Laser IR fragmentation of molecular clusters: the role of channels for energy input and relaxation, the influence of surroundings, and the dynamics of fragmentation

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<u>Abstract.</u> The results of research into the infrared (IR) laser fragmentation of molecular clusters by resonant vibrational excitation of their constituent molecules are presented with special attention given to the role of cluster environment, the energy input and relaxation channels, and dynamical aspects. For this purpose, the results of experiments with free homogeneous and mixed molecular clusters and of experiments with clusters inside or on the surface of large inert gas clusters are analyzed, the laser excitation pulses varying in wavelength and duration. Data on the character and rate of cluster fragmentation, and on the intramolecular and intracluster vibrational energy relaxation times in clusters are discussed. Results of an

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Received 19 April 2016, revised 7 June 2016 Uspekhi Fizicheskikh Nauk **187** (3) 241–276 (2017) DOI: https://doi.org/10.3367/UFNr.2016.06.037821 Translated by Yu V Morozov; edited by A Radzig investigation into the structure and dynamics of molecular clusters and atomic-molecular complexes obtained by IR photodissociation spectroscopy and the spectroscopy of photofragments are analyzed. Methods for generating heterogeneous molecular clusters, for size-selecting clusters. and for studying the IR dissociation and IR fragmentation of clusters are also briefly considered.

Keywords: atoms, molecules, clusters, nanoparticles, molecular and cluster beams, laser IR photodissociation and photofragmentation of molecular clusters, intramolecular and intracluster vibrational energy relaxation in clusters, time dynamics of cluster decay

1. Introduction

Ongoing efforts in the area of cluster and cluster beam research have brought this issue to the forefront of modern physics and chemistry (see, for instance, monographs and volumes of collected articles [1–17] as well as reviews [18–59]). Special interest in cluster studies arises from their being intermediate structures between single particles (atoms,

molecules) and bulk liquids or solids. The discrete structure of their energy levels and the high surface-to-volume ratio of clusters taken together account for their properties differing from those of their constituent particles and bulk matter. Clusters can be regarded as a new state of matter organized at the nanoscale. Clusters of identical elemental compositions may represent a variety of bonding and structure types and therefore exhibit very different chemical and physical (optical, electrical, magnetic, and thermodynamic) properties [9, 19, 23, 29, 56]. The possibility of changing the number of atoms and molecules in a cluster, as well as its environment, opens up unique opportunities for the observation of the state and characteristics of matter.

The ever-increasing interest in cluster and cluster beam studies is attributable to the rapid development of nanotechnology [60–65], a relatively new area of research of great practical significance. Cluster beams find application in micro- and nanotechnologies for the production of thin films, the creation of new materials, and the treatment of surfaces [1–3, 5, 19–21, 25, 48]. Cluster beams are used to study both cluster properties and processes involving clusters [23, 50–53, 65].

Developments in cluster science gave rise to a variety of new research areas and practical applications [1–3, 19–24], such as (1) excitation of clusters by ultrashort superpower laser pulses [66–104] for the production of highly ionized atoms and high-energy ions, the observation of Coulomb and hydrodynamic cluster explosions [66–83], the generation of X-ray radiation [84–95] and neutrons [96–104], (2) the interaction of high-energy clusters and cluster ions with solid surfaces [19–21, 25, 41] and between themselves [105– 107], intended for applications in nuclear synthesis [108–112] and initiation of chemical reactions [113–122], and (3) use of cluster beams for the film deposition [5, 19–21, 25, 123–139] and creation of new materials [131–139], and, finally, for the treatment of surfaces [140–154].

Equally important in the context of practical applications is the study of fullerenes, i.e., closed-structure carbon clusters [6, 12, 13, 31, 43–46], carbon nanotubes [40, 47, 57–59], and graphenes [54, 55, 155–161]. In 1996, the Nobel Prize in Chemistry was awarded to a group of researchers (R E Smalley, R F Curl, H Kroto) "for the discovery of fullerenes" [43–45], and the Nobel Prize in Physics 2010 to A Geim and K Novoselov "for groundbreaking experiments regarding the two-dimensional material graphene" [160, 161]. Many aspects of cluster research are highlighted in monographs and reviews [1–59].

The advent of powerful broadly tunable lasers emitting ultrashort light pulses [162-164] made possible research on dynamic processes in atomic and molecular clusters, as well as real-time analysis of electron and nucleus movements in them, as in the case of free electrons and molecules. Short pulses with controlled amplitudes and phases can be used to induce ion and electron motions inside clusters and thereby to study in real time intracluster processes under extreme conditions [18, 19, 24]. It also makes possible investigations into electron relaxation processes and the temporal evolution of collective modes. Cluster irradiation with intense laser pulses transforms these structures into well-insulated nanoscale plasma [68-77] and permits studying their Coulomb and hydrodynamic explosions [68-70, 74-76]. The absence of channels for energy transfer into the environment, regardless of cluster excitation regime, creates conditions for accurate analysis of reaction products induced in a cluster, such as electrons, ions,

cluster fragments, and emitted photons [24]. Laser-induced processes in atomic and molecular clusters have recently been considered in several review articles [18, 24].

Internal physical and chemical processes in molecular van der Waals clusters and their fragmentation under the effect of resonant excitation of intercluster molecules by intense IR laser pulses have lately been thoroughly investigated in Refs [26, 165–172]. These investigations are interesting in that such excitation permits us to create conditions that are difficult to realize in a gas or a macroscopic condensed medium. Particle's environmental effects in gases are usually insignificant and not infrequently disregarded. In contrast, the influence of the environment in a condensed medium is much more pronounced, but the energy absorbed by the particles is rapidly transferred to the surroundings. Dimensional effects play an important role in clusters, because the absorbed energy is confined within a small volume. Therefore, clusters interacting with resonant laser radiation can undergo strong heating, which facilitates the investigation of many intracluster processes associated with strong excitation, e.g., environmental effects, energy relaxation times and channels, ionization, dissociation, and fragmentation [165-1671

Furthermore, environmental conditions for surface and intracluster particles are quite different, which has important implications for their excitation and relaxation processes. Specifically, it is not difficult to lay the groundwork for particles of interest to exist in either a homogeneous or heterogeneous environment. Experiments are also conceivable in which clusters may be homogeneous or located either inside other clusters or on their surface [171, 172]. In other words, the use of clusters opens up ample opportunities for studying the interplay between matter and laser radiation.

