which begins at relatively low vibrational excitation energies (3000–5000 cm^{-1}) and which a molecule enters after simultaneous absorption of 3–5 infrared photons (Fig. 2c).

The resonant nature of collisionless dissociation of BCl_2 observed by us[35] suggested a further series of experiments designed to prove dissociation of an isolated molecule in a strong infrared field by observing isotopic selectivity of the dissociation in a natural mixture of $^{10}BCl_3$ and $^{11}BCl_3$ isotopic molecules. After many initially unsuccessful experiments, designed to detect this effect by direct observation of a change in the isotopic composition of BCl_3, we carried out experiments in which the isotopic effect was studied in the primary products employing the chemiluminescence spectrum of the BO radical with a time resolution better than 10^{-7} sec. This eliminated the indeterminacy in the interpretation of the results associated with the loss of selectivity in the final dissociation products because of secondary processes. It was reported for the first time in Ref. 36 that isotopically selective dissociation of the BCl_3 molecule was achieved. This was important for two reasons. Firstly, it became finally clear that it is possible to dissociate an isolated molecule by a strong infrared field even in the absence of collisions. Secondly, another practical method has been found for separating isotopes within our photodissociation approach to laser separation.[37,38] The resonant nature of the dissociation was observed also by others[39] where preferential (the difference amounted to 15%) dissociation of trans-2-butane molecules mixed with cis-2-butane was achieved by CO_2 laser radiation. However, the results reported there were too limited to identify the relevant mechanism among several, one of them including collisions.

The discovery of isotopically selective dissociation of BCl_3 molecules in strong infrared fields made it clear that this effect is fairly common and should be observed also for other polyatomic molecules. In fact, successful experiments on isotopically selective dissociation of SF_6 molecules and macroscopic enrichment with the sulfur isotopes were soon carried out[40] at the Institute of Spectroscopy of the USSR Academy of Sciences. These experiments were soon reproduced at the Los Alamos Laboratory in the U.S.A.[41] Isotopically selective dissociation was also achieved for heavy isotopes (osmium isotopes in the OsO_4 molecule[42]). In this last work it was possible to observe directly (from changes in the ultraviolet absorption spectra) the excitation of high vibrational levels of the OsO_4 molecule in an infrared field of moderate intensity (about 10^6 W/cm^2). Clearly, this excitation of vibrational levels below the dissociation limit can account for the experimental observation[43] of an isotopically selective chemical reaction of BCl_3 molecules with H_2S (or D_2S) under the action of CO_2 laser pulses.

These successful experiments on isotopically selective dissociation of polyatomic molecules[36,40–42] met with a major response from experimenters working on methods for isotope separation and control of chemical reactions and from theoreticians interested in the nontrivial effect of collisionless resonant dissociation of polyatomic molecules in a strong infrared field. Essentially, a new method has been developed for creating a strong nonequilibrium distribution of molecules between the vibrational levels directly by an intense infrared field without translational heating (Fig. 2c) and this has become the main trend in the photochemistry of molecules in the ground electronic state. The radiation intensity required in this case is intermediate between the other approaches discussed above and shown schematically in Fig. 2: radiative multiphoton excitation of simple molecules, which needs 10^9–10^{12} W/cm^2, and radiative–collisional excitation, which needs only a relatively low intensity of 10–10^3 W/cm^2.

3. MAIN PROCESSES

Multiphoton excitation and dissociation of polyatomic molecules in strong infrared fields are fairly difficult to describe theoretically and so far only an approximate semiquantitative theory has been developed. The difficulties are mainly due to the fact that practically nothing is known about vibrational–rotational transitions between excited vibrational states of polyatomic molecules. The attempts to explain and describe quantitatively the phenomena of multiphoton excitation and dissociation of molecules have yielded the first experimental data on the spectra of transitions between excited (and particularly highly excited) vibrational states of polyatomic molecules, and the phenomena themselves have become the main methods for obtaining this spectroscopic information.

We shall use a relatively simple model of multiphoton excitation and dissociation of polyatomic molecules, which is capable of explaining qualitatively the main features of these phenomena. Figure 3 shows in a simplified manner the main stages of multiphoton excitation and subsequent dissociation of polyatomic molecules in a strong resonant infrared field, as now accepted by all the investigators.

Resonant multistage excitation of a molecule in an infrared field of moderate intensity occurs in the range

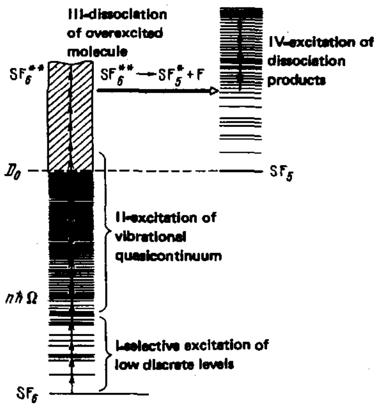

FIG. 3. Model of the process of dissociation of a polyatomic molecule by an intense infrared field. Stage I: resonant excitation of low-lying vibrational transitions; stage II: strong excitation (vibrational heating) of molecules by transitions between high-lying states; stage III: unimolecular decay of an overexcited molecule; stage IV: subsequent strong excitation (and dissociation) of polyatomic decay products.

of lower vibrational transitions. This is the result of compensation of the anharmonic detuning of the frequencies of successive vibrational transitions by changes in the rotational energy of a molecule, anharmonic splitting of the excited degenerate vibrational states, etc. In those cases when at some of the lower transitions the anharmonicity is not compensated exactly, both two- and three-photon vibrational transitions with near-resonant intermediate levels occur at slightly higher intensities. Resonant and, in particular, isotopically selective excitation of molecules is possible during this first stage.

As a polyatomic molecule is excited to higher vibrational levels, the number of possible vibrational transitions from a given vibrational–rotational state increases rapidly. This is due to the high density of vibrational levels of a molecule which has a large number of degrees of freedom and due to the interaction between these levels. Therefore, the spectrum of vibrational transitions between highly excited states does not have such a definite resonant nature as in the case of lower transitions. We shall adopt the term vibrational quasicontinuum to denote the wide-band and, consequently, relatively weak spectrum of transitions between such levels. If the intensity (or, more exactly, the energy flux) in the absence of relaxation of the absorbed energy of infrared pulses is sufficiently high, a polyatomic molecule can move up the levels of this quasicontinuum, in spite of the small absorption cross sections for transitions between the levels.

We thus find that a molecule can acquire energy comparable with the dissociation limit. This energy is distributed between many vibrational degrees of freedom because numerous composite vibrations can participate in the absorption resulting from transitions in the vibrational quasicontinuum. A molecule dissociates during a laser pulse (usually of 10^{-7} sec duration) if its rate of dissociation exceeds 10^7 sec^{-1}. For this purpose, a molecule should have a certain excess of the vibrational energy above the dissociation limit, as is known from thermochemical data. In other words, the energy of transident dissociation is slightly higher than the energy of steady-state dissociation when an unlimited time is available. This dissociation of a vibrationally overexcited molecule is the third stage of the process.

If one of the molecular fragments (products) is itself polyatomic, it can participate in multiphoton absorption of infrared radiation and break up into simpler fragments. This is possible at the expense of an excess vibrational energy transferred by an overexcited molecule to its polyatomic fragment, since it finds itself immediately in the vibrational quasicontinuum, or due to retention of resonant coupling to the infrared radiation by the polyatomic fragment. In both cases such a fragment (for example, SF_5) can itself absorb the infrared radiation. Successive dissociation of a polyatomic molecule and its fragments is the fourth possible stage of the breakup of a polyatomic molecule in a strong infrared field.

It should be stressed that this division of the process into stages is in many respects arbitrary, since these stages are superimposed on one another but it is convenient for the understanding of the main features of such a complex process of the interaction of a radiation field with a quantum system which has a large number of degrees of freedom and breaks up under the action of a nonlinear external force. This relatively simple model of the process has been developed gradually as a result of synthesis of several key ideas suggested by different investigators. "Soft" compensation of the anharmonicity at lower vibrational transitions, particularly because of a change in the rotational energy, was suggested in Ref. 44. The role of multiphoton processes at lower levels was discussed in Refs. 45 and 46. The idea of nonresonant excitation of a molecule by transitions between highly excited states forming a vibrational quasicontinuum was put forward in Ref. 34 and then discussed in Refs. 47–50. Direct experimental studies[50] of selective dissociation of molecules in a two-frequency field (resonant infrared field + infrared field nonresonant for lower transitions) confirmed the validity of these qualitative ideas. The role of mixing (or stochastization) of various vibrational modes in the course of strong excitation by infrared radiation of one vibrational degree of freedom was discussed in Ref. 51. The extent of vibrational overexcitation of a molecule above the dissociation limit and the possibility of subsequent dissociation of molecular fragments were considered and investigated in Refs. 52 and 53. These experiments on molecular beams showed that the dissociation occurred by breaking of the weakest molecular bond and the appearance of simpler fragments was due to the subsequent dissociation of the primary products.

Numerous subsequent investigations of the characteristics of multiphoton excitation and dissociation of a large number of different molecules confirmed the validity of the above qualitative picture. In particular, special selection of the molecules made it possible to study changes in the contribution of each of the stages to the multiphoton process of excitation and dissociation. For example, a systematic study was made of more complex molecules, particularly S_2F_{10} (Ref. 54), for which the boundary of the vibrational quasicontinuum is very low and is located in the region of the first excited multiphoton state (Fig. 4a). In this case the first stage of multiphoton excitation is practically absent and a molecule of this kind begins to exhibit directly transitions to the quasicontinuum. A similar situation occurs also in the case of polyatomic molecular ions under the conditions preventing collisions when these ions dissociate under the action of cw laser radiation of relatively low power (amounting to several watts).[55]

In the case of simple polyatomic molecules the boundary of the vibrational quasicontinuum corresponds to 3–5 vibrational quanta but dissociation occurs when the vibrational energy received from the infrared field exceeds slightly the dissociation limit (1–2 infrared photons) and the dissociation products cannot absorb efficiently infrared radiation in the multiphoton process (Fig. 4b). For such molecules (for example, CF_3I) the dissociation process is not complicated by a strong overexcitation of a molecule above the dissociation limit and by the secondary processes of fragment dissociation. In this case it is possible to compare theory and experiment quite accurately.[56]

Many polyatomic molecules have excited electronic states below the dissociation limit of the ground electronic state. In such cases there is unavoidable mixing of the wave functions of the higher vibrational states of the ground electronic state and of the lower vibrational states of an excited electronic state. When a large number of infrared photons is absorbed, such mixed electronic–vibrational states may be excited. Therefore, we may find a molecule in an excited electronic state and the probability of this happening depends both on the degree of the electronic–vibrational interaction and on the ratio of the statistical weights of the vibrational states in the quasicontinuum and in an excited electronic state. In this state a molecule can fluoresce (Fig. 4c), which clearly occurs when the OsO_4 molecule is excited with CO_2 laser radiation and which accounts[57] for its fluorescence even without the need for dissociation and for the appearance of electronically excited fragments. It may be necessary to review the interpretation of the results of earlier experiments on SiF_4 (Ref. 34) from this point of view. Moreover, an electronically excited molecule may continue to absorb many infrared photons at the same time until the dissociation limit of the excited electronic state is reached (Fig. 4b) and it can thus dissociate in another channel with a higher energy barrier. This is the probable explanation of the collisionless appearance of C_2 radicals as a result of dissociation of C_2H_4 molecules by CO_2 laser radiation.[58,59]

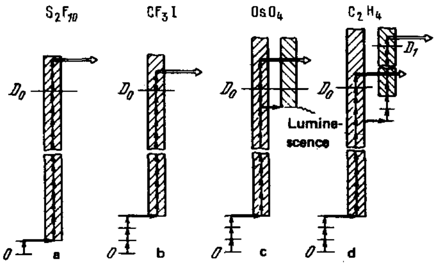

FIG. 4. Various limiting cases of multiphoton excitation and dissociation of polyatomic molecules by infrared radiation: a) multiphoton excitation of a molecule with a very low boundary of a vibrational quasicontinuum (shaded region below dissociation limit D_0 under steady-state conditions); b) decay of a molecule in the case of slight overexcitation ($E - D_0 \ll D_0$) above the dissociation limit D_0 in the region of real continuum (shaded region above D_0); c) excitation of mixed electronic–vibrational molecular states capable of emitting visible or ultraviolet luminescence; d) multi-photon excitation of mixed electronic–vibrational states and subsequent multiphoton vibrational excitation to an electronically excited state.

We can thus see that even this simplified classification demonstrates a great variety of the processes which occur when a polyatomic molecule is in a strong infrared field. Therefore, in the initial analysis of the behavior of a specific polyatomic molecule in an infrared field we have to understand first which of the above simplified cases (Fig. 4) applies. However, this requires at least an investigation of the characteristics of multiphoton excitation and dissociation of such molecules over a wide range of infrared field intensities and frequencies.

4. MULTIPHOTON ABSORPTION OF INFRARED RADIATION AND TRANSITION OF MOLECULES THROUGH LOWER VIBRATIONAL LEVELS

In accordance with the above model of dissociation of molecules in a strong infrared field (Sec. 3, Fig. 3) and classification of the main processes (Sec. 3, Fig. 4) we shall now consider the first stage of the process when multiphoton absorption vibrational transitions between the lower vibrational states bring a molecule to a vibrational quasicontinuum.

In the simplest approximation the process of multiphoton absorption of radiation and excitation of a molecule can be described by an average energy $\bar{\varepsilon}$ absorbed by a molecule or by the average number $\bar{n} = \bar{\varepsilon}/\hbar\Omega$ of the absorbed infrared photons of energy $\hbar\Omega$. This characteristic is determined by measurements of the absorbed (in the irradiated volume) energy from an infrared radiation pulse, when the absorbed energy is shared equally among all the molecules in the irradiated retion. Determination of the dependence of $\bar{n}$ on the energy density Φ (or on the radiation intensity P for a given pulse duration τ_p) and on the radiation frequency Ω gives directly the most important characteristics which are the unsaturated and resonant nature of multiphoton absorption by polyatomic molecules (Sec. 4.a).

Such an average description of the multiphoton absorption process by the quantity $\bar{n}(\Phi, \Omega)$ is useful but it is far too simplistic and, strictly speaking, valid only in the limit of very high intensities when we know that all the molecules in the irradiated region are participating in the multiphoton absorption process. In fact, at moderate intensities certainly not all the molecules participate effectively in this absorption process or are capable of being raised to high vibrational states. This is related to the initial distribution of molecules between many vibrational states and is known[33,60] as the "rotational bottleneck" in the excitation of molecular vibrations by monochromatic infrared radiation pulses. Determination of the fraction q of molecules excited by the multiphoton process and of its dependence on the energy density Φ (or on the intensity P) and the frequency Ω of infrared radiation pulses gives a fuller description of multiphoton excitation (Sec. 4.b below). Naturally, the most complete description of multiphoton excitation is provided by the distribution function $F(\varepsilon)$ of the vibrational energy ε acquired by molecules from the infrared field. In this section we shall consider multiphoton excitation employing average characteristics $\bar{n}(\Phi,\Omega)$ and $q(\Phi,\Omega)$. An analysis of the distribution function of the vibrational energy $F(\varepsilon)$ will be given later (Sec. 5) in the course of description of multiphoton excitation of molecules in a vibrational quasicontinuum.

a) Characteristics of multiphoton absorption

An interesting observation was made in the early experiments[61] on multiphoton excitation of the SF_6 molecule in an infrared field: the absorbed energy $\bar{\varepsilon}$ increased monotonically on increase in the pulse intensity. This behavior of the absorption differs greatly from the familiar behavior of a two-level system which begins to absorb linearly and then, because of saturation, ceases to absorb at all. A similar behavior is expected also for a molecule because of anharmonicity of the vibrations. Naturally, at very high intensities one can expect a strong power-law dependence because of the n-photon processes. However, in the case of SF_6 the rise is monotonic and slightly sublinear. This shows that the excitation of the $v=1$ level is accompanied simultaneously or subsequently by the excitation of higher vibrational states, i.e., the average level of vibrational excitation increases gradually as the intensity P or the energy density Φ is increased. Saturation of such a multiphoton absorption occurs for levels $\bar{n} \gg 1$ because of dissociation of the excited molecules.

Similar dependences were reported subsequently for several other polyatomic molecules.[62] It was found[62] that multiphoton absorption by simple molecules (OCS, D_2O) is of similar nature to that of a two-level saturable system with the maximum number of absorbed photons given by $\bar{n}<1$ (Fig. 5). Direct determinations of the dependence $\bar{n}(\Phi)$ have now been made for many molecules. A summary of such measurements[63] supplemented by other results[64,65] is plotted in Fig. 5. The energy density at which the average number of absorbed photons is $\bar{n} \gg 1$, ranges from 10^{-3} J/cm² for complex molecules (SF_5NF_2, S_2F_{10}) and molecules with a heavy atom (UF_6) to tens of joules per square centimeter for less complex molecules with a large rotational constant (C_2H_4).

These complex molecules are characterized by an almost linear rise of the average number of absorbed photons, i.e., the dependence $\bar{n}(\Phi)$ is linear. This linearity is explained in Refs. 66–69, where reports are given of systematic measurements of the multiphoton absorption by complex molecules: the linear dependence is explained by a high density of vibrational states at low energies because of the presence of low-frequency vibrations and, consequently, because of the descent of the lower boundary of the vibrational quasicontinuum to the region of the $v=1$ level (Fig. 4a).

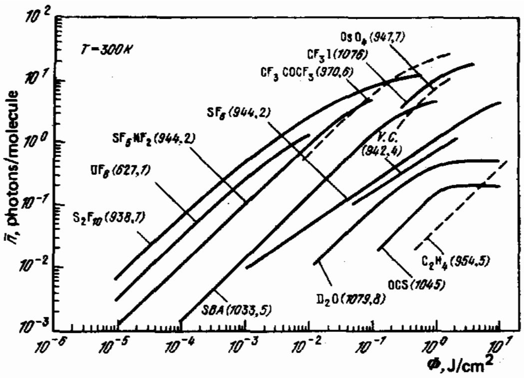

FIG. 5. Comparison of the dependences of the average number $\bar{n}$ of absorbed infrared photons (per molecule) on the energy density Φ of infrared pulses interacting with different molecules. The results represent those summarized in the review in Ref. 63 supplemented with data from Refs. 64 and 65.

We shall note some deviations from the monotonic dependences $\bar{n}(\Phi)$. In the case of the OsO_4 molecule the dependence $\bar{n}(\Phi)$ is step-like with several saturation regions.[57,70] This is attributed to the step-like dependence on Φ of the fraction of the molecules interacting with the infrared field.[70] In the case of the SF_6 molecule at a low temperature (137°K) the dependence of $\bar{n}$ on Φ is superlinear.[71] This is explained by the role of two- and three-photon processes of the excitation of lower vibrational states.

The dependence of the number of absorbed photons on the frequency $\bar{n}(\Omega)$, known as the multiphoton absorption spectrum, is strongly resonant. This accounts for the possibility of selective multiphoton excitation of molecules and, in particular, for its use in laser isotope separation. Therefore, the resonant characteristics of multiphoton absorption are important in practice and considerable attention is given to them. We now know the multiphoton absorption spectra of about ten molecules, but mainly in the 9–11 μ range because of the use of CO_2 laser radiation. The main features of the multiphoton absorption spectra are as follows: the spectra are highly sensitive to the radiation intensity, broadening and shift of the resonance in the direction of the red part of the spectrum result from an increase in the intensity, and narrow resonances appear in the spectra in a certain range of intensities. We shall illustrate this by two examples.

Figure 6 shows the evolution of the multiphoton absorption spectrum of two molecules (SF_6 and OsO_4) when the intensity increases. In the SF_6 case there is a clear shift of the absorption maximum toward longer wavelengths and broadening of the absorption band. This result was obtained[62] by the optoacoustic method and later confirmed[72] by transmission measurements. The shift and broadening of a multiphoton absorption

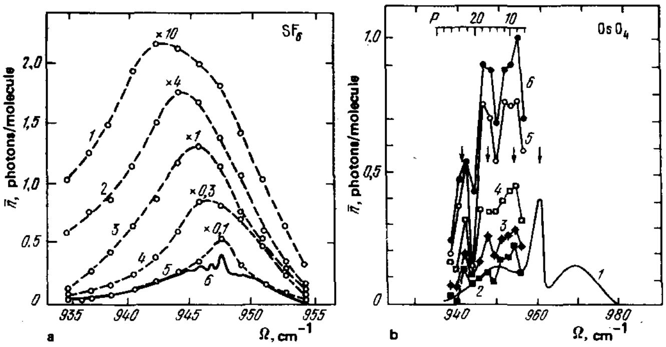

FIG. 6. Evolution of multiphoton absorption spectra of SF_6 and OsO_4 molecules resulting from an increase in the energy density of infrared pulses at 100°K. Experimental conditions: a) SF_6 pressure 0.45 Torr, CO_2 laser pulse duration 100 nsec, intensity 60, 10, 1.2, 0.15, and 0.035 MW/cm^2 for curves 1-5, respectively, curve 6 represents the linear absorption spectrum, real scale of the curves is indicated by a factor alongside each of them[62]; b) OsO_4 pressure 0.18 Torr, pulse duration 90 nsec, energy densities 0.31, 0.64, 0.94, and 1.26 J/cm^3 for curves 2-5, respectively, curve 1 represents the linear absorption spectrum, arrows identify the positions of successive anharmonic shifts $2|x_{33}|\,\omega_3$ taken from Ref. 70.

band on increase in the intensity can be explained qualitatively by the anharmonicity of the vibrations. In fact, an increase in the infrared radiation intensity increases the average degree of excitation of the interacting molecules and, consequently, it increases the contribution of all the higher vibrational transitions to the multiphoton absorption process. Since the spectrum of transitions between high vibrational levels shifts (because of the anharmonicity) on increase in the level number toward longer wavelengths, a gradual "red" shift and broadening of the multiphoton absorption band are observed.

At room temperature only 30% of the molecules are in the ground vibrational state and the others are distributed in an equilibrium manner between low vibrational states. This gives rise to "hot" bands in the linear absorption spectrum (long-wavelength peaks superimposed on the continuous curve in Fig. 6a). The distribution of molecules between many initial states naturally complicates the multiphoton absorption spectrum, since there are then many different ways of multiphoton excitation of a molecule. Cooling of SF_6 reduces the width of the linear infrared absorption spectrum[73] because of a reduction in the intensity of these "hot" bands and also because of a reduction in the width of the distribution of the molecules between the vibrational levels. This immediately alters the multiphoton absorption spectrum, which acquires a structure.[71,74]

In some cases the structure of the multiphoton absorption spectrum appears in a certain range of intensities even at room temperature: this is true, for example, of the OsO_4 molecules (Fig. 6b).[70] If the energy density of infrared pulses is $\Phi > 0.03$ J/cm^2, the absorption by OsO_4 deviates from linearity and the multiphoton absorption spectrum has three peaks at the wavelengths of the P(8), P(16), and P(22) lines of a CO_2 laser. The positions of the peaks are in agreement with the successive anharmonic shifts ($2|x_{33}| = 5.98$ cm^{-1}) of the ν_3 mode. An increase in Φ does not alter the positions of the peaks but the contrast between them decreases and the width of the multiphoton absorption band increases. The appearance and such evolution of narrow resonances in the multiphoton absorption spectrum were investigated[64,75] for the C_2H_4 molecules. When the energy density of the laser pulses was $10^{-3}-10^{-2}$ J/cm^2, very narrow (about 10^{-2} cm^{-1} wide) multiphoton absorption resonances were observed. A high-pressure CO_2 laser with a continuous frequency tuning was used in these measurements. Narrow multiphoton absorption resonances were recently revealed also by a similar technique in the case of the SF_6 molecule.[76]

b) Fraction of molecules which become excited

At low energy densities of infrared pulses, when multiphoton excitation of high vibrational states is not yet important, a monochromatic infrared field interacts (in the absence of rotational relaxation) with just a small proportion of the molecules which are at rotational levels J and which can undergo a $v=0 \to v=1$ transition at the field frequency Ω. Thermal population of these rotational levels determines the maximum fraction of the molecules f which can be excited by a short pulse to the level $v=1$ in the case of saturation of a vibrational-rotational transition. This effect is known as the rotational bottleneck: it was predicted by the present authors[33] and detected experimentally later.[60] The value of f estimated for different molecules lies within the range 0.1-0.001 and depends strongly on the gas temperature.

An attempt to allow for this effect in estimating the true number of the photons absorbed by the SF_6 molecules participating in multiphoton excitation was made in the first investigations of multiphoton absorption.[61,77] The absorbed energy was assumed to be shared only by a fraction f of the molecules in the irradiation region. Such a rough estimate gave initially strongly overestimated numbers of the infrared photons absorbed by molecules. Observation of bleaching of an infrared absorption band for many vibrational-rotational transitions at the same time[78] led to the conclusion that many initial rotational states were emptied by a high-power infrared pulse. This experiment showed that the number $q(\Phi)$ of the SF_6 molecules participating in the multiphoton absorption process in the case when $\Phi = 10^{-2}-1.0$ J/cm^2 was considerably greater than the fraction of the molecules f interacting with the infrared field in the linear limit, i.e.,

$$q(\Phi) \gg f = q(0). \tag{4.1}$$

The question of how close was $q(\Phi)$ to unity remained unresolved.

Soon after investigations were made of the OsO_4 (Ref. 79), SF_6 (Ref. 80), and CF_3I (Ref. 81) molecules by a variety of methods, it was established that the value of $q(\Phi)$ in the case of multiphoton excitation increased on increase in Φ from relatively low values to the maximum amounting to unity. It was thus found that typically multiphoton excitation creates two ensembles of molecules. A fraction of the molecules q participating in multiphoton excitation forms an ensemble of vibrationally "hot" (i.e., highly excited) molecules. The remainder $(1-q)$ remains at lower vibrational levels and forms an ensemble of vibrationally "cold" molecules under conditions probably little different from the initial (Fig. 7a).

In other words, it was found that the distribution function $F(\varepsilon)$ of the vibrational energy of molecules after multiphoton excitation can be represented approximately by

$$F(\varepsilon) = q(\Phi) F_e(\varepsilon) + (1-q) F_0(\varepsilon), \tag{4.2}$$

where $F_0(\varepsilon)$ is the initial vibrational distribution of the molecules which describes an ensemble of "cold" molecules and $F_e(\varepsilon)$ is the vibrational distribution of highly excited molecules describing a "hot" ensemble. The average (over all the molecules) number of absorbed infrared photons $\bar{n}$ introduced earlier

$$\hbar\Omega\bar{n} = \int_0^\infty \varepsilon\,[F(\varepsilon) - F_0(\varepsilon)]\,d\varepsilon \tag{4.3}$$

is related to the average number of photons $\bar{n}_q$ absorbed by molecules in the "hot" ensemble

$$\hbar\Omega\bar{n}_q = \int_0^\infty \varepsilon\,[F_{\rm B}(\varepsilon) - F_0(\varepsilon)]\,d\varepsilon \tag{4.4}$$

by the simple expression

$$\bar{n}(\Phi, \Omega) = \bar{n}_q(\Phi, \Omega)\, q(\Phi, \Omega), \tag{4.5}$$

where it is assumed that the average energy of molecules in the "hot" ensemble $\bar{\varepsilon}_q = \bar{n}_q\hbar\Omega$ is much higher than the average energy $\bar{\varepsilon}_0$ of molecules in the "cold" ensemble.

Figure 7b shows the dependences of the fraction q of molecules excited to a vibrational quasicontinuum on the energy density Φ in the case of three molecules investigated in Refs. 80–82. We can clearly see that for typical (of the majority of experiments) values of the energy density of infrared pulses (0.1–1.0 J/cm^2) only a certain proportion of molecules reaches the vibrational quasicontinuum. Therefore, a correct determination of the average energy of the excited molecules $\bar{\varepsilon}_q$ cannot be made without allowance for the rotational bottleneck or, in the present case, the effect of formation of two molecular ensembles. However, as the energy density is increased to a few joules per centimeter squared, it is clear from the example of the molecules mentioned above that multiphoton excitation affects all the molecules, i.e., a single "hot" ensemble is formed. Under these conditions when $q \approx 1$ we can ignore the formation of two ensembles. Bloembergen *et al.*[83] used subnanosecond CO$_2$ lasers in multiphoton excitation of SF$_6$ in order to remove indeterminacy in the estimate of the fraction q of the molecules participating in multiphoton excitation and to find correctly the absorbed energy. Pulses of this kind are characterized by a high intensity (in excess of 10^9 W/cm^2) for a moderate energy density $\Phi \approx$ J/cm^2 and, therefore, one can expect multiphoton excitation of all the molecules, i.e., that the condition $q \approx 1$ is attained. This makes it possible to find the dependence of the dissociation yield of molecules on the energy acquired from the infrared field without determining the value of q.