A topical problem deals with investigations into resonant IR laser-induced fragmentation of molecular clusters placed under different environmental conditions [49, 171, 172]. Such investigations can be expected to provide detailed information about the character and times of cluster fragmentation, depending on laser excitation parameters, cluster structure, composition, and environment. Resonant excitation of molecular clusters by short IR laser pulses yields extensive information on energy migration inside clusters and permits kinetics of their decay to be observed in real time [49,168–172, 174, 175].

The present review provides the results of research on dissociation and fragmentation of molecular clusters in response to resonant vibrational excitation of their constituent molecules by IR laser radiation. The data of comparative experiments on resonant excitation of molecular clusters by nanosecond, picosecond, and femtosecond IR laser pulses are discussed. Much attention is given to the analysis of results obtained in studies on the migration of the energy absorbed inside clusters and the kinetics of their monomolecular decomposition under the effect of excitation. In addition, results of research into the dependence of cluster IR dissociation efficiency on the structure and environment of both homogeneous and heterogeneous (mixed) molecular clusters, involving those located in a bulk or on the surface of other clusters are presented. Methods for the production of heterogeneous molecular clusters, their size selection, dissociation and fragmentation by IR laser radiation are summarized.

The paper outline is as follows. Section 2 is designed to briefly discuss methods for the production of homogeneous and mixed molecular clusters used in the studies surveyed in the present paper. Methods of cluster generation in supersonic and gas-dynamic jets are described, along with laserassisted techniques for the production of heterogeneous clusters containing metal atoms and ions and the method for the generation of mixed clusters based on the cluster trapping of molecules and atoms.

Section 3 deals with methods for size (mass)-selecting homogeneous and heterogeneous molecular clusters, including mass-spectrometry, cluster deflection in the beam by means of angular momentum transfer from atoms upon cluster collision with an atomic beam, and cluster doping (tagging) with fluorescent molecules or low-ionization energy atoms.

Section 4 concerns methods for the study of dissociation and fragmentation of molecular clusters by IR laser radiation. Special attention is given to molecular beam depletion by a spectroscopic technique with the use of bolometers and mass-spectrometers for beam detection, and to the detection of clusters and their fragments by mass-spectrometry.

Section 5 is devoted to discussing the results of experimental studies on the spectra, constitution, and structure of molecular clusters and atomic-molecular complexes by IR photodissociation spectroscopy and spectroscopy of photofragments. The application of vibrational IR predissociation of van der Waals molecules for laser-assisted isotope separation is considered in brief.

Section 6 is focused on the analysis of results of investigations into dissociation and fragmentation of homogeneous and heterogeneous molecular clusters by intense IR laser pulses and the role of energy input and relaxation channels in cluster fragmentation and the influence of the environment on its efficiency.

Section 7 is designed to consider the dynamics of molecular clusters excited by short IR laser pulses. Direct real time measurements of *intramolecular* and *intracluster* energy relaxation rates in molecular clusters are described along with the influence of energy input and relaxation channels on cluster fragmentation time.

Section 8 summarizes the main results for the studies encompassed by the present review; the most important achievements and prospects for further studies are highlighted.

2. Production of homogeneous and mixed molecular clusters

Many methods are currently available for the production of atomic and molecular clusters [1-3, 7, 19, 22, 23, 27, 28, 30, 176, 177]. The most popular are generation in gas-dynamic jets, gas aggregation, surface erosion, ionic sputtering, laser ablation, pulsed arc discharge, and magnetron and laser methods for metal cluster generation [1, 14, 19, 22, 27, 178]. Molecular and mixed (heterogeneous) atomic-molecular clusters on which the present review is focused are most frequently obtained by means of gas condensation during gas-dynamic expansion, laser-assisted methods, and trapping of atoms and molecules by clusters. The laser techniques are employed to produce both homogeneous metal and heterogeneous atomic-molecular clusters and complexes containing atoms or clusters (including charged ones) of metals or refractory elements. These methods are briefly reviewed below.

2.1 Generation of clusters in gas-dynamic jets

Gas condensation during supersonic expansion in a nozzle appears to be currently the most widespread method for cluster formation [1-3, 7, 19, 22, 27, 28, 30, 176-180]. A gas initially at rest over the nozzle exit area at temperature T_0 and pressure p_0 expands as it outflows through the nozzle orifice into a vacuum chamber. The gas is accelerating and cooling adiabatically as it expands. As soon as it becomes supersaturated, clusters begin to grow. As a result, a mixture of uncondensed gas and cluster particles forms in the jet. The molecular-cluster beam is extracted from the expanding jet with a skimmer usually positioned roughly 1–3 cm from the nozzle exit. To avoid beam scattering on the skimmer, the leading edges of its walls must be made as thin as possible. Normally, electrophoretically deposited skimmers are used with an inlet opening diameter ranging 0.5-2 mm. In this way, narrow directional molecular-cluster beams are produced in which free clusters collide neither with one another nor with atoms or molecules present in the beams. Due to this, the interaction between laser radiation and cluster beams is usually unaffected by particle collisions and energy transfer from the clusters into their environment. The relative number of clusters in a beam, i.e., the degree of clusterization of atoms or molecules, depends on a variety of factors, in the first place gas composition, pressure, and temperature over the nozzle, as well as the latter's shape.