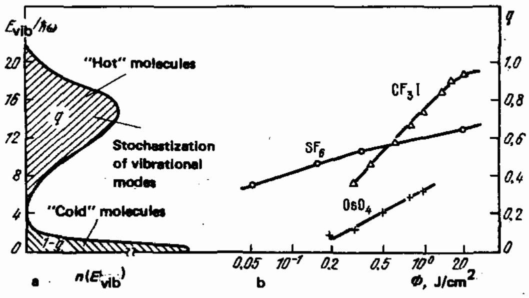

FIG. 7. Formation of two ensembles of vibrationally "hot" and "cold" molecules by multiphoton excitation with a high-power infrared radiation pulse: a) distribution of the vibrational energy of molecules after multiphoton excitation; b) dependence of the relative fraction q of strongly excited molecules on the energy density of CO$_2$ laser pulses interacting with SF$_6$ (Ref. 80), OsO$_4$ (Ref. 82), and CF$_3$I (Ref. 81) molecules.

The frequency dependence of q had been determined only for two molecules: OsO$_4$ (Ref. 82) and CF$_3$I (Ref. 56). Figure 8 shows the dependence $q(\Omega)$ obtained in Ref. 82 for a fixed value of the energy density $\Phi = 1.2$ J/cm^2 of infrared pulses. At the maximum of the linear infrared absorption band the fraction was $q = 0.6$ and it fell considerably at the long-wavelength edge of the band. The frequency dependence of the average energy of the molecules $\bar{\varepsilon}_q$ in the "hot" ensemble is also plotted in Fig. 8. The number of infrared photons absorbed by the "hot" molecules rises at the long-wavelength edge. This is due to an increase in the absorption cross section in a vibrational quasi-continuum at long wavelengths. We can thus conclude that the resonant nature of the multiphoton absorption spectra, i.e., of the quantity $\bar{n}(\Omega)$ governed—according to Eq. (4.5)—by the product of $\bar{n}_q(\Omega)$ and $q(\Omega)$, is related to the resonant dependence of the fraction of molecules reaching a vibrational quasicontinuum.

c) Theory of transition through lower levels in multiphoton excitation of molecules

Excitation of the lower vibrational levels of molecules right up to the edge of a vibrational quasicontinuum has

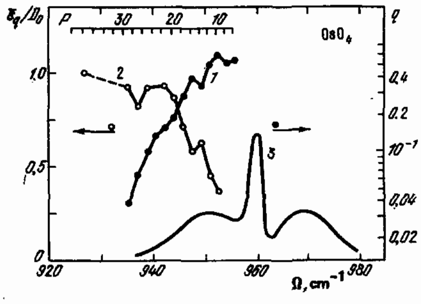

FIG. 8. Dependences of the relative fraction q of strongly excited OsO$_4$ moleucies (curve 1) and of their average energy $\bar{\varepsilon}_q = \bar{n}_q\hbar\Omega$ in units of the dissociation energy D_0 (curve 2) on the frequency Ω of infrared radiation pulses of energy density $\Phi = 1.2$ J/cm^2 incident on a gas at 0.03 Torr (curve 3 is the linear absorption spectrum); based on data from Ref. 92.

been considered theoretically in many papers on the basis of a very great variety of models. It has been found that this stage of excitation is most difficult to tackle quantitatively and this is due to a number of factors. Firstly, the spectroscopic information on the lower vibrational states with $v \geqslant 2$ and on transitions between them is practically nonexistent and suitable experimental methods for acquiring such information are being currently developed. Secondly, in a strong field we have to consider multistage and multiphoton transitions (for brevity, we shall call them always collectively multiphoton transitions) from a large number of states between which molecules are distributed in a gas at a realistic temperature. Thirdly, a theory should describe not only the resonant characteristics of passing through lower vibrational levels but also the fraction of molecules $q(\Phi, \Omega)$ reaching a vibrational quasicontinuum. Therefore, investigations of the first stage of multiphoton excitation of molecules—resonant passing through lower vibrational levels—are still continuing and are far from complete.

In the case of lower vibrational transitions a monochromatic laser radiation field cannot be simultaneously in exact resonance with several successive vibrational-rotational transitions from many rotational states because vibrations are anharmonic and molecules are distributed between rotational levels. Therefore, all the theoretical models are designed to account for a resonant multiphoton excitation of molecules to the vibrational quasicontinuum when the infrared field frequency is not tuned exactly to the frequencies of vibrational-rotational transitions. All the models proposed in the literature can be divided into three types: a) a model of multiphoton transitions from the ground vibrational state to a vibrational quasicontinuum; b) different models of compensation of the anharmonic shift; c) a model of weak vibrational-rotational transitions. However, one should point out once again that these models do not give a complete quantitative interpretation of the effect of excitation of a molecule to a vibrational quasicontinuum. It is perhaps better to consider them as testing various theoretical approaches to explain qualitative aspects of the phenomenon and as a necessary base for further searches.

1) *Model of multiphoton transitions.* The existence of a quasicontinuous spectrum of transitions in the case of sufficiently high vibrational levels in a quasicontinuum (Sec. 5 below) clearly makes possible a multiphoton resonant transition from the ground state directly to a vibrational quasicontinuum. This mechanism of excitation of molecules, first considered in Refs. 49 and 84 and then in many other studies,[85-88] can be understood quite readily if we adopt the language of quantum-mechanical "leakage."

Let us consider an excited vibrational level $|a\rangle$, whose energy differs from the nominal lower edge of a vibrational quasicontinuum by an amount smaller than $\hbar\Omega$. The probability W_{0a} of filling this level is low because the infrared field frequency Ω is always detuned by $\Delta_1, \Delta_2, \ldots$ relative to the frequencies of successive vibrational-rotational transitions from the ground vibrational state to $|a\rangle$ (in Fig. 9a the last discrete $|a\rangle$ level is $v=3$). It follows from all the experiments on multiphoton excitation that the intensity of an infrared pulse is insufficient to compensate all the detuning differences by the "brute force" method, i.e., by field broadening of the transitions. However, in spite of the fact that $W_{0a} \ll 1$, if many elementary events involving irreversible decay of the $|a\rangle$ level to the vibrational quasicontinuum take place during a laser pulse of duration τ_p, the excitation of a molecule may be quite considerable. The rate of "leakage" from the lower states to the quasicontinuum is given by the simple relationship

$$\mathscr{K} = W_{0a}\sigma_{ak}P, \tag{4.6}$$

where σ_{ak} is the cross section for a radiative transition from the level $|a\rangle$ to the quasicontinuum and P is the radiation intensity (in photons per centimeter squared per second). The probability of "leakage" during a pulse τ_p is[87]

$$\xi = 1 - \exp(-\mathscr{K}\tau_p) = 1 - \exp(-W_{0a}\sigma_{ak}\Phi). \tag{4.7}$$

We can thus find that $\xi \approx 1$ even for $W_{0a} \ll 1$ if $\sigma_{ak}\Phi \gg 1$, i.e., induced decay of the last discrete vibrational level to the quasicontinuum is fairly fast.

The same mechanism of excitation of molecules to a vibrational quasicontinuum has been considered in several papers[89-] in terms of decay of an excited anharmonic mode to other vibrational degrees of freedom of a molecule.

The process can also be described in terms of direct multiphoton (four-photon in Fig. 9a) transitions of a molecule from various rotational states of the $v=0$ level to a vibrational quasicontinuum. In this case we can consider the effect of emptying of many rotational levels. Naturally, the probabilities of transitions are not the same for different initial states and, as is always true of multiphoton processes (see, for example, Refs. 92 and 93), they depend on the detuning Δ_k relative to

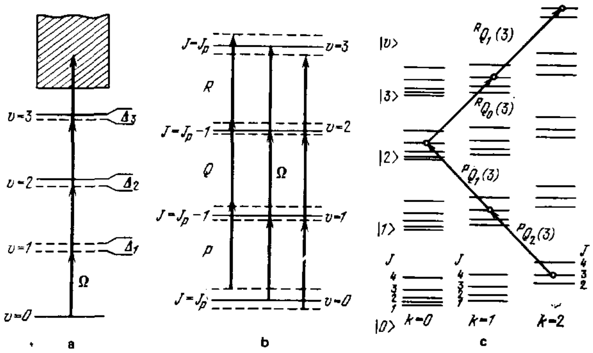

FIG. 9. Models of resonant excitation of molecules from the ground vibrational state to a vibrational quasicontinuum: a) four-photon excitation directly to the quasicontinuum of three-photon excitation of the $v = 3$ discrete level followed by induced leakage to the quasicontinuum; b) rotation compensation of anharmonicity in a three-stage PQR transition (transitions between continuous levels) and a three-photon resonance for many rotational states (transitions between levels shown dashed); c) multiple resonance due to rotational compensation of anharmonicity in vibrational-rotational transitions of perpendicular bands of molecules of the symmetric top type.

an intermediate resonance (Fig. 9a). The probability of such a process is given by the following formula

$$\mathscr{K}=\frac{\sigma_{ak}I}{2\pi c\hbar\Omega}\left(\frac{I}{2\hbar^2\pi c^3}\right)^{n-1}\prod_{k=1}^{n-1}\left(\frac{\mu_{k-1,\,k}}{\Delta_k}\right)^2, \tag{4.8}$$

where $\mathscr{K}$ is expressed in reciprocal seconds, n is the number of photons required to excite a molecule to the quasicontinuum, and $I = P\hbar\Omega$.

An estimate obtained from Eq. (4.8) shows that if the intensity is $I = 10^8$ W/cm^2 for $\tau_p = 100$ nsec a four-photon PQQR transition can excite molecules from all the initial states with a probability $\mathscr{K}\tau_p \approx 1$. This is in agreement with the experimental results because for $\Phi \approx 10$ J/cm^2 we indeed have $q \approx 1$. However, when the intensity is reduced just severalfold, the probability of excitation to the quasicontinuum becomes negligible because of the strong dependence of $\mathscr{K}$ on the intensity ($\mathscr{K} \propto I^4$ in the example considered). This is no longer in agreement with the experimental results which show that the dependence of q on I is relatively weak (Fig. 7b).

2) *Model of anharmonicity compensation.* It has been suggested that the anharmonicity of lower vibrational transitions can be compensated by a change in the rotational energy of a molecule and anharmonic splitting of vibrational states, which do not require a very strong infrared field. Therefore, these are sometimes called "soft" anharmonicity compensation schemes.

The rotational compensation of anharmonicity[44] is based on the possibility that the frequency of an infrared field Ω is identical with the frequencies of three successive vibrational-rotational transitions (Fig. 9b)

$$|v_i=0,\ J=J_r\rangle \xrightarrow{P(J_r)} |1,\ J_r-1\rangle \xrightarrow{Q(J_r-1)} |2,\ J_r-1\rangle \xrightarrow{R(J_r-1)} \to |3,\ J_r\rangle, \tag{4.9}$$

if the frequency Ω is tuned to a resonance with the Q branch of the $v_i = 1 \to v_i = 2$ transition. Such a chain of transitions is possible only for molecules with a specific "resonance" value of the rotational quantum number J_r satisfying the condition

$$2BJ_r = 2\omega^i\,|x_{ii}|, \tag{4.10}$$

where B is the rotational constant and $|x_{ii}|$ is the anharmonicity constant of the excited i-th vibrational mode.

Such rotational compensation may also increase the effectiveness of multiphoton resonances considered above.[46] This is due to the fact that if allowance is made for rotation, combinations of intermediate levels are possible in the case of multiphoton transitions and these are characterized by much smaller detuning relative to intermediate exact resonances. The three-stage PQR resonance described by Eq. (4.9) is a degenerate case when detuning vanishes for all the intermediate transitions. If we consider the PQR transitions for the molecules with $J \neq J_r$ (between the dashed levels in Fig. 9b) at the same frequency Ω, we find that for $B_{v_i} = B = \text{const}$ the frequency 3Ω is exactly equal to the frequency of the three-photon resonance transition. The fairly high effectiveness of four-photon resonances of the PPRR and PQQR types is mentioned in Ref. 46. The last case is the one considered in the above example of a multiphoton transition to a vibrational quasicontinuum. According to the estimates of Ref. 46 the rates of transitions in the SF$_6$ molecule in a field of $I = 2.5 \times 10^7$ W/cm^2 intensity is at least 10^9 sec^{-1} for the majority of the populated rotational levels of the ground vibrational state.

Estimates become more definite if we take into account that the rotational constants vary from one vibrational state to another. This is manifested by the finite width of the Q branch of linear infrared absorption ($\Delta\nu_Q \gtrsim 1$ cm^{-1} for SF$_6$). Therefore, we again reach the conclusion that in the model of rotational compensation of anharmonicity only a relatively small fraction of molecules can be excited effectively from all the lower rotational levels at a given field frequency Ω even if allowance is made for multiphoton resonances.

In the case of symmetric-top molecules with two rotational constants B_{v_i} and A_{v_i} there is another possibility of compensation of anharmonicity when the field frequency Ω is tuned to perpendicular bands.[62,94] The rules governing electric dipole transitions in such bands admit the possibility of a change not only in respect of the J but also of the K projection of the angular momentum onto the axis of a molecule ($-J \leqslant K \leqslant J$): $\Delta K = \pm 1$. Therefore, if the condition

$$A - B = |x_{ii}|\,\omega_i \tag{4.11}$$

is satisfied, we can expect a multiple resonance of the field frequency Ω with a sequence of transitions (Fig.9c):

$$\begin{gathered}|v_i=0,\ J_0,\ K_0\rangle \xrightarrow{^PQ_{K_0}} |1,\ J_0,\ K_0-1\rangle \xrightarrow{^PQ_{K_0-1}} |2,\ J_0,\ K_0-2\rangle \to \\ \ldots \to |K_0,\ J_0,\ 0\rangle \xrightarrow{^RQ_0} |K_0+1,\ J_0,\ -1\rangle \xrightarrow{^RQ_1} \\ \ldots \xrightarrow{^RQ_{K_0}} |2K_0,\ J_0,\ -K_0\rangle.\end{gathered} \tag{4.12}$$

Such a $2K_0$-fold vibrational-rotational resonance may occur everytime that the field frequency Ω coincides with the center of the $^PQ_{K_0}$ branch. Therefore, the multiphoton absorption spectrum in the case of this anharmonicity compensation mechanism should be periodic. A periodic structure of the multiphoton absorption spectrum was observed for the perpendicular ν_7 band of the C$_2$H$_4$ molecule.[62] True, this mechanism cannot account for the multiphoton absorption in the case of the parallel bands of molecules of the symmetric-top type ($\Delta K = 0$) observed in CF$_3$I (Ref. 95) and CF$_3$Br (Ref. 96) molecules.

The possibility of anharmonicity compensation at lower transitions of molecules of the spherical-top type by anharmonic splitting was pointed out in Refs. 85, 97, and 98. In the case of these molecules the modes active in infrared absorption are triply degenerate (for example, this applies to the ν_3 mode of the SF$_6$ molecule). Allowance for the anharmonic terms in the Hamiltonian corresponding to the triply degenerate mode not only gives the usual shift of the levels but also results in a partial lifting of degeneracy (Fig. 10). If the splitting of the degenerate levels is sufficiently strong, it may compensate the anharmonic shift. The anharmonic splitting of the levels gives rise to new

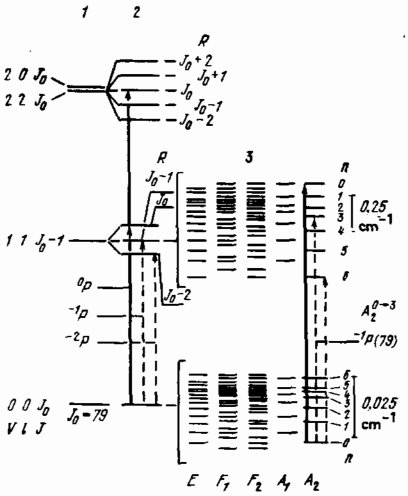

FIG. 10. Structure of vibrational-rotational levels of triply degenerate vibrations of spherically symmetric molecules (shown for the specific case of the ν_3 vibration of SF_6): 1) structure allowing for anharmonic splitting; 2) Coriolis splitting of levels; 3) tensor (octahedral) structure of levels. The continuous vertical lines correspond to allowed transitions and the dashed lines represent weak forbidden transitions. Examples of transitions with $\Delta n \neq 0$ (taken from Ref. 64) are shown on the right for the components with A_2 symmetry.

multiphoton resonances which complicate greatly the structure of the multiphoton absorption spectrum. Rotational motion has the effect that each anharmonic splitting component has a rotational structure. Multiphoton absorption spectra were calculated allowing for all these effects in the case of the SF_6 molecule[99-101] and using the dipole moments of the allowed transitions calculated in Ref. 102. It was pointed out in Refs. 99 and 101 that the results of calculations for the SF_6 temperature of 300°K were insensitive to the anharmonic splitting. Experiments carried out at 140°K demonstrated[76] some structure in the multiphoton absorption spectrum of SF_6 which was attributed to the anharmonic splitting effect. Further studies are needed.

3) *Model of weak transitions*. The selection rules governing the rotational quantum numbers of allowed electric-dipole transitions are[103]

$$\Delta J = 0, \pm 1, \quad \Delta R = 0, \tag{4.13}$$

where $R = J + l$ is the total angular momentum of a molecule; J is the rotational angular momentum; l is the angular momentum due to the vibrational excitation of degenerate vibrations (which is typical of triply degenerate modes of symmetric tops).

Forbidden transitions with $\Delta R \neq 0$ were observed in the linear absorption spectra of the CH_4 molecule.[104,105] Therefore, it was suggested in Refs. 65 and 106 that such transitions occur in a strong infrared field causing multiphoton excitation of spherical-top molecules. It was recently shown[107] that the selection rule $\Delta R = 0$ may be violated in higher order of the vibrational-rotational interaction. According to approximate estimates, the probabilities of transitions with $\Delta R \neq 0$ in heavy molecules (SF_6, UF_6) represent $\sim(10^{-8}-10^{-10})J^4$ of the probability of allowed transitions with $\Delta R = 0$. In the case of the SF_6 molecule the upper estimate gives $\mu \approx 0.7 \times 10^{-2}$D for the dipole moments of the transition with $\Delta R \neq 0$ if $J \approx 50$. This value of μ results in induced transitions at a rate of 2×10^7 sec^{-1} already for infrared field intensities of 10^5 W/cm^2. Consequently, weak transitions with $\Delta R \neq 0$ may become saturated even in fields of moderate intensity.

In the case of spherical-top molecules each rotational component of an anharmonically split degenerate state (Fig. 10) has a fine structure due to the so-called octahedral splitting.[108] This splitting exceeds the rotational splitting, as indicated by high-resolution measurements and identification of the linear absorption spectra of the SF_6 molecule.[109] It was shown in Ref. 108 that for each octahedral component of a lower vibrational-rotational state there is only one allowed transition to an exactly defined component of an upper vibrational-rotational state. In terms of the notation used in Ref. 108, octahedral components of symmetry of type C are labeled by an index n and the following selection rules apply:

$$C' = C'', \quad \Delta n = 0. \tag{4.14}$$

As pointed out in Ref. 108, the selection rule $\Delta n = 0$ is not stringent. Therefore, in Refs. 65 and 106 a study was made of the possibility of participation of weak $\Delta n \neq 0$ transitions in the process of multiphoton excitation of lower vibrational transitions. A theoretical model of multiphoton excitation allowing for $\Delta n \neq 0$ transitions was also considered in Ref. 110. If there are weak transitions with $\Delta n \neq 0$, then a fairly large ($\sim J$) number of transitions becomes possible for a given octahedral splitting component. This may result in the participation of a considerable proportion of molecules in the process of resonant interaction with an infrared field of fixed frequency. It was shown in Ref. 106 that allowance for weak transitions with $\Delta R \neq 0$ and ($\Delta n \neq 0$) in the SF_6 molecule increases q from a value of the order of 0.01 to one of the order of 0.1. It will be necessary to consider to what extent the $\Delta n = 0$ rule has to be rigorously obeyed and to study experimentally transitions with $\Delta n \neq 0$.

Finally, it is necessary to mention the possibility of forbidden (in the case of one-photon selection rules) vibrational-rotational transitions with $|\Delta J| > 1$, considered in Ref. 111. These $|\Delta J| > 1$ transitions can be treated as multiphoton transitions in which all the intermediate steps are allowed but detuned from exact resonances. For example, the $|v = 0, J_0\rangle \to |v = 1, J_0 - 3\rangle$ transition with $\Delta J = -3$ corresponds to a three-photon transition in which the intermediate states are the levels $|v = 1, J = J_0 - 1\rangle$ and $|v = 0, J = J_0 - 2\rangle$. Estimates indicate that if the infrared field intensity is 10^7 W/cm^2, the rate of such a three-photon transition may reach 10^7 sec^{-1}. Consequently, transitions of this kind can contribute to depopulation of rotational levels in a strong infrared field.

d) Future research trends

We can at present compare only qualitatively the experimental results with the theoretical models of resonant passing of molecules through lower vibrational states. A quantitative interpretation of multiphoton absorption, particularly of the dependences given above (Figs. 6–8), is still a very difficult problem for a number of reasons. Firstly, in the case of many polyatomic molecules, particularly heavy molecules with a small rotational constant, and in the case of molecules of the asymmetric top type the spectra of even linear absorption have not yet been identified. Such identification requires determination of the spectra with a resolution of the order of 10^{-3} cm^{-1}, which has become possible only recently as a result of development of the technology of semiconductor diode lasers. The first successful work on the SF_6 (Ref. 109) and OsO_4 (Ref. 112) molecules was done only a short time ago. Secondly, at present there are almost no spectroscopic data for vibrational levels of molecules with $v \geqslant 2$. Therefore, it is so far very difficult to predict theoretically the structure of a multiphoton absorption spectrum which appears as a result of summation of multistage and multiphoton transitions in a system of lower vibrational levels from many initial states (Fig. 11a).

Experiments should be carried out at low temperatures so as to facilitate interpretation of the data on multiphoton excitation of molecules. Several studies have been made on SF_6 at 140°K (Refs. 74 and 76). Investigations of multiphoton absorption spectra employing strongly cooled free molecules in supersonic jets[113] is a particularly promising approach. In this case the rotational and vibrational temperatures may amount to a few degrees Kelvin and it should be possible to determine the spectrum of multiphoton transitions from a very specific initial quantum state (Fig. 11b). In combination with a continuously tunable infrared laser this approach should give much useful information on the probability of multiphoton transitions via various intermediate states. Moreover, experimental studies are needed of multistage excitation of vibrational levels with the aid of several tunable infrared lasers (Fig. 11c). This is desirable because it can give information on the spectrum of transitions between excited vibrational levels and on the development of methods for multiphoton highly selective excitation of molecules to a vibrational quasicontinuum in the infrared fields of moderate intensity, even at a normal gas temperature. This makes it possible to compare the contributions of multistage and multiphoton transitions to multiphoton excitation. Only successful development of these two approaches will give the spectroscopic information necessary for a quantitative comparison of the experimental results with various theoretical models and, in the final analysis, for a theoretical description and prediction of the already observed characteristics of multiphoton absorption in the form of $\bar{n}(\Omega, \Phi)$, $q(\Omega, \Phi)$, and $\bar{n}_q(\Omega, \Phi)$ for specific molecules.

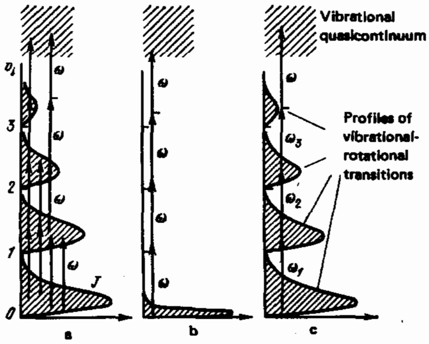

FIG. 11. Possible multiphoton excitation schemes for low vibrational levels of a polyatomic molecule: a) multiphoton excitation by a one-frequency field from many initial states (wide resonance of multi-photon absorption, difficult to interpret theoretically); b) multiphoton excitation by a one-frequency field at low temperatures (narrow resonances of multiphoton absorption, theoretical interpretation easier); c) multistage excitation by a multifrequency field (narrow multiphoton absorption resonances, theoretical interpretation easy).

5. MULTIPHOTON EXCITATION OF MOLECULES IN THE VIBRATIONAL QUASICONTINUUM AND DISTRIBUTION OF VIBRATIONAL ENERGY

a) Properties of the vibrational quasicontinuum

A quasicontinuum of vibrational transitions in polyatomic molecules in highly excited states forms for two physical reasons. The first of these reasons is a high density of vibrational states of polyatomic molecules, which rises quite rapidly on increase in the vibrational energy of a molecule. This situation is typical of any quantum system with many degrees of freedom when the same energy can be obtained by a very large number of excitation paths. For example, it is known that the density of levels in highly excited nuclei is very high[114] and there is a close analogy between the behavior of a highly excited molecule and a highly excited nucleus. The second reason is the anharmonic interaction of various vibrational modes, which has the result that—in principle—transitions are possible between any vibrational levels.

Several good approximations are available for a quantitative description of the density of levels in a vibrational quasicontinuum of polyatomic molecules. The best known is the Whitten–Rabinovitch approximation (see, for example, Ref. 115) which describes the dependence of the density of states ρ on the vibrational energy $E_{\rm vib}$ in terms of the frequencies of normal vibrations of a molecule. The expression for the function $\rho(E_{\rm vib})$ is of the following form:

$$\rho(E_{\rm vib}) = \frac{[E_{\rm vib} + E_0 - \beta w(\eta) E_0]^{s-1}}{(s-1)! \prod_{i=1}^{s} \omega_i} [1 - \beta w'(\eta)], \tag{5.1}$$

where s is the number of vibrational degrees of freedom of a molecule, whose vibrational energy $E_{\rm vib}$ is measured from the zero-point vibration energy:

$$E_0 = \frac{1}{2} \sum_{i=1}^{s} \omega_i, \tag{5.2}$$

the parameter β is given by

$$\beta = \frac{s-1}{s} \frac{\langle \omega^2 \rangle}{\langle \omega \rangle^2}, \tag{5.3}$$

and the numerical parameter $w(\eta)$ dependent on the variable $\eta = E_{\rm vib}/E_0$ assumes the values ranging from 0.3–0.1 (for $0 < \eta < 1$) to 0 for $\eta > 8$. Figure 12 shows the dependences $\rho(E_{\rm vib})$ for a series of polyatomic mol-

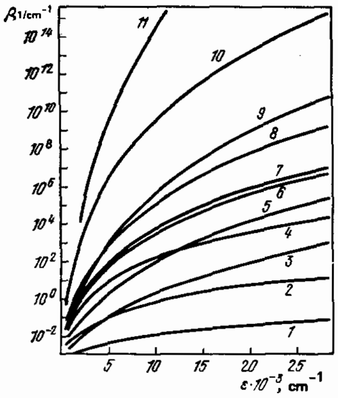

FIG. 12. Dependences of the density of vibrational levels on the vibrational energy plotted for different molecules: a) D_2O; 2) OCS; 3) CH_3F; 4) BCl_3; 5) C_2H_4; 6) CF_3I; 7) OsO_4; 8) C_2F_3Cl; 9) SF_6; 10) UF_6; 11) S_2F_{10}.

ecules with different numbers of atoms, that have been investigated on many occasions.

The formation of a vibrational quasicontinuum depends on a high density of vibrational states and also on the anharmonic interaction which should overlap at least several intermode resonances that determine the degree of mixing of wave functions of various normal vibrations. The efficiency of the anharmonic interaction is governed by the degree of the difference between the sets of quantum numbers of two levels in a vibrational quasicontinuum. The greater the difference between these two sets, the higher the order of anharmonicity of the term which may be responsible for the interaction of vibrational states. The strongest are the three-frequency Fermi resonances, i.e., resonances of the $\omega_1 + \omega_2 \approx \omega_3$ or $2\omega_1 \approx \omega_2$ type, which result in the interaction of vibrational states with the sets of quantum numbers $|a\rangle = |n_1, n_2, n_3, n_i\rangle$, $|b\rangle = |n_1 - 1, n_3 + 1, n_i\rangle$ in the former case, and $|a\rangle = |n, n_2, n_i\rangle$, $|b\rangle = |n_1 - 2, n_2 + 1, n_i\rangle$ in the latter case. The three-frequency interaction $\omega_1 + \omega_2 - \omega_3$ is described by the operator

$$\hat{V} = \alpha \hat{x}_1 \hat{x}_2 \hat{x}_3, \qquad (5.4)$$

where $\hat{x}_i$ are the operators of the normal coordinates and α is the interaction constant. The matrix element is $V_{ab} \propto (n_1 n_2 n_3)^{1/2}$. In addition to the Fermi resonances, we must also allow for other types of resonance, for example, the Coriolis resonance (for details on intermode resonances in molecules see the monograph of Herzberg[103] and also the work of Nielsen[116]).