Gas condensation and cluster generation processes in nozzle sources are known fairly well [181–184]. Both cluster formation process and size depend on the expansion conditions in the jet [181, 183]. To characterize the cluster formation process, Hagena introduced a dimensionless parameter (Hagena parameter) [181, 183] expressed as

$$\Gamma^* = k \, \frac{(d/\tan\alpha)^{0.85} p_0}{T_0^{2.29}} \,, \tag{2.1}$$

where *d* is the nozzle diameter in μ m, α is the expansion halfangle of the conical nozzle, p_0 is the gas pressure above the nozzle (in mbar), T_0 is the pre-expansion temperature, and *k* is a constant dependent on a sort of gas. Constant *k* (in K^{2.29} mbar⁻¹) may be calculated from molar enthalpy of the gas at zero temperature and solid state density [179]. *k* equals 5500 for Xe, 2900 for Kr, 1700 for Ar, 180 for Ne, and 4 for He [179, 185].

The results of many studies give evidence that gas clustering starts when parameter Γ^* becomes higher than 300. Then, the mean cluster size increases roughly in proportion to $\sim (\Gamma^*)^{2.0-2.5}$ [181, 186]. Large clusters (containing more than 10⁴ atoms) are formed for $\Gamma^* > 5 \times 10^4$ [185]. Parameter Γ^* reflects clusterization efficiency, which is higher for heavy inert gases, such as Kr and Ar, than for Ne and He. A gas pressure of about 1.5 atm over a nozzle with an inlet diameter of 1 mm is enough for Kr or Ar cluster formation in the jet at room temperature, whereas helium undergoes clusterization at a pressure above 10 atm. It also follows from relation (2.1) that cluster formation greatly depends on the nozzle expansion angle. The possibility of enhancing clustering efficiency with the exploitation of supersonic nozzles has been demonstrated for many gases [187]. It was shown that Ar, Kr, Xe, and N_2 give rise to especially large clusters.

Relation (2.1) holds only for monoatomic gases. It is not fulfilled for molecular gases due to the rather strong temperature dependence of their thermal capacity and specific heat ratio (different exponents for d and T_0). Various methods for the evaluation of the degree of molecular clusterization and the mean size of resultant clusters in a beam are employed in the case of molecular cluster generation [167–169]. They allow the production of homogeneous atomic or molecular clusters and heterogeneous or mixed molecular and atomic-molecular clusters, depending on the gas (gaseous mixture) composition and partial-to-total pressure ratio above the nozzle [178, 188, 189]. A combination of these methods with laser vaporization of a metallic sample at the exit from the nozzle yields mixed atomicmolecular clusters and cluster ions [178]. In addition, nanoscale superfluid helium droplets (clusters) are formed in molecular beams [50–53, 190].

To enhance the probability of cluster generation in supersonic jets, the particles studied are usually diluted by mixing with an inert carrier gas, the atoms of which are needed to cool the growing clusters and withdraw condensation heat. In this way, they stabilize the clusters subject to evaporation. Under poor cooling conditions, the clusters are stabilized as a result of evaporation of one or several particles. The carrier gas exerts a similar effect in the case of molecular cluster formation [191].

Given that the energy of cluster-cluster interaction does not differ significantly from the energy of interaction between these particles and carrier gas atoms, heterogeneous clusters can form [191, 192]. Notice that cluster formation also depends on the mass of atoms in the carrier gas. A heavy gas expands more slowly than a light one, which provides more time for aggregation to proceed; therefore, larger clusters can be generated [27].

In gas-dynamic jets, as in the majority of other methods, cluster formation proceeds as a statistical process [1, 3, 7, 27], which accounts for their log-normal distribution over size [1, 190, 194, 195]. This is, in fact, a Gaussian distribution in the coordinate system with the logarithmic *x*-axis. The half-width of the asymmetric distribution is roughly equal to the mean cluster size. The presence of clusters with different sizes in a beam markedly complicates experimental studies, especially when they are designed to elucidate the properties of clusters of a given size and processes with their participation. The available methods of size-selecting clusters (see Section 3) make it possible to resolve this problem.

2.2 Laser-assisted method for the production of atomic-molecular complexes in molecular beams

The method for the production of atomic-molecular complexes in molecular beams is based on laser-induced evaporation of the material used to generate cluster or nanoparticle beams. Atoms, ions, and small clusters of the target material obtained by laser ablation are taken up by the carrier gas and cooled as a result of gas-dynamic expansion, thereby giving rise to clusters and nanoparticles. Smalley and co-workers were the first to design sources for the generation of supersonic metal cluster beams by laser vaporization [196–199]. At the beginning, it was a very simple source [199], but in the course of time it underwent a number of modifications taking account of the shape of the sample subjected to evaporation and the atomic clusterization conditions [44, 178, 200-202]. Vaporization is effected with the use of either an excimer laser or an Nd:YAG laser and the latter's second harmonic. The pulse energy is usually 30-50 mJ, and pulse duration 5-50 ns. The method itself and its physical principles are considered in much detail in Refs [19, 22, 178, 188, 189].



Figure 1. (a) Schematic of a 'standard' source of clusters with laser evaporation of the sample [178]. (b) Schematic of a cluster source in the so-called cutaway configuration with laser evaporation of the sample [178].

With this technique, a sample of the material from which clusters are prepared is placed near the channel through which the gas outflows from the nozzle and evaporates under the effect of laser irradiation (Fig. 1). The sample is usually a round metal rod rotated about and translationally moved along its axis by a motor. A pulsed nozzle (General Valve series) is usually applied to generate a molecular beam [178]. The gas flows out from the nozzle through a narrow channel over the sample surface. Laser radiation responsible for sample evaporation is focused onto its surface in the gas flow area. The channel (not infrequently referred to as the cluster growth channel) extends beyond the sample vaporization site (Fig. 1a); it serves to localize the expansion of gas flow and sample vapors and thus enables particle-particle collisions, further gas cooling, and cluster formation and growth. The variable parameters of such a source influencing cluster beam characteristics are the sort of the carrier gas (helium, argon, etc.), its pressure over a nozzle, nozzle opening time, its synchronization with laser pulses, pulse energy and wavelength, and quality of laser radiation focusing. Other key parameters varying with the type of a sample are its shape and material, cluster growth channel length and diameter [19, 178].