The first direct experimental evidence of the existence of a vibrational quasicontinuum in polyatomic molecules and information on the spectrum of transitions in this quasicontinuum were obtained from multiphoton dissociation of molecules in a two-frequency infrared field.[50,117] A relatively weak infrared field of frequency Ω_1 excited molecules resonantly from the ground vibrational state to a quasicontinuum, whereas a second sufficiently strong infrared field of frequency Ω_2, detuned from the frequency of resonance with unexcited molecules, performed multiphoton excitation to the quasicontinuum right up to the dissociation limit. In this method the operations of selective excitation of molecules via lower transitions and the excitation to a vibrational quasicontinuum were performed by separate pulses of different frequencies and intensities, so that the spectrum of transitions to a quasicontinuum could be investigated independently. The frequency dependence of the dissociation yield β can be used to determine the efficiency of excitation to a quasicontinuum at various frequencies. This has been done for the molecules of SiF_4 (Ref. 118), SF_6 (Refs. 118 and 119), and OsO_4 (Ref. 79), and a strong shift of the maximum of the dependence $\beta(\Omega_2)$ to the long-wavelength part of the spectrum has been observed. An example of the dependence $\beta(\Omega_2)$ for the OsO_4 molecule is plotted in Fig. 13. We can clearly see an increase in the efficiency of excitation as a result of a shift of the frequency Ω_2 toward longer wavelengths, which reflects an increase in the cross section of transitions to the quasicontinuum. An exponential dependence of the dissociation yield β on the absorbed energy (see Chap. 6) results in a strong increase in β for a relatively small increase in the absorption cross section resulting in transitions to the quasicontinuum. Therefore, in determining the absorption spectrum in the quasicontinuum it is more correct to determine the frequency dependence of the energy density $\Phi_2^{sat}(\Omega_2)$ causing a high degree of excitation (saturation) of transitions to the quasicontinuum and, consequently, molecular dissociation. Measurements of this kind have been made for the OsO_4 (Ref. 79) and SF_6 (Ref. 118) molecules; a reduction in the value of Φ_2^{sat} from about 1 J/cm² to about 0.1 J/cm² was observed as a result of a shift of Ω_2 to the red range.

Experimental studies of multiphoton dissociation of molecules in a two-frequency infrared field and determination of the infrared absorption spectrum of a heated SF_6 gas[120] indicate that the spectrum of transitions in an excited molecule which is in a vibrational quasicontinuum is concentrated near the frequencies active in the infrared absorption process. It should be stressed particularly that this property of the spectrum of transitions in the quasicontinuum is not in any way in conflict with the hypothesis of a strong mixing of the vibrational modes of a molecule because of the anharmonic interaction but it simply means that in reality each harmonic state is mixed effectively only with sufficiently close

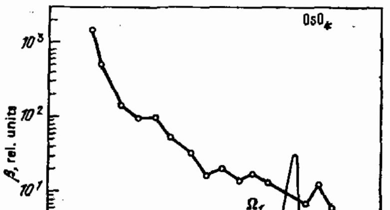

FIG. 13. Dependence of the dissociation yield of OsO_4 molecules in a two-frequency field on the frequency Ω_2 of the second pulse for fixed other parameters of the pulses: $\Omega_1 = 954.5$ cm⁻¹, $\Phi_1 = 0.24$ J/cm², $\Phi_2 = 0.22$ J/cm². There is a strong shift of the maximum of the frequency dependence $\beta(\Omega_2)$ toward longer wavelengths.[79]

states, so that the width of the mixing zone remains considerably less than the differences between molecular frequencies.

Maxima of the absorption bands in a vibrational quasicontinuum naturally shift toward longer wavelengths on increase in the vibrational energy E because of the anharmonicity of the vibrations. Theoretical models of the absorption spectrum in such a quasicontinuum have been considered[56,121] and it has been found that the experimental results can be described by a Lorentzian profile for the spectral density of the square of the modulus of the matrix element of the dipole moment $|\mu_\Omega|^2$ of the transitions:

$$\mu_\Omega^2(E) \approx \frac{1}{\pi}\frac{\langle\mu^2(E)\rangle\,\delta(E)}{[\Omega-\nu(E)]^2+\delta^2(E)}, \tag{5.5}$$

where $\nu(E)$ and $\delta(E)$ describe the frequency at the center and the half-width of the profile representing absorption from a state in a vibrational quasicontinuum whose energy is E. Simple model representations make it possible to estimate approximately the energy dependences $\delta(E)$ and $\nu(E)$.

We shall consider, for example, a molecule in a state of energy E in a vibrational quasicontinuum. In the harmonic approximation this molecule can undergo a dipole-allowed transition upward to a state of energy $E+\hbar\omega_i$, where ω_i is the frequency of a molecular vibration active in the infrared absorption. Mixing of the harmonic wave functions due to the Fermi-type resonances has the effect that the resonance broadens and its characteristic half-width $\delta(E)$ can be estimated as a half-sum of the intervals of "strong" mixing in the vicinity of the energy E and of the energy $E+\hbar\omega_i$ (Refs. 56 and 122):

$$\delta(E) \approx \frac{1}{2}[\Delta_0(E)+\Delta_0(E+\hbar\omega_i)] \approx \langle V_{ab}(E)\rangle + \langle V_{ab}(E+\hbar\omega_i)\rangle. \tag{5.6}$$

The dependence $\delta(E)$ should be considered separately for each molecule. For example, in the case of CF_3I the three-frequency Fermi resonances described by the operator (5.4) are clearly of the main importance. Therefore, the dependence $\langle V_{ab}\rangle \propto E^{3/2}$ has been adopted for this molecule in Ref. 56.

The transition frequency $\nu(E)$ at the center of an absorption profile for an initial state of energy E can be estimated from[56,123]

$$\nu(E) = \omega_i - |x_0|\,E, \text{where } x_0 = \sum_k x_{ik}\frac{\omega_i}{\omega_k}(1+\delta_{ik}), \tag{5.7}$$

where we have employed the usual spectroscopic notation for the anharmonicity constant x_{ik}.

It should be pointed out that a Lorentzian profile of transitions in a vibrational quasicontinuum is also a consequence of a model approach developed in a number of papers.[89-91,124,125] These papers have been concerned with coherent excitation of an infrared-active absorption mode of a molecule and the contribution of the remaining modes has been allowed for by phenomenological terms describing relaxation of nondiagonal elements of the density matrix.

The simple formula (5.5) ignores the rotational structure of the absorption bands. This structure can be allowed for if we know the dependence of the rotational constant of a molecule on its vibrational energy. For example, in the case of molecules of the spherical top type and also in the case of parallel bands of molecules of the symmetric top type the absorption profile of a molecule with a given rotational quantum number J should be the result of superposition of three profiles of the (5.5) type corresponding to the P, Q, and R branches. The more complex absorption profile is used in Ref. 56 to calculate multiphoton excitation and dissociation of CF_3I molecules.

b) Excitation of distribution of molecules in the vibrational quasicontinuum

The high density of states and their mixing in a vibrational quasicontinuum allow us to regard the process of excitation of molecules in the continuum as noncoherent. This can always be done if the rate of induced transitions is less than the rate of loss of the phase memory in the initial and/or final state of a transition:

$$\omega_R = \frac{\mu_\Omega E}{\hbar} \ll \frac{1}{T_2}, \tag{5.8}$$

where ω_R is the Rabi frequency equal to the induced-transition rate; T_2 is the transverse relaxation time which is in this case governed by the high density and mixing of quantum states in the quasicontinuum that interact with an infrared field.

The noncoherent interaction of molecules in a vibrational quasicontinuum with an infrared field can be described by simple rate equations. For example, irreversible loss of a molecule from the last discrete level in the lower system of vibrational levels in a quasicontinuum can be described by the simple equation

$$\dot{z} = -W_{ak}z, \tag{5.9}$$

where z is the population of the discrete level and W_{ak} is the probability of an induced transition to states in the quasicontinuum whose energies differ from the energy of the discrete level by an amount $\hbar\Omega$ (Fig. 14a). The large differences between the densities of states of a discrete level and the excited part of the quasicontinuum makes it unnecessary to allow for the reverse transitions from the quasicontinuum to the discrete level.

In a vibrational quasicontinuum induced molecular transitions occur—because of the law of conservation

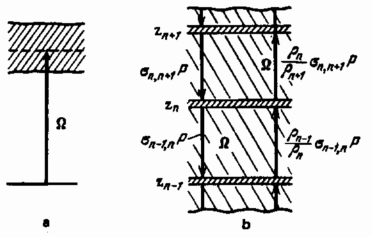

FIG. 14. Induced transitions from a discrete vibrational level to a vibrational quasicontinuum (a) and between a level and a quasicontinuum (b).

of energy—between narrow zones of the quasicontinuous spectrum separated by the photon energy.[126-128] Therefore, it is necessary to allow not only for the direct but also for the reverse transitions (Fig. 14b). The relationship between the rates of the direct and reverse transitions is governed, in accordance with the principle of detailed balance, by the relationship between the densities of the levels in the upper ρ_{n+1} and lower ρ_n parts of the quasicontinuous spectrum (zones). The kinetics of the level populations z_n in a vibrational quasicontinuum is described by the equations

$$\dot{z}_n=\sigma_{n-1,\,n}P\left[z_{n-1}-\frac{\rho_{n-1}}{\rho_n}z_n\right]-\sigma_{n,\,n+1}P\left[z_n-\frac{\rho_n}{\rho_{n+1}}z_{n+1}\right], \quad (5.10)$$

where P is the radiation intensity (photons·cm^{-2}·sec^{-1}) and σ are the successive transitions which can be expressed in terms of the spectral density of the square of the dipole moment of the transition at the field frequency Ω:

$$\sigma_{n-1,\,n}=\mu_\Omega^2(E_{n-1})\frac{8\pi^2\Omega}{\hbar c}. \quad (5.11)$$

In the specific case of a Lorentzian profile the value of $\mu_\Omega^2(E_{n-1})$ is given by Eq. (5.5). The system (5.10) has been used to describe the excitation of the SF_6 molecule to a vibrational quasicontinuum.[52]

The properties of solutions of these equations are considered in Refs. 88, 129, and 130. The most important of these properties is the difference between the rates of the direct and reverse transitions ($\rho_n > \rho_{n-1}$). For example, in the limiting case of $\rho_n \gg \rho_{n-1}$ the solution of the system (5.10) has the simple form

$$z_n=\frac{(\sigma P\tau_p)^n}{n!}\exp(-\sigma P\tau_p)=\frac{\bar{n}^n}{n!}e^{-\bar{n}}, \quad (5.12)$$

where $\bar{n}=\sigma P\tau_p=\sigma\Phi$ is the average degree of vibrational excitation created by a pulse of duration τ_p and energy density Φ.

The distribution of the vibrational energy of molecules in a quasicontinuum, i.e., in an ensemble of "hot" molecules—described by the solution of the system (5.10), has been determined on a number of occasions both analytically[121,129,130] and numerically.[52,53,56,122,128,132] It has been found that for realistic values of the ratio of the probabilities of the direct and reverse transitions the nature of the distribution $z(n)$ is quite close to the Poisson distribution given by Eq. (5.12). The difference between the level densities, which is only a factor of 1.5–2 when the energy of a molecule is altered by the energy equal to one CO_2 laser photon $\hbar\Omega$, is a very important aspect. Figure 15 shows, for the specific case of the CF_3I molecule, the vibrational distribution calculated in Ref. 56 using the system (5.10) and the Boltzmann distribution for identical values of the absorbed energy and two values of the energy density of the laser pulses. We can see that the actual distribution of molecules in a hot ensemble differs from the Boltzmann distribution mainly in the tail. The tail of the vibrational distribution lying above the dissociation limit D_0 contributes to the dissociation yield of the molecule (see Sec. 6). Therefore, the difference between the real and Boltzmann distributions is manifested clearly in the dependence of the dissociation yield β on the absorbed energy.

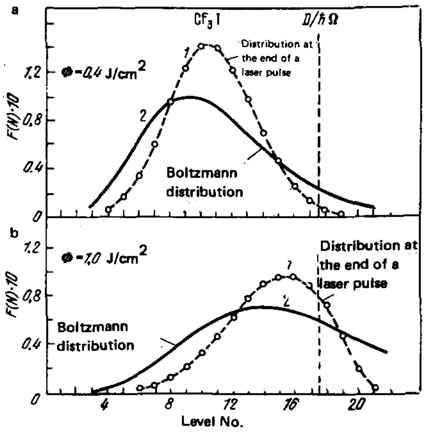

FIG. 15. Vibrational energy distributions after multiphoton excitation of the CF_3I molecule calculated using a semiempirical model (curves denoted by 1) compared with the Boltzmann distributions for the same average internal energy of the molecules (curves denoted by 2): a) $\bar{\varepsilon}$ = 10 500 cm^{-1}; b) $\bar{\varepsilon}$ = 16 000 cm^{-1} (from Ref. 56).

We can thus see that a vibrational distribution of molecules created by a high-power infrared pulse becomes strongly nonequilibrium in two respects. Firstly, two ensembles of molecules are formed: those vibrationally excited to a quasicontinuum (hot ensemble) and those remaining at the lower levels (cold ensemble). Secondly, the actual vibrational distribution in the hot ensemble differs somewhat from the Boltzmann distribution, particularly in the tail. Therefore, after the end of a laser pulse a vibrational equilibrium is established by two types of molecular collisions. Collisions of hot and cold molecules result in a vibrational exchange of energy between two ensembles and their merging into one. This process has been deduced experimentally from changes in the infrared absorption spectrum[80] and ultraviolet absorption spectrum[133] of excited SF_6 and CF_3I molecules.