A source of the so-called cutaway configuration (Fig. 1b) was developed [178, 203, 204] to prepare clusters containing a metal atom or an atomic ion and surrounded by more weakly bound molecular ligands or inert gas atoms. The cluster growth channel in such a source is truncated (cutaway) and extends only as far as the sample to be evaporated. Nozzles designed in such a way were utilized to obtain complexes



Figure 2. Mass spectra of $CuAr_n$ and $Cu(H_2O)Ar_n$ clusters obtained by laser vaporization of the sample with a nozzle in a cutaway configuration and directly detected with a time-of-flight mass spectrometer [178, 203].

composed of a metal atom cation and a water molecule tagged with argon atoms (Fig. 2) [178, 203, 204]. Other changes in the design of the source are also possible, depending on the objective of the work [178].

To obtain homogeneous atomic clusters by this method, monoatomic carrier gases (helium, argon) are usually employed, whereas molecular clusters containing atoms or clusters of metals, semiconductors, refractory elements, and molecules or atoms of gaseous substances are produced by doping a carrier gas with molecular gases. For example, metal carbide clusters are produced by evaporating metal targets (usually of transition metals, such as titanium, vanadium, or zirconium) in a gas flow containing hydrocarbons (methane, acetylene) [205, 206]. Oxygen doping (2-4%) of a gaseous mixture is a method with which to obtain clusters containing metal oxides [205, 206]. Mixed molecular clusters containing metal atoms and molecules (e.g., CO, NO, CO₂, H₂O, C₂H₂) are generated by evaporating the meal samples in a carrier gas flow with a small (2-5%) amount of the respective molecular gas [178, 203-206].

2.3 Formation of mixed and tagged clusters as a result of cluster trapping of atoms and molecules

Mixed and tagged (doped) molecular and atomic-molecular clusters can also be generated by taking advantage of their ability to capture molecules and atoms. This method, first proposed by Scoles and co-workers [207, 208], finds wide application in cluster spectroscopy and other studies with molecular and cluster beams [1–3]. It is frequently called the method of cluster doping with molecules and atoms. In this method, the cluster beam to be doped with the desired molecules or atoms is crossed by a beam (frequently an effusion beam) of these molecules (atoms) or passed through a cell (5–10 cm in length) containing a rarefied gas ($\sim 10^{-3} - 10^{-5}$ Torr) of these particles. Since the clusters in the beam have a rather low temperature, the molecules and atoms with which they collide become trapped and go off with the beam. The trapping is accompanied by the captured

particle momentum and energy transfer onto clusters (see Section 3.2). This method is widely applied in doping molecular clusters and complexes with atoms and molecules (see Sections 5.1 and 5.2), in putting tags on clusters, and in doping helium nanodroplets [50–53, 190].

3. Methods for size-selecting clusters

In many experiments designed to study the physical and chemical properties of clusters (structure, spectra, stability, state, internal dynamics), as well as their interaction with particles or radiation, it is convenient to exploit clusters of a given size and obtain information regarding exactly these clusters. At the same time, size-selecting clusters by means of their ionization and subsequent separation in a mass spectrometer according to masses encounters difficulty due to cluster fragmentation [209]. This is especially true of systems with van der Waals, hydrogen or ionic bonds, in which interaction potentials for neutral and ionized particles are vastly shifted relative to each other. As a result, ionization can be associated with highly excited vibrational states responsible for cluster fragmentation (evaporation) [27].

Extraction of clusters of a given size from a beam remains in the general case an unresolved problem. Therefore, special experiments are needed to separate clusters by size (mass). There are a few methods for cluster selection according to their sizes. Some of them allow clusters to be separated prior to detection, whereas others imply separation during detection in a mass spectrometer.

3.1 Mass spectrometry

Isolation of clusters of a definite size generated in a beam under conditions of their wide distribution by size is a sufficiently difficult task. Clusters of a desired size can be extracted from the beam with the use of a transmission quadrupole mass spectrometer. Cluster ions passed through the spectrometer are then neutralized, if appropriate, in a cell for the charge exchange and used in further experiments, e.g., to study their interaction with atoms or laser radiation. Therefore, two quadrupole mass spectrometers are employed in certain experiments [210, 211]: one to extract clusters of a given size from the beam, the other to detect them, their fragments, or reaction products resulting from interaction between particles and laser radiation. By way of example, the method in question was applied in Refs [210, 211] to measure the temperature and melting heat of aluminum clusters containing 49-63 [210] and 63-83 [211] particles.

3.2 Size-selecting clusters by atomic beam diffraction

The possibility of size-selecting smaller clusters was postulated in Refs [212, 213]. This method is based on the transfer of angular momentum from an atom to a cluster upon their single collision. Such a method is usually realized in crossed atomic and cluster beams. Clusters scattered by an atomic beam are deflected by different angles θ in accordance with the relation

$$\tan \theta = \frac{\sin \alpha}{m_1 v_1 / m_2 v_2 + \cos \alpha}, \qquad (3.1)$$

where m_1 , m_2 and v_1 , v_2 are the masses and velocities of clusters and atoms in the beams, respectively, and α is the angle between the cluster and atomic beams.

However, the method has limitations arising from angular resolution problems [214] that reduce its application only to smaller clusters (e.g., $(H_2O)_n$ clusters, having the size $n \le 12-13$ [215]).

3.3 Attachment of chromophore molecules to clusters

Another approach to cluster selection proposed and implemented in Refs [216–218] consists in the attachment to the clusters of an aromatic chromophore molecule with a relatively low ionization energy ($\leq 7-8$ eV), which is ionized by resonant two-photon and two-frequency excitation at a laser wavelength sparing the clusters fragmentation [216–218]. Relevant electronic transitions need to occur in the chromophore molecule for the method to be realized.

Its disadvantage consists in the fact that it is applicable only to clusters of approximately the same size as in the method based on cluster deflection by atoms. Moreover, the molecule attached to a cluster tends to interact with it and cause its perturbation. A different technique of putting tags on clusters is reported in Ref. [219] where absorption spectra of neutral and negatively charged water clusters were studied based on argon atoms-mediated soft electron trapping by neutral clusters.

3.4 Doping clusters with low-ionization energy atoms

A new method for the measurement of IR spectra of totally mass-separated clusters was proposed in Ref. [215] when studying water clusters. The method imposes no limitation whatever upon the cluster size and can be applied to elucidate the size distribution of clusters and for spectroscopy of any weakly bound complexes. The method is based on doping clusters with single Na atoms having a low ionization energy (5.14 eV) and their subsequent ionization by a single laser photon [220, 221] (Fig. 3). Cluster excitation to a state lying near ionization threshold gives rise to ionization of clusters practically without their fragmentation, because the potential curves for neutral metal atoms and ions are virtually identical and unshifted relative to each other.

This method was utilized to study ammonia and water clusters [220], as well as clusters of inert gases (argon, krypton, and xenon) [221]. Due to a low ionization energy of sodium clusters (even smaller in complexes with water and ammonia clusters than that of a free atom), intracluster molecules and atoms avoid ionization, despite their much higher ionization potentials. As a result, the cluster beam will contain singly ionized clusters of various sizes that are readily separated in a beam-detecting mass spectrometer.

4. Experimental methods

for investigations into IR dissociation and fragmentation of van der Waals molecules and molecular clusters

4.1 Processes behind the study methods

Van der Waals molecules are referred to as the bound states of a small number of atoms and/or molecules resulting from a weak long-range (van der Waals, hydrogen, or ionic) interaction. Systems including many such particles are termed clusters and sometimes van der Waals molecular complexes (systems).

Van der Waals molecules and molecular clusters have energies of van der Waals and hydrogen bonds much lower



Figure 3. (a) Schematic representation of the mechanism behind IR pumping–UV probing of clusters doped with low-ionization energy atoms (sodium) used for size-selecting clusters. IP—atomic ionization potential [215]. (b) Signals in the absence and presence of IR excitation of clusters. Left scale — the number of ionized particles with and without IR excitation of clusters. Right scale (dashed line)—difference signal expressed in percent [215].

than the energies of chemical bonds in clusters of monomeric molecules ($E_b \approx 3-5$ eV [222]). The difference between binding energies is so conspicuous that vibrational quanta energies conditioned by chemical bonds linking molecules-monomers exceeds the weak bond dissociation energy. For example, the binding (dissociation) energy E_b of van der Waals molecules formed by polyatomic molecules ranges between 0.1–0.5 eV [223–225], while the dissociation energy of van der Waals molecules composed of a polyatomic molecule and a noble gas atom is $E_b \leq 0.1$ eV [223–225]. As a result, such molecules exhibit metastable state properties in the case of vibrational excitation of a single monomer.

Assuming that the vibrationally excited state of a monomer is related to its ground state via the intramolecular potential, a vibrationally excited van der Waals molecule (cluster) must dissociate. IR vibrational predissociation of the molecule or the cluster takes place. In other words, absorption of one or several IR radiation quanta with a wavelength of $3-10 \,\mu\text{m}$ by an intracluster molecule results in weak bond dissociation. It is this property of van der Waals molecules and molecular clusters that provides the basis for the methods invoked to study their properties, such as structure, spectra, internal dynamics, dissociation and fragmentation processes [28, 32, 33, 36, 223–225] (see Sections 5–7).

4.2 The study methods

Experiments are carried out with the employment of cluster beams. Molecules inside the clusters are vibrationally excited by IR radiation of a CO₂-laser (in the wavelength range $\lambda \approx 9-11 \mu$ m), a CO laser ($\lambda \approx 5-6.5 \mu$ m), or an optical parametric generator (oscillator) operated in the wavelength range $\lambda \approx 2-5 \mu$ m. Sometimes, the second harmonic of CO₂-laser radiation ($\lambda \approx 4.5-5.5 \mu$ m) or diode laser radiation is used as well.

The methods developed for studying cluster dissociation and fragmentation are, in essence, as follows. Vibrational excitation of intracluster molecules by IR laser irradiation leads to cluster dissociation or fragmentation. In the course of cluster dissociation due to a contribution from recoil processes, the fragments (monomers) escape from the beam (Fig. 4) and become distributed in the laboratory reference frame within a rather large solid angle determined by their mass and velocity, whereas intact clusters remain in the beam. Observation of a molecular cluster beam with a mass spectrometer, bolometer, or pyroelectric sensor reveals its depletion of excitable particles. On this account, this method is frequently referred to as molecular beam depletion spectroscopy (MBDS).

The possibility of detecting IR vibrational predissociation of clusters from the decay of a cluster beam signal was predicted by Klemperer [226]. Scoles et al. were the first to apply this technique in experiment [227]. It can also be exploited to study molecular dissociation in a beam.

IR laser induction of cluster dissociation and fragmentation in a beam makes up the basis for two other methods, viz. IR laser photodissociation spectroscopy (IRLPDS) and IR laser photofragment spectroscopy (IRLPFS). The employment of a bolometer or pyroelectric sensor as a beam detector makes it possible to measure the energy of



Figure 4. (a) Layout of the experimental setup for IR laser molecular (cluster) beam depletion spectroscopy (IRLMBDS). The detector is installed on the beam axis ($\theta = 0$) to measure beam depletion (signal attenuation) associated with cluster (molecule) fragmentation by laser irradiation and fragment fly out from the beam. This is the basic scheme behind IR photodissociation spectroscopy of clusters [33]. (b) Layout of the experimental setup for IR laser photofragment spectroscopy (IRLPFS). The detector mounted outside the beam axis ($2^{\circ} \leq \theta \leq 4^{\circ}$) measures laser-induced dissociation products responsible for signal amplification [33].