The most direct data have been obtained recently in an experimental study of the spectra of the Raman scattering by vibrations of molecules excited by a CO_2 laser pulse.[134] Figure 16 shows the results of these experiments confirming clearly the main physical effects in the multiphoton excitation molecules described above. At the top of this figure we show the spectrum of the Raman scattering by the ν_1 vibration of the SF_6 molecules in the Stokes region in the absence of any excitation. Excitation of these molecules by a CO_2 laser pulse gives rise to an additional Raman peak which is due to the hot molecular ensemble and which is somewhat smaller because of the anharmonic shift of the vibrations to the Stokes region (Fig. 16b). This spectrum demonstrates also the formation of two ensembles of vibrationally excited molecules immediately after the end of a CO_2 laser pulse. An increase of the delay between the CO_2 laser and probe pulses up to 3 μsec (Fig. 16c) causes merging of both ensembles into one because of the vibrational exchange. Finally, when a buffer gas is added, the rotational relaxation during multiphoton excitation ensures that all the molecules are transferred from the lower levels to a vibra-

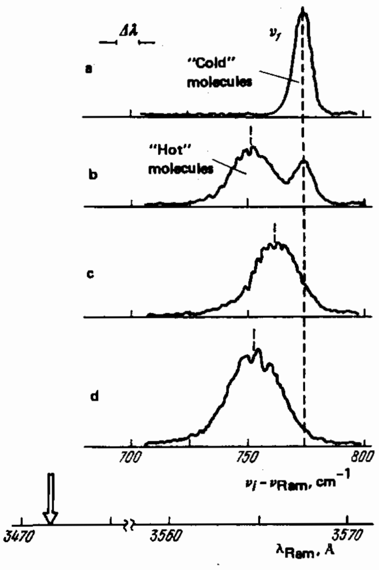

FIG. 16. Spectra of the Stokes signal of the Raman scattering of the second harmonic of ruby laser radiation of the ν_1 vibration of the SF_6 molecule: a) unexcited SF_6 molecule; b)–d) SF_6 molecules excited by a CO_2 laser pulse of 0.5 J/cm^2 density. The delay of a ruby laser probe pulse relative to the CO_2 laser excitation pulse was $\tau_d = 50$ nsec (b, d) and $\tau_d = 4\,\mu$sec (c). This last spectrum (d) was obtained in the presence of a buffer gas (Xe at 120 Torr).[134]

tional quasicontinuum and then only one ensemble of vibrationally hot molecules is formed (Fig. 16d).

The other relaxation process observed after the end of a laser pulse is the establishment of a Boltzmann equilibrium of populations in a hot molecular ensemble. This gives rise to an exponential tail in the distribution (Fig. 15a) and can make a considerable contribution to the dissociation of molecules after the end of a laser pulse.[56] The authors are not aware of any experimental determination of the form of the vibrational distribution of molecules in a hot ensemble. It follows indirectly from the dissociation yield (Sec. 6) that this vibrational distribution does indeed differ from the Boltzmann form.

c) Stochastization of vibrational energy

A strong vibrational excitation of a polyatomic molecule affects energy levels which represent complex (near-random) combinations of various normal vibrations. Consequently, the motion of the nuclei also becomes complex and near-stochastic. This can be understood by the example of "chain-wise" mixing of vibrations for the concrete case of Fermi resonances in the CF_3I molecule.[56] There is a large number of three- and four-frequency combinations which can give rise to the Fermi resonances. Figure 17 shows the beginning of a chain which appears because of coupling between three three-frequency resonances which have the lowest energy defect and which occur in the vicinity of a level $n\nu_1$ of the excited vibration ν_1 on the assumption that the level positions are harmonic. An allowance is made for the states whose harmonic positions are separated from the level $n\nu_1$ by not more than 11 cm^{-1}. It is clear that if the matrix elements of operators of the (5.4) type responsible for the anharmonic interaction exceed this value (11 cm^{-1}), resonances overlap and vibrational wave functions should be described by superpositions of the harmonic wave functions of the modes ν_1, ν_3, ν_5, and ν_6, which are random. In classical language, this means that the motion of the nuclei becomes random or stochastic.[53,135]

It is known that in the case of molecules with ≥4 atoms the vibrational motion near the dissociation limit is stochastic and can be described by statistical methods. On the other hand, in the case of low vibrational levels the motion is described in terms of normal coordinates of a molecule. The position of the energy limit of stochasticity is very important in this context but it has been given little attention. This problem is important in molecular spectroscopy, multiphoton laser chemistry, and theory of nonlinear oscillations of systems with many degrees of freedom.

There have been several experimental investigations[136-138] carried out by the method of double infrared resonance which has made it possible to study the effect of stochastization of the vibrational energy of the SF_6 molecule. An SF_6 gas was excited by a laser pulse and infrared absorption of a probe laser beam was resolved on the time scale. However, in our opinion, caution should be exercised in quantitative interpretation of any attempts to observe stochastization of the vibrational energy by the double infrared-infrared resonance method. This is because the integral absorption in a band concentrated near a vibrational mode active in the infrared spectrum should depend weakly on the energy of this mode. This dependence is related solely to the anharmonic terms which give rise to a difference between the probabilities of upward and downward molecular transitions.

A reliable investigation of the stochastization of the vibrational motion of molecules requires separation of the upward and downward molecular transitions. This can be done by, for example, the method of spontaneous Raman scattering. The first experiment in which the process of multiphoton excitation of molecules was investigated by Raman spectroscopy had been described in Ref. 139. In this experiment the average energy of the SF_6 and CF_3I molecules in a hot ensemble was approximately 10 000 cm^{-1} and it was found that the second harmonic of a ruby laser experienced anti-Stokes Raman scattering by all the vibrational modes active

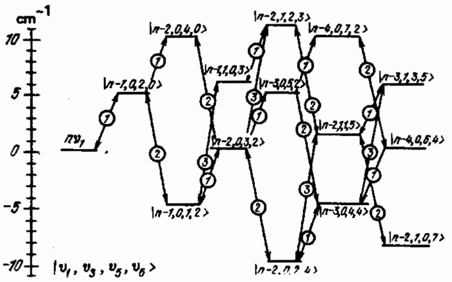

FIG. 17. Mechanism of chainwise mixing of wave functions of vibrational states of the CF_3I molecule due to three-frequency Fermi resonances: 1) $2\nu_5-\nu_1$; 2) $2\nu_6-\nu_5$; 3) $\nu_3-\nu_5+\nu_6$.

in the scattering. This was a clear demonstration of the excitation of these modes and the degree of excitation remained constant when the delay of a test pulse (relative to the exciting pulse) was varied between 20 nsec and 10^{-6} sec, i.e., up to time intervals when the distribution of the vibrational energy between all the modes should reach equilibrium because of collisional vibrational exchange. Stochastization of vibrational motion under the experimental conditions of Ref. 139 occurred in the multiphoton excitation process itself. Hence, the energy limit of stochastization of the vibrational motion in the SF_6 and CF_3I molecules was located below 10 000 cm^{-1}. Our most recent measurements[140] by the Raman method made it possible to lower this estimate to 3900 cm^{-1} in the case of SF_6 and 6000 cm^{-1} in the case of CF_3I.

d) Future research trends

A quantitative description of multiphoton excitation of molecules in a vibrational quasicontinuum can be provided if we have direct experimental data on the absorption spectrum of molecules in the quasicontinuum, at least the dependences of $\nu(E)$ and $\delta(E)$ on the absorbed energy E. New laser spectroscopy methods suitable for highly excited vibrational states are needed to obtain such data. One can use the method of excitation of molecules by two infrared pulses of different frequencies Ω_1 and Ω_2 (Refs. 50 and 117). However, one has to go outside the tuning range of a CO_2 laser, particularly when probing the absorption in a vibrational quasicontinuum.

The stochastization time of the vibrational energy τ_{stoch} is governed by the anharmonic interaction and probably lies in the picosecond range. This range of infrared pulse durations is very difficult to use in the determination of τ_{stoch}. Nevertheless, there are still several promising opportunities. In particular, it is very interesting to consider the situation when only some of the vibrational degrees of freedom participate in a quasicontinuum or vibrational transitions near the frequency of the mode being excited. This situation may appear, for example, in complex molecules which have different spatially separated functional groups.[141] Then, the anharmonic interaction between the vibrational modes of these functional groups may be sufficiently weak. Moreover, we cannot exclude the situation when for some particular molecular mode there is no suitable Fermi resonance coupling it to the other modes. In both cases we can probably observe partial stochastization of the vibrational motion in a molecule even in a time of the order of 10^{-8}–10^{-9} sec. In the subnanosecond range of pulse durations the probability of such partial stochastization rises considerably.

Excitation of molecules by infrared radiation to higher vibrational states lying in a quasicontinuum is closely related to the general problem of response of nonlinear systems with many degrees of freedom to an external alternating force, which has been investigated for a long time (see, for example, the review given in Ref. 135). Therefore, it should be possible to investigate systematically polyatomic molecules, which represent the smallest nonlinear vibrational systems with many degrees of freedom which exhibit a variety of structures, and which are available in unlimited amounts to experimenters; in particular, it should be possible to investigate the energy limit and time of total stochastization of the vibrational energy, which is of fundamental interest. Methods should be developed for such investigations. A very promising approach is the Raman scattering, particularly if the durations of the exciting and probe pulses are reduced to the subnanosecond range.

It would also be interesting to consider methods of excitation of molecules to states in a vibrational quasicontinuum other than multiphoton excitation, which by its very nature excites many vibrational modes at the same time. In particular, it may be promising to excite vibrational overtones of higher order by near-infrared or visible laser radiation[142] or to excite molecules in cooled jets characterized by few rotational states (see Sec. 4.d). This should make it possible, at least in principle, to study stochastization of the vibrational energy for different initial populations of the vibrational levels.

6. DISSOCIATION OF HIGHLY EXCITED MOLECULES

A highly excited molecule with a large store of vibrational energy may undergo transitions even without collisions with other reacting partners and such transitions are known as unimolecular reactions. They include dissociation, isomerization, dissociative ionization, etc. Since we are interested in the physical aspects, we shall confine our discussion to one most important and thoroughly studied unimolecular process, which is the dissociation of highly excited molecules.

a) Characteristics of multiphoton dissociation

The main characteristics of the dissociation process are the yield β, i.e., the probability of breakup by a single infrared radiation pulse, and the dissociation channel which governs the decay products. The yield β has two very characteristic features: a steep almost threshold-like dependence on the energy density Φ of a laser pulse and a resonant dependence on the frequency Ω of such a pulse. The dependence $\beta(\Phi, \Omega)$ is naturally governed by the corresponding dependences of multiphoton absorption. We shall now consider these characteristics of multiphoton dissociation in greater detail.

Already the earliest investigations[34,35] resulting in the discovery of visible luminescence of molecules in a strong infrared field under collisionless conditions showed that the dependence of the luminescence intensity on the laser pulse intensity was steep and threshold-like. The threshold properties of multiphoton dissociation were first investigated carefully[143] in the case of the SF_6 molecule. The dependence of the dissociation yield $\beta(\Phi)$ on the energy density of a laser pulse obtained in this investigation is plotted in Fig. 18a. We can see that there was a clear dissociation threshold at $\Phi = 2.1$ J/cm². A reduction in the pulse energy by just

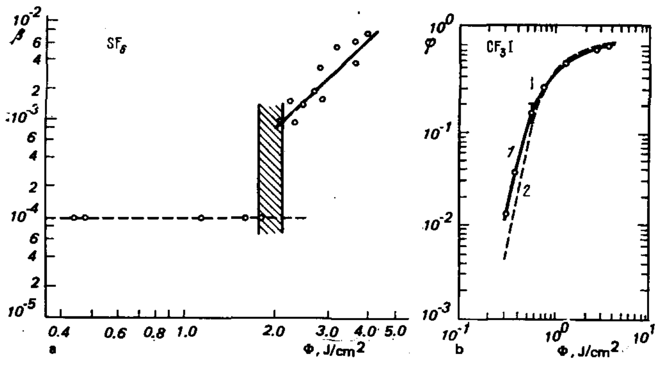

FIG. 18. Dependence of the multiphoton dissociation yield β and of the efficiency φ on the energy density Φ of CO_2 laser pulses interacting with the molecules of: a) SF_6 (taken from Ref. 143, β in rel. units); b) CF_3I (taken from Ref. 56). The dashed curve in Fig. 18b shows the results of calculations carried out using a semiempirical model developed in Ref. 56.

8% did not produce any significant dissociation although at energy densities below the threshold the number of pulses increased greatly. The dependence of the dissociation yield above the threshold was $\beta \propto \Phi^3$. The dissociation yield of the SF_6 molecule subjected to CO_2 laser pulses of durations 0.5 nsec and 100 nsec was investigated in Ref. 144. It was found that the dissociation threshold was governed by the energy density of laser pulses and not by the intensity of these pulses. The terminology was modified in Ref. 144. Up to then the multiphoton dissociation threshold was expressed in terms of the laser radiation intensity (see, for example, Refs. 34, 35, 143, and 145). Figure 18a taken from Ref. 143 was plotted using the more correct (energy density) terminology.

In the very first theoretical treatments of the multiphoton dissociation effect an attempt has been made to explain the occurrence of the threshold. In these treatments the threshold has been attributed to the passage of a molecule through lower levels (lying below the boundary of a vibrational quasicontinuum) as a result of field broadening[47,48] or of multiphoton transitions,[45,46] apparently reflecting the powerlaw dependence $\beta(\Phi)$. However, if this explanation is adopted, a similar steep dependence on Φ should be observed also for the absorbed energy $\bar{n}(\Phi)$, which is in direct conflict with the experimental results (see Sec. 4).

The key to the correct explanation of the threshold nature of the multiphoton dissociation effect was found in Ref. 145, where a comparison was made of the dependences $\beta(\Phi)$ for the SF_6 molecule in the case of excitation of the band of the strong infrared absorption mode ν_3 and a weak composite vibration $\nu_2+\nu_6$. It was found that, although the dissociation yield for the excitation of the $\nu_2+\nu_6$ band was considerably less than for ν_3, the thresholds were practically the same for both cases. This experimental observation made it possible to relate the threshold to the excitation of molecules to a vibrational quasicontinuum, which was independent of the degree of ease with which a molecule passed through a range of energies lying below the boundary of the quasicontinuum.[49,84] A subsequent theoretical investigation of the excitation of molecules to a vibrational quasicontinuum demonstrated that excitation produced a distribution (Sec. 5) exhibiting a steep exponential fall in the direction of higher energies. The position of the distribution tail was proportional to the laser pulse energy density Φ and, consequently, the dissociation threshold was associated physically with the value of Φ_{th} at which the tail of the distribution reached the dissociation limit (Fig. 15). This explanation of the multiphoton dissociation threshold is now regarded as correct for the molecules whose vibrational quasicontinuum is located not too high and which, therefore, dissociate at readily attainable densities of the laser energy pulses (1–100 J/cm^2).

Since the absorption spectrum in a vibrational quasicontinuum depends on the frequency, the dissociation threshold should also depend on the frequency. In particular, the conclusion[145] of the identity of the dissociation thresholds of SF_6 in the case of interaction with the ν_3 and $\nu_2+\nu_6$ bands was modified later[144] and it was found that the threshold in the case of interaction with the $\nu_2+\nu_6$ band was about half that for the interaction with ν_3. Moreover, even within the same absorption band the inhomogeneity of absorption in a vibrational quasicontinuum (see Sec. 5) could play a role in modifying the threshold so that it was different for different laser frequencies.[146,147]

When the laser energy density exceeds the threshold, the dissociation yield rises rapidly. After the yield β has reached a significant value, for example, when it becomes of the order of 0.2–0.3, the rise of $\beta(\Phi)$ slows down and then reaches saturation. An example of such a dependence is shown in Fig. 18b for the CF_3I molecule. It should be noted that in this figure the ordinate does not give the dissociation yield per pulse β but the so-called quantum efficiency of multiphoton dissociation:

$$\varphi=\beta\frac{D_0}{\bar{\varepsilon}}, \qquad (6.1)$$

which provides a physically more correct description of the process of decay of a highly excited molecule and is more convenient for the comparison of theory with experiment. The dissociation yield per pulse β is influenced by two factors: the fraction of molecules q in a vibrational quasicontinuum and the probability of decay of a strongly excited molecule, which depends on the energy $\bar{\varepsilon}_q=\bar{\varepsilon}/q$ absorbed by this molecule. Clearly, the value of φ is independent of q, since both β and $\bar{\varepsilon}$ are proportional to the fraction q of the molecules which have reached a vibrational quasicontinuum.

The relationship between multiphoton dissociation and multiphoton absorption effects is manifested clearly in the similarity of the spectral dependences of the dissociation yield and absorbed energy. Figure 19 shows the dependence of the dissociation yield of the $^{32}SF_6$ molecule on the frequency Ω of laser pulses causing excitation in the ν_3 band.[143] The maximum of this dependence and of the corresponding dependence of the absorbed energy (Fig. 6a) are both shifted toward longer wavelengths. Although the multiphoton dissociation $\beta(\Omega)$ and multiphoton absorption $\bar{\varepsilon}(\Omega)$ spectra are considerably wider than the linear infrared absorption

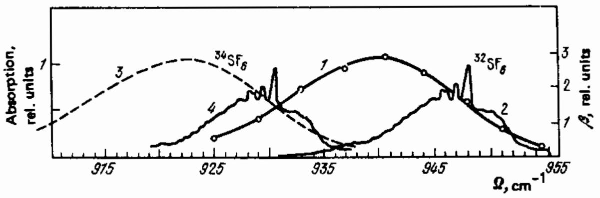

FIG. 19. Dependence of the yield of multiphoton dissociation of SF_6 on the carrier frequency of infrared pulses, explaining the isotopic selectivity of multiphoton dissociation: 1) experimental dependence $\beta(\Omega)$ for the $^{32}SF_6$ molecule; 2) linear absorption spectrum of $^{32}SF_6$; 3) postulated dependence $\beta(\Omega)$ for the $^{34}SF_6$ molecule; 4) linear absorption spectrum of the $^{34}SF_6$ molecule.[143]

spectrum, in many cases the width of $\beta(\Omega)$ is considerably less than the isotopic shift of the absorption bands of various isotopic molecules. A typical spectrum obtained in such a situation is shown in Fig. 19 for the two isotopes ^{32}S and ^{34}S of the SF_6 molecule.[143] It is clear from this figure that irradiation of an SF_6 gas containing a mixture of the $^{32}SF_6$ and $^{34}SF_6$ isotopic molecules should not result in selective dissociation at the radiation frequency Ω_0, at which the relative dissociation yields of both isotopic molecules are equal. A shift toward longer wavelengths relative to Ω_0 should result in preferential dissociation of $^{34}SF_6$, whereas a shift toward shorter wavelengths should have the same result in the case of $^{32}SF_6$. The dependences $\beta(\Omega)$ play a key role in the selection of the radiation frequency when the multiphoton infrared dissociation effect is used in laser isotope separation.

b) Multiphoton dissociation in a two-frequency infrared field

Considerable progress in the understanding of the process of multiphoton dissociation was made after experiements[50,117] were carried out using two infrared pulses with different frequencies Ω_1, Ω_2 and different energy densities Φ_1, Φ_2, as mentioned earlier in Sec. 5a (Fig. 20). They made it possible to separate for the first time and to investigate independently multiphoton excitation of molecules involving lower vibrational transitions (Ω_1, Φ_1) and a vibrational quasicontinuum (Ω_2, Φ_2). These experiments provided the principal confirmation of the model of multiphoton dissociation process shown in Fig. 3. In particular, the absence of a threshold in respect of the energy density of the first pulse Φ_1 observed in Refs. 50 and 117 and investigated in Ref. 119 confirmed that the lower vibrational levels of the molecule were crossed in a gradual manner and the dissociation threshold was due to the excitation of molecules to the quasicontinuum. Investigations of the frequency dependences $\beta(\Omega_1, \Omega_2)$ reported in Refs. 50, 79, 117, and 118 demonstrated that the resonant nature of the dissociation was related mainly to the passage through the lower vibrational levels, but at the same time transitions to a vibrational quasicontinuum also were of weakly resonant nature (Fig. 13).

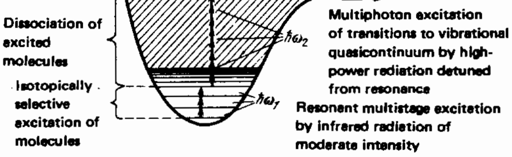

FIG. 20. Multiphoton to dissociation scheme of a molecule subjected to a two-frequency infrared field with separation of a resonant excitation of lower vibrational states by a relatively weak pulse of frequency Ω_1 and excitation of levels in a vibrational quasicontinuum by a high-power pulse of frequency Ω_2.

Multiphoton dissociation in a two-frequency infrared field has also properties of practical importance. A reduction in the energy density Φ_1 of the first pulse causing resonant excitation of molecules in the course of lower transitions can increase the selectivity of the excitation of molecules in a vibrational quasicontinuum because of the associated reduction in the width of the multiphoton absorption spectrum. This was also demonstrated in the successful experiments on the separation of heavy isotopes in molecules with a small isotopic shift (Os isotopes in OsO_4 molecules[148]). The frequency of the second pulse Ω_2 was, firstly, detuned from Ω_1 so as not to broaden the multiphoton absorption spectrum involving lower transitions and, secondly, tuned to the frequency of the absorption maximum in a vibrational quasicontinuum, which ensured reduction in the multiphoton dissociation threshold. This was demonstrated successfully in the experiments on OsO_4 (Ref. 148) and SF_6 (Ref. 118).

c) Statistical theory of unimolecular dissociation of molecules

A strong infrared pulse establishes a nonequilibrium distribution of molecules between the vibrational levels (see Sec. 5b) and the tail of the distribution reaches the boundary of the real continuum of states corresponding to the decay of the molecules. If the vibrational energy of a molecule exceeds the dissociation energy D_0 (or, in other words, the energy of breaking the weakest bond x_0), such a molecule can dissociate spontaneously into fragments. The rate of this dissociation is clearly a function of the state of the molecule. For example, if the energy of vibrational excitation is localized at the bond x_0, the dissociation should occur very rapidly, approximately in one vibrational period. However, if a considerable part of the energy is in other vibrational degrees of freedom of the molecule, dissociation requires a fluctuation as a result of which the energy becomes concentrated at the bond x_0. Realization of such a fluctuation requires a longer time than one vibrational period.

A statistical approach in which an excited molecule is regarded as a closed equilibrium system and its dissociation is considered to be the result of thermodynamic fluctuations was first formulated by Landau.[149,150] Subsequently, the calculations were carried out in much greater detail and the terminology was modified somewhat. The concept of an activated complex was introduced and this was understood to be the configuration of nuclei in a molecule when energy sufficient for the dissociation is localized at the bond x_0. The excess of the energy above the dissociation limit may be distributed also between the internal degrees of freedom of an activated complex. The main assumption of the statistical theory is (see, for example, Ref. 151) that the lifetime of an activated complex is long compared with the characteristic time for the exchange of energy between the various vibrational degrees of freedom by nonlinear couplings. It readily follows from this assumption that in the case of a molecule of energy $E > D_0$ the rate of dissociation should be proportional to the total number $W(E - D_0)$ of the levels of a complex that have internal energies in the interval between D_0 and E or, in other words, it should be proportional to the number of energetically allowed dissociation channels. Moreover, the rate of dissociation should be inversely proportional to the number $\rho(E)$ of vibrationally excited levels of a molecule per unit energy interval in the vicinity of the energy E. It was also found that the coefficient of proportionality can be expressed in terms of physical constants and the formula for the dissociation rate is simply

$$k(E) = \frac{cW(E-D_0)}{\rho(E)}, \tag{6.2}$$

where $\rho(E)$ has the dimensions of reciprocal frequency (cm) and c is the velocity of light.

The formula (6.2) is very general but it can be used only if we know the energy spectra of a vibrationally excited molecule and an activated complex. The theory based on the quantum-mechanical approach to the determination of the characteristics of a vibrational spectrum is usually called the RRKM theory in accordance with the initial letters of the authors' surnames.[152] Estimates which often describe the observed dissociation rates with sufficient accuracy can be obtained using one of the variants of the RRKM theory based on the harmonic model of a molecule. According to this model, the density of levels ρ can be expressed in terms of s values of the frequencies of normal vibrations of a molecule and the number of dissociation channels W can be expressed in terms of $s-1$ values of the normal vibration frequencies of an activated complex. In the harmonic approximation the functions $\rho(E)$ and $W(E - D_0)$ can be calculated numerically when the frequencies are known. There are also available sufficiently accurate simple approximation formulas and of these the generally accepted one is the expression (5.1) for $\rho(E)$ in the Whitten–Rabinovitch approximation.[115] However, satisfactory estimates can also be obtained using the semiclassical approximation, which yields the following formula for the rate of unimolecular dissociation (decay)[153]:

$$k(E) = \mathscr{K} \left(\frac{E - D_0 + E_0^{\text{comp}}}{E + E_0^{\text{mol}}} \right)^{s-1} = \mathscr{K} f(E), \tag{6.3}$$

where s is the number of vibrational degrees of freedom of a molecule; E_0^{mol} and E_0^{comp} are the energies of zero-point vibrations of a molecule and an activated complex, respectively; the frequency factor $\mathscr{K}$ (with the dimensions of reciprocal second) can be expressed in terms of the frequencies of normal vibrations of a molecule ω_m^{mol} and an activated complex $\omega_m^{\text{comp.}}$:

$$\mathscr{K} = cL \left(\prod_{m=1}^{s} \omega_m^{\text{mol}} \right) \left(\prod_{m=1}^{s-1} \omega_m^{\text{comp}} \right)^{-1}, \tag{6.4}$$

where L is the number of decay paths (for example, when an SF_6 molecule decays into an SF_5 radical and an F atom, the number of paths is $L = 6$).

The frequency factor $\mathscr{K}$ is clearly of the same order of magnitude as the frequency of molecular vibrations, i.e., $\mathscr{K} \approx 10^{13}$–$10^{14}$ sec^{-1}. The factor $f(E)$ in Eq. (6.3) describes the rapid rise of the rate of decay of a molecule on increase in its energy above the dissociation limit because of an increase in the number of energetically allowed channels. However, the numerical values of $f(E)$ are small and they decrease on increase in the number of molecular degrees of freedom, which readily follows from the fluctuation mechanism of molecular decay.

The above simple formulas allow us to estimate how strongly a molecule may be overexcited above the dissociation limit due to the interaction with a laser infrared pulse under typical experimental conditions when the pulse duration is $\tau_p \approx 100$ nsec. If the energy density of a laser pulse does not exceed greatly the threshold value, the number of absorbed photons is equal to the ratio $D_0/\hbar\Omega$. In this case we can estimate the rate k_0 of passage through each successive transition related to the absorption of one infrared photon by assuming that $k_0 \approx (D_0/\hbar\Omega)\tau_p^{-1}$. Since typical values are $(D_0/\hbar\Omega) \approx 20$–$50$, it follows that $k_0 \approx (2$–$5) \times 10^8$ sec^{-1}. The rapid rise of the decay rate $k(E)$ allows us to estimate the characteristic energies E to which a molecule can be excited by an infrared pulse from the relationship $k_0 \approx k(E)$, which corresponds approximately to $f(E) \approx 10^{-4}$. Figure 21 shows the dependences $f(E)$ plotted for different values of s ignoring the energies of zero-point vibrations. We can see that, for example, in the case of molecules with five atoms the values of $f(E) \approx 10^{-4}$ are obtained already for $(E - D_0) \lesssim 0.1D_0$, whereas for molecules with six and seven atoms, this occurs for $(E - D_0) \lesssim 0.2D_0$, and $(E - D_0) \lesssim 0.3D_0$, respectively. Thus, in the case of molecules with ≤7 atoms a realistic overexcitation above the dissociation threshold resulting from the action of a pulse of $\tau_p \approx 10^{-7}$ sec duration may amount to $(0.1$–$0.3)D_0$. For the more complex molecules and/or shorter pulses the degree of overexcitation may be even greater than the dissociation energy D_0. This is the special feature of infrared photodissociation under transient (pulsed) conditions.

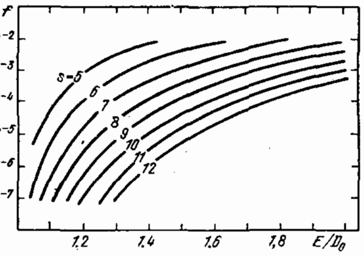

FIG. 21. Dependence of the function $f(E)$, occurring in Eq. (6.3) representing the rate of unimolecular decay, in the ratio E/D_0 of the vibrational energy to the energy of dissociation of molecules with different numbers s of atoms.