Figure 5. Layout of the experimental setup for the study of laser IR and UV fragmentation of homogeneous and heterogeneous molecular clusters [167, 172]; SEM — secondary electron multiplier.

incoming particles but does not allow identifying them. Beam depletion resulting from cluster dissociation is determined from signal decay. The use of a quadrupole or timeof-flight mass spectrometer for the purpose of detection not only reveals beam depletion of concrete particles but also permits measuring the particle time-of-flight spectra in the beam, identifying constituent particles, and analyzing beam composition before and after laser irradiation. In the method of IR laser photofragment spectroscopy, the mass spectrometer is frequently set at an angle to the cluster beam to selectively detect fragments (Fig. 4b). In this case, the spectrometer records signal enhancement associated with cluster dissociation in the beam.

Ionization of clusters and molecules or atoms in mass spectrometers is induced by either an electron beam or UV laser radiation. To prevent strong fragmentation of the clusters or molecules by UV radiation, the resonance enhanced multiphoton ionization (REMPI) technique is employed [228, 229]. This method, in combination with making use of a time-of-flight mass spectrometer (TOFMS), provides a very sensitive selective tool for detecting molecular and cluster beams.

Figure 5 presents a schematic of an experimental setup for the study of laser IR- and UV-induced dissociation and fragmentation of molecules and molecular clusters described in Refs [167–169, 171–173] and considered in Section 6. The setup was exploited to excite molecules and clusters in a beam by IR irradiation of particles along and across the beam axis. To ionize beam molecules and clusters in the mass spectrometer, the authors used wavelength-tunable UV radiation in the 215–240-nm spectral range of the second harmonic of an excimer XeCl laser-pumped dye laser (generation wavelength $\lambda = 308$ nm), which enabled them to study the parameters of the molecules and molecular clusters, measure particle velocities, obtain time-of-flight spectra of the molecules and clusters, and observe their dissociation and fragmentation induced by IR and UV laser pulses [167-169, 171-173] (see Section 6).

5. IR laser photodissociation spectroscopy of molecular clusters and atomic-molecular complexes

5.1 Early experiments.

Estimates of the lifetime of molecular complexes from IR vibrational predissociation spectra

IR vibrational predissociation of van der Waals molecular clusters was observed for the first time in Ref. [227] in connection with $(N_2O)_2$ dimer excitation near the v_3 vibrational mode of the N_2O molecule by radiation of a tunable diode laser. Photodissociation of van der Waals C_2H_4 complexes with He, Ar, Kr, C_2H_4 , C_2F_4 , and larger ones was studied in Refs [230, 231], where they were excited by continuous radiation of a CO₂-laser near the v_7 vibrational mode of the C_2H_4 molecule. It was shown that the shape and the width of predissociation spectral bands are consistent with the mechanism of their homogeneous broadening due to complex dissociation. For ethylene complexes studied, predissociation lifetimes corresponding to the spectra were found to fall into a range from 0.3 to 1 ps.

In molecular cluster experiments, much attention was given to the excess excitation energy distribution over dissociation fragments [232, 233]. Many later studies involved measuring IR absorption spectra of clusters by tunable IR lasers with the use of molecular beam depletion spectroscopy (MBDS) [32, 36, 223-225]. The spectra thus obtained were analyzed in terms of the cluster spatial structure [234-236]. Moreover, IR photodissociation spectra were used to derive information about intracluster dynamics, including the cluster decay rate, based on data on spectral width and the displacement of spectra relative to free molecule spectra [225, 234]. Relatively simple HF (DF) dimer- and trimer-based systems [237, 238] were studied with special reference to complexes of these molecules with noble gases [239, 240]. The lifetimes of dimers with respect to decay varied roughly from 0.5 to 30 ns [240]. More complex systems, e.g., polyatomic molecular clusters such as C₂H₄, CH₃OH, and N₂H₄ were examined, too [225, 241]. The lifetimes of these systems ranged from $\sim 10^{-6}$ to 10^{-12} s.

It is worthwhile to note that the interpretation of the results of spectral measurements for estimating the lifetime of excited complexes causes controversy arising from the difficulty of temporal information retrieval from spectral measurements, when the nature of line broadening and/or the contribution of various mechanisms to the homogeneous constituent of this line width are unknown. In the case of polyatomic molecular clusters, the contribution to the homogeneous width may come from a number of processes including intramolecular vibrational relaxation (IVR-1) in an excited 'chromophore' molecule, energy relaxation from the latter to the cluster intermolecular vibrations—intracluster vibrational relaxation (IVR-2), and vibrational predissociation (VP) of the cluster. A conclusion as regards vibrational predissociation lifetimes can be drawn only for simple clusters with the well-resolved rotational structure, based on the measured line widths. Measurements of both the line width (fluorescence excitation) [242] and predissociation lifetimes [243] were performed for the dimethyl-tetrazine (DMT)₂ dimer ($[C_2N_4(CH_3)_2]_2$). The intracluster vibrational relaxation lifetime was estimated to be 66 ± 22 ps from the measurements of the line width [242], and 35 ± 10 ps from direct measurement of the relaxation lifetime [243]. These

results are in reasonable agreement. However, the most reliable method for determining the cluster fragmentation rate is direct measurement of cluster kinetics from the decay of the clusters themselves and/or the emergence of disintegration products (free particles). This approach was employed in experiments considered in Section 7.

5.2 Certain results of investigations into IR photodissociation spectra and the molecular complex structure

IR photodissociation and photofragment spectroscopies provide copious valuable information on the composition and structure of molecular clusters and complexes [28, 32, 33, 225, 234, 244–249], bond strengths [250, 251], energy relaxation channels [250, 251], stable configurations and coordination numbers of the complexes [251], cluster and complex fragmentation channels [252], influence of the environment on their fragmentation [253], photofragmentation spectra [165, 254], and energy distribution in the resulting fragments [168, 255]. Specifically, the number of IR-active bands and their relative intensity and frequency location contain information about the structure and bonding nature in complexes consisting of metal cations and a carbonyl group, e.g., $M(CO)_n^+$ (M = Ti, Zr, Hf; n = 6-8) [256].

IR photodissociation spectra permit us to examine phase transitions in large clusters [33, 257–261]. Let us consider this issue by the examples of water and methanol clusters, as well as complexes of metal cations with molecules and molecular ligands.

5.2.1 IR photodissociation spectroscopy of water and methanol clusters. Water clusters are of special interest, bearing in mind that water is fundamental to life on Earth. Clusters of water and methanol are equally interesting in the context of atmospheric research and astrophysics. Both are the most widely used solvents. Their structure and dynamic properties were studied by IR photodissociation and photofragment spectroscopies in numerous papers [32, 33, 244–246, 257–262]. The data obtained are paramount for the elucidation of water properties in the liquid and solid states, as well as the characteristics of water and methanol as solvents.

Buck and Huisken [33] report the results of research on size-selected water and methanol clusters containing from n = 2 to n = 10 and from n = 2 to n = 9 particles, respectively. These data were obtained for both free clusters and those inside or on the surface of argon clusters [33, 245], as well as for clusters inserted into superfluid helium nanodroplets [33, 246].

Experiments with clusters of a definite size yield more extensive and detailed information than those using sizedistributed clusters. Moreover, work with size-matched clusters facilitates theoretical calculations and comparisons of its results with experimental data.

The main objective of cluster IR photodissociation research, according to paper [33], is to address the following issues: how do photodissociation spectra and their frequency shifts relate to the cluster structure? How do the internal dynamics of clusters depend on the excitable mode? What is the difference, if any, between photodissociation of free clusters and those inside or on the surface of other clusters? What are the causes behind the difference? The answers to these questions can be found in the aforementioned studies, including those considered in the present review.



Figure 6. (Color online.) (a) Observed 'depletion' spectra of size-selected water clusters containing from 7 to 10 molecules excited in the O–H bond valent vibrational frequency range [33, 264, 265]. Top: cluster distribution over size from n = 10 to n = 20 [33, 266]. Green color denotes the region on the frequency axis in which the parametric oscillator was not operated to excite clusters [33]. Spectra obtained for free $(H_2O)_n$ clusters (b) and small water polymers inserted into large helium clusters (c) [33, 246].

In Refs [32, 33], homogeneous $(H_2O)_n$ and $(CH_3OH)_n$ clusters were generated by supersonic expansion of a 5–20% mixture of these molecules with helium through an opening 100 µm in diameter of a conical nozzle at a fixed temperature of 273–373 K under a total pressure of 2 atm. Vibrational excitation of intracluster molecules was effected by a frequency-tunable (in the 1020–1090 cm⁻¹ range) CO₂-laser or an Nd:YAG laser-pumped optical parametric oscillator (OPO) tunable within the frequency range of 2800–3800 cm⁻¹. Clusters were size-selected by means of their deflection under the effect of helium atoms in crossed beams (see Section 3.2). The collinear scheme of cluster excitation in a beam was realized for the purpose (Fig. 4a).

IR radiation excited vibrations in symmetric (v₁, frequency 3657.05 cm⁻¹) and asymmetric (v₁, 3755.97 cm⁻¹) O-H bonds of water molecules [263], and O-H (v, 3680.5 cm⁻¹) and C-O (v, 1033.5 cm⁻¹) bonds in CH₃OH molecules [247]. In clusters, these absorption bands were shifted to the red side of the spectrum with respect to those of free molecules [33]. IR photodissociation spectra were obtained for water clusters of a given size (from n = 2 to n = 10) in [264, 265], and for larger clusters in paper [266]

(Fig. 6a). Experimental findings were compared with theoretical ones, and the structure of the clusters was determined in Ref. [267]. Water dimers were shown to have a linear structure, while clusters containing n = 3-5 particles were cyclic and those with n = 7-10 had a three-dimensional cellular structure [33].

Studies with small water clusters formed upon the trapping of water molecules by argon clusters (mean size n = 50) showed that water clusters are located on the surface rather than inside argon clusters [33, 245, 268]. This inference is based on the fact that the O-H bond vibrational frequency shift in surface water clusters with respect to that in free molecules is less pronounced than inside the argon matrix. Water clusters inside helium nanodroplets have very narrow IR photodissociation spectra (Fig. 6c) [33, 246] attributable to low droplet temperature (T = 0.38 K) [50–53, 190] compared with roughly 80 K in a beam [33], and a small red shift of absorption bands (IR photodissociation) as a result of a rather low binding energy between water clusters and the surrounding helium atoms.

IR photodissociation spectra of free $(CH_3OH)_n$ clusters containing from n = 2 to n = 9 particles were obtained in



Figure 7. (a) Evolution of IR spectra of size-selected $(H_2O)_n$ clusters composed of 85–475 particles. The spectra are averaged over 10 cluster sizes (for n = 85 and n = 95), 25 sizes (n = 113 and n = 137), 50 sizes (n = 175), and larger sizes including n = 475. Clusters were generated by supersonic expansion of water vapors (40%) mixed with helium under a total pressure above nozzle of 3.9 ± 0.1 atm. Cluster photoionization was performed at a wavelength of 390 nm [257]. (b) Comparison of calculated and measured IR spectra of water clusters (n = 600 [273] and $n = 475 \pm 25$ [257], respectively).