The dissociation yield β can be calculated by supplementing the rate equations (5.10) with the term $-k_n(E)z_n$ describing the decay of states above the dissociation limit at a rate $k_n(E)$ governed by Eq. (6.3), where $k_n = 0$ for all the levels above the dissociation limit. Then, the solution of the system (5.10) including this term allows us to find the dissociation yield during a laser pulse

$$\beta(\tau_p)=\sum_n\int_0^{\tau_p}k_nz_n(t)\,dt. \qquad (6.5)$$

The molecules which are at levels above the dissociation limit D_0 at the end of a laser pulse may dissociate subsequently making an additional contribution to the dissociation yield. The total dissociation yield can be calculated using Eq. (6.5) in which integration with respect to time is limited by the time needed for unavoidable relaxation of the vibrational excitation. The dashed curve in Fig. 18b shows the results of a calculation of the dissociation yield of the CF_3I molecule made using the quantum efficiency φ of the dissociation process described by Eq. (6.1) This calculation was carried out in Ref. 56 using the model concepts concerning the vibrational quasicontinuum discussed in Sec. 5 and on the basis of the above assumptions on the rate of multimolecular decay. The variable parameters were the average anharmonicity constant x_0 and the average three-frequency Fermi interaction constant V_0. It was found that the theoretical and experimental dependences $\varphi(\Omega, \Phi)$ agreed within the limits of the experimental error for the following values of the parameters of a vibrational quasicontinuum of CF_3I: $\nu_1|x_0| = 3.8 \pm 0.2\ \text{cm}^{-1}$, $V_0 = 0.73 \pm 0.03\ \text{cm}^{-1}$. Thus, one could say that it has now become possible to investigate theoretically in a self-consistent manner all the stages of multiphoton dissociation and to obtain quantitative data by calculation.

d) Products of multiphoton dissociation

According to the statistical theory of dissociation presented above, the observed dissociation products should correspond to the breaking of the weakest bonds in molecules. Direct diagnostics of radicals formed as a result of multiphoton dissociation of molecules has become possible on introduction of the molecular beam method.[52,154,155] For example, this method was used to establish[52] that in the case of SF_6 an atom of F is detached first and then multiphoton dissociation of the SF_5 radical produces the radical SF_4 (Fig. 3). An alternative dissociation mechanism $SF_6 - SF_4 + F_2$ does not occur because this method failed to reveal the presence of the F_2 molecules. Determination of the distribution function of the kinetic energy of the newly formed radicals $g(E_{\text{kin}})$ made it possible to obtain[52] data on the vibrational energy of the resultant radicals and, consequently, on the degree of overexcitation of the dissociating SF_6 molecules above the dissociation limit. In particular, when the laser pulse energy density was $\Phi = 4\text{–}10\ \text{J/cm}^2$, the excess of E over D_0 was 6–10 CO_2 laser photons. This was in good agreement with the statistical theory predictions.

In several cases there were two dissociation channels with similar energies ΔH. A characteristic example is the C_2H_4FCl molecule which can undergo the following dissociation reactions:

$$C_2H_4FCl\ \begin{cases}\longrightarrow C_2H_3Cl + HF & (\Delta H = 21\,280\ \text{cm}^{-1}),\\ \longrightarrow C_2H_3F + HCl & (\Delta H = 22\,330\ \text{cm}^{-1}).\end{cases} \qquad (6.6)$$

The rates of decay calculated in Ref. 156 showed that the RRKM theory was in agreement with the measured ratios of the concentrations of C_2H_3F and C_2H_3Cl.

In the presence of adjacent dissociation channels, one of which is accompanied by the detachment of an atom and the other by the detachment of a molecule, the former is frequently more likely even if it is not favored by the energy considerations. A typical example is the CF_2Cl_2 molecule which can undergo the following dissociation reactions:

$$CF_2Cl_2\ \begin{cases}\longrightarrow CF_2Cl + Cl & (\Delta H = 28\,700\ \text{cm}^{-1}),\\ \longrightarrow CF_2 + Cl_2 & (\Delta H = 24\,850\ \text{cm}^{-1}).\end{cases} \qquad (6.7)$$

In this case the probability of dissociation in accordance with the first channel is approximately an order of magnitude higher than in the case of the second channel.[157,158] The reason for this effect is the presence of a potential barrier for the second reaction. The proof is provided by a determination[159] of the distribution of the vibrational energy of the CF_2 radical. It was found that the vibrational temperature of this radical remained constant ($T_v = 1050\,^\circ\text{K}$) although variation of Φ altered the yield of the radicals by an order of magnitude. Hence, the dissociation of these molecules occurred near the top of the barrier whose height was 6900 cm^{-1}.

e) Future research trends

The RRKM theory was developed on the assumption that the lifetime of an activated complex is relatively long and it ignored the above situation when the configuration of the nuclei corresponding to an activated complex is separated by a potential barrier from the configuration of nuclei in a molecule. In this case the rate of dissociation should be described in terms of quantum tunneling across a barrier. The numerical rates of dissociation in the subbarrier range become considerably less than the estimates given above and in reality the dissociation occurs only when a molecule reaches the top of the barrier in the process of multiphoton excitation. A typical example is the dissociation producing a diatomic molecule whose atoms are not bound to one another in the original molecule. It would be desirable to investigate experimentally the dissociation as a result of subbarrier passage of a molecule to the continuum. This could be done by developing methods for investigating highly excited molecules under conditions of slow (10^{-1}–10^{-5} sec) relaxation of the excitation, probably using molecular beams.

It would be of considerable interest to investigate multiphoton excitation of polyatomic molecules by ultrashort pulses when a strong vibrational overexcitation of molecules above the dissociation limit takes place. In this case one can expect the discovery of many dissociation channels with energies considerably greater than the energy of breaking of the weakest bond. Transient multiphoton dissociation effects provide many new opportunities for producing a variety of radicals, as indicated by a detailed comparison of the existing theory of monomolecular dissociation with the experimental results.

As pointed out in Sec. 5.d, multiphoton excitation by ultrashort pulses makes it possible to acquire strong excitation in a time shorter than the stochastization time of the vibrational energy and thus cause breaking of molecular bonds which are not the weakest. Particularly interesting results should be obtained in experiments on complex molecules, for which one could expect partial stochastization of the vibrational energy and a major difference between the experimental results and predictions of the statistical theory.

All the experiments and calculations reported so far have been concerned only with the average values of various properties or parameters when one is dealing with an ensemble of a very large number of molecules. New methods of laser spectroscopy have been developed recently and these make it possible to detect single atoms with a nanosecond time resolution.[160] If such methods could be used to detect atoms formed as a result of dissociation of a molecule, it would be possible—in principle—to investigate fluctuations of, for example, the molecular dissociation time after fast multiphoton excitation. A study of fluctuations should allow a more thorough checking of the statistical theory of the dissociation of molecules.

7. APPLICATIONS

Applications of the phenomena which appear as a result of interaction of infrared laser pulses with polyatomic molecules cover a fairly wide range of problems ranging from spectroscopy to nuclear chemistry. A detailed discussion of possible applications which are being investigated by hundreds of scientists in many countries would require an independent review. We shall confine ourselves to a brief listing of potential applications.

a) Molecular spectroscopy

As pointed out earlier, it is the multiphoton excitation of molecules with high-power infrared radiation pulses that has made it possible to investigate systematically high vibrational states of molecules and transitions between them. Essentially, this has led to the development of molecular spectroscopy of excited vibrational states both discrete (below the boundary of a vibrational quasicontinuum) and those forming the quasicontinuum. The first tasks for this new branch of spectroscopy and molecular physics have been listed above (Sec. 4.d and Sec. 5.d).

We shall draw attention to the possiblity of investigating "reverse nonradiative" transitions in which a strong vibrational excitation is transformed into an electronic excitation, in contrast to the well-known process of nonradiative relaxation of the electronic into vibrational energy. Processes of this type have already been investigated experimentally.[57]

Multiphoton dissociation makes it possible to generate high concentrations (10^{14}–10^{16} cm^{-3}) of radicals of a given kind. The very first investigations have led to the suggestion of utilizing this effect as a method for infrared photolysis of molecules. Employing various polyatomic molecules one can vary the nature of radicals within very wide limits even when conditions are restricted to breaking of the weakest molecular bonds. This provides an opportunity for a systematic investigation of the spectra of radicals from the microwave to the vacuum ultraviolet range.

b) Chemical physics

Pulsed generation of free radicals of a specific kind provides a convenient method for investigating elementary processes in which these radicals participate in a gaseous medium, including kinetics and dynamics of chemical reactions.[161] Excitation of the fluorescence of such radicals by tunable laser radiation makes it possible to determine the quantum state of a free radical with nanosecond time resolution. For example, it was found[58,59] that the C_2 radicals appeared in the ground ($a^3\Pi_u$) and metastable ($d^3\Pi_g$) electronic states as a result of multiphoton dissociation of C_2H_4 molecules by high-power CO_2 laser pulses. This trend in the study of gaseous reactions has now become highly topical (for reviews see Refs. 162 and 163).

Controlled rapid acquisition of laser energy by the vibrational degrees of freedom of polyatomic molecules provided a unique opportunity for investigating monomolecular dissociation and isomerization reactions, and for comparing their rates with the predictions of the RRKM theory.[152] Some of the currently pursued investigations have already been mentioned in Sec. 6.e. Once again it will be particularly valuable to combine the method of multiphoton excitation with the methods of laser-spectroscopic diagnostics[164] of the electronic, vibrational, and rotational states of photodissociation products.

c) Nuclear chemistry

One of the most important tasks in nuclear chemistry and technology is isotope separation. Rapid development of multiphoton methods for the excitation and dissociation of molecules has been stimulated precisely by the isotopic selectivity of these methods discovered by Ambartsumyan *et al.*[36] The possibility of separation has now been demonstrated for a great variety of isotopes ranging from the light isotopes H/D as a result of highly selective dissociation of CF_3Cl_2H molecules[165] to the heavy Os isotopes as a result of dissociation of OsO_4 molecules in a two-frequency infrared field.[148] The problem of laser isotope separation is one of the most important specific tasks of selective interaction between laser radiation and atoms or molecules (for a review see Ref. 11). It has been considered in detail in many reviews[166-169] and monographs.[15,170]

We shall mention here that, for example, our recent experiments[56,81,171] on the CF_3I molecule have demonstrated the possibility of attaining the following practical parameters of the method of multiphoton isotopically selective dissociation: 1) minimal energy losses equal to the dissociation energy of the weakest molecular bond (2 eV of infrared radiation energy); 2) maximal (almost 100%) dissociation yield of molecules in the irradiated region for a moderate energy of infrared radiation pulses; 3) a high isotopic selectivity of the dissociation (in excess of 30) at a relatively high (5–10 Torr) total pressure of the CF_3I gas; 4) a considerable degree of extraction (about 50%) of the target rare isotope (${}^{13}C$) without significant decomposition (less than 2%) of the remaining molecules (${}^{12}CF_3I$); 5) suppression of secondary photochemical processes destroying the high selectivity of the dissociation process. All this has made it possible to develop methods for the separation of light and moderately heavy isotopes on a practical scale, based on the use of a TEA CO_2 laser with a high (up to 200 Hz) frequency of pulse repetition at an average power of 1 kW (Refs. 172 and 173). The simplicity and technological ease of this method of laser isotope separation allows us to expect its introduction in industry in the near future.

Separation of light and intermediate-mass isotopes present in concentrations of 1% or more is a relatively simple task. There are more complex and important problems such as the extraction of rare isotopes (for example, the D isotope with a relative abundance of 1/5000) and of heavy-element isotopes from molecular compounds characterized by a small isotopic shift (for example, extraction of ${}^{235}U$ from UF_6). A practical method for the separation of the hydrogen isotopes should be characterized by a very high separation selectivity. At the very least, the isotopic selectivity of dissociation $\alpha(D/H)$, defined as the ratio of the dissociation yields of molecules with the required target isotope D and without it (H):

$$\alpha\left(\frac{D}{H}\right)=\frac{\beta_D}{\beta_H}, \tag{7.1}$$

should exceed 1000. The recent successful experiments[165] on multiphoton dissociation of a series of deuterated molecules by CO_2 laser radiation have yielded promising results.

Such highly selective laser technology should also in future have a considerable influence on the purification of nuclear reactor waste from the radioactive impurities which contaminate such waste and the ambient atmosphere. Laser technology is still at the early stages of development from the point of view of such large-scale applications. However, the scientific foundations of such progressive technology are already being established.

d) Chemical synthesis

Multiphoton excitation with high-intensity infrared radiation can be used to transfer an energy of the order of several electron volts only to molecules of a selected kind in a mixture without transmitting the same high energy to other molecules. This situation differs from thermal excitation when all the molecules in a gas mixture acquire the same store of vibrational energy. Therefore, one would expect to find new chemical reactions involving highly excited molecules or their dissociation products. It is the strong excitation of a selected molecule under transient reaction conditions and the appearance of products of its dissociation before thermalization of the excitation that can make unusual reaction paths, studied earlier under equilibrium conditions, more competitive. In fact, under steady-state conditions the composition of the initial and final products is governed by thermodynamics. In the case of pulsed excitation under transient (non-steady-state) conditions, not only the thermodynamic factors but also the time factors are important, i.e., the ratio of the rate of a reaction along any given path to the rate of relaxation of the nonequilibrium state of the molecular mixture becomes important.

An example of highly efficient infrared photochemical synthesis is described in Ref. 174, where a report is given of a study of selective infrared multiphoton dissociation of CF_3Br and CF_3I molecules in the presence of acceptors. In particular, the possiblity of very efficient (practically 100%) photochemical conversion of CF_3Br in a mixture with I_2 (at an I_2 pressure in excess of 10 Torr) into CF_3I molecules was demonstrated. In this case the photochemical reactions occurred in accordance with the scheme

$$\begin{aligned} CF_3Br + n\hbar\Omega &\rightarrow CF_3 + Br,\\ CF_3 + I_2 &\rightarrow CF_3I + I,\\ CF_3 + I &\rightarrow CF_3I,\\ Br + Br &\rightarrow Br_2. \end{aligned} \tag{7.2}$$

On the basis of this and other[175] investigations one could draw a far-reaching conclusion concerning the promising nature of laser photochemical synthesis based on radical reactions. Application of infrared laser radiation to suitable molecules should make it possible to generate rapidly any desired concentrations of a great variety of radicals. This should allow one to direct the reaction of synthesis along the shortest path ensuring the maximum yield of the required product for the minimum use of the original materials. In the case of infrared multiphoton dissociation employed in the preparation of radicals of the required kind one should bear in mind that the excited molecules dissociate as a result of breaking of the weakest bonds. Nevertheless, this still provides a wide scope for laser chemical synthesis.

In conclusion, we take the opportunity to express our deep gratitude to our colleagues at the Institute of Spectroscopy of the USSR Academy of Sciences for their cooperation in the work on the problems discussed above during the last decade. One of the authors (V.S. Letokhov) is grateful to Prof. É. Yu. Salaev for his help and cooperation in writing this paper.

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Translated by A. Tybulewicz