Refs [269–271] under conditions of vibrational excitation of O-H and C-O bonds in methanol molecules. The shifts of their absorption bands were detected and compared with those of free molecules. Photodissociation spectra and the configurations of clusters were calculated [249]. It was established using data on the observed and theoretical spectra and the model potential that all the studied clusters barring dimers with a linear chain structure, had minimumenergy cyclic configurations.

Cluster doping with sodium atoms characterized by low ionization energy [215] (see Section 3.4) provided a basis for elucidating the structure and properties of large water clusters [215, 257-261, 272, 273]. In Ref. [272], O-H band vibrational spectra in large water clusters were measured by photofragment spectroscopy making use of tunable (in the 3000-3800 cm⁻¹ frequency range) pulsed laser radiation. The mean cluster size ranging from n = 20 to n = 1960 was determined by means of threshold (soft) ionization of doped clusters [215]. The dependence of fragment composition and intensity on the cluster size was measured at different excitation energies and temperatures of the clusters. It was shown that fragmentation of large clusters yields many more hexamers than pentamers and tetramers. The number of hexamers in the products increases with cluster size up to n = 70, but begins to decrease as it continues to grow up to n = 300. Such behavior is due to the relationship between the cluster size and the number of interconnected 3-coordinated molecules in water clusters, needed for hexamers to form. The formation of large fragments is in contrast to fragment distribution observed for many other clusters whose fragmentation results from successive evaporation of their molecules (see Sections 6 and 7).

One of the most interesting and important problems in cluster research consists in determining the size at which phase transition occurs. Such knowledge in regard to water clusters would allow the nature of hydrogen bonds responsible for the macroscopic properties of water to be clarified. It was believed that the number of water molecules necessary for the preparation of the smallest possible ice crystals is all but impossible to determine in experiment. The authors of

Ref. [257] obtained, utilizing sodium-doped water clusters, IR absorption spectra of size-selected $(H_2O)_n$ clusters containing from 85 to 475 particles by IR radiationmodulated photoionization spectroscopy, as described in Ref. [215] (see Section 3.4 and Fig. 3). This study was the first to demonstrate characteristic spectral features indicating the onset of crystallization of clusters with $n = 275 \pm 25$; for clusters with $n = 475 \pm 25$, the well-known ice crystal band at a frequency of 3200 cm⁻¹ became predominant in the vibrational O-H stretch spectrum (Fig. 7). The absorption peak in the O-H vibrational spectrum at 3200 cm⁻¹ was especially apparent in large water clusters of a mean size from $n = 10^3$ to $n = 10^5$ [273]. To recall, electron diffraction experiments [274] allowed the size of water clusters at which transition between amorphous and crystalline states occurred to be determined; such a transition was deemed possible "somewhere between n = 200 and n = 1000" [33].

The water crystallization process depends on cluster temperature [259]. Surprisingly, crystallization at high temperatures begins when n < 200, and at low temperatures when n > 400. The structure and stability of water cluster isomers consisting of appr. 20 particles were deduced from IR absorption spectra in the vibrational O-H stretch region [260]. It was shown that $(H_2O)_{20}$ clusters exist, in agreement with the theoretical prediction, as two different highly stable isomers: one in the form of a droplet-like structure with perfectly coordinated inner molecules, and the other being an angled structure resembling a pentagonal prism with all the molecules located on the cluster surface. Structural transitions in size-selected water clusters with n = 10 - 125were studied in Ref. [261]. The spectral structure suggested the formation of perfectly coordinated water molecules inside a cluster. It was shown that structural transitions are activated in clusters containing from 40 to 65 particles, with structural changes taking place largely among surface water molecules, i.e. on the cluster surface.

5.2.2 IR photodissociation spectroscopy of molecular complexes containing metal ions. IR photodissociation and photofragment spectroscopies, in combination with theoretical calculations of spectra by the density functional method, are extensively used in research on the structure, nature, and bond energies, as well as coordination numbers of cations in molecular complexes, such as metal carbonyls $[M(CO)_n^+,$ where *M* is the metal atom], and solvation of metal cations $(M^+(H_2O)_n)$ [178, 250, 251, 275]. Simultaneously, fragmentation and energy relaxation channels are investigated in laser-excited complexes. Such studies attract interest because metal carbonyls find wide application as catalytic agents in the chemical industry [276]. Transition metal carbonyls are a classical example of metallic linkage in organic and inorganic chemistry [276–280]. Solvatation of metal cations by water is a fundamental process in the chemistry of aqueous solutions [281].

The processes involving the above complexes are difficult to interpret at the molecular level based on studies in macroscopic media. Therefore, cluster beams need to be exploited. The binding energy of molecular ligand-metal ion complexes (around 1-2 eV) being much higher than the vibrational quantum energy in the molecules composing the complexes, the latter are tagged by inert gas atoms (mostly those of argon) that are more weakly bound to metal ions and molecules of the complexes. As a result, a decay channel forms, characterized by low vibrational predissociation energy and making it possible to obtain IR-photodissociation spectra of complexes containing vibrationally excited molecules [275, 282].

Complexes are generated in pulsed molecular beams by laser vaporization of metal samples using a nozzle in cutaway configuration (see Section 2.2, Figs 1b and 2). Complexes and their analogs tagged by inert gas atoms, $[M(CO)_n(RG)_m^+]$, where *RG* is the noble gas metal], were studied by massselective IR photodissociation spectroscopy in Refs [178, 275, 282] to measure the number of IR-active bands, their frequency, and their relative intensities. A comparison of the observed and theoretical values provided reliable information about the geometric and electronic structures of the complexes [275, 282].

In all metal-carbonyl complexes, the vibrational frequency of C–O stretch is the main indicator of the nature of the metal–ligand linkage, including the electronic structure and geometric arrangement of their constituent particles [178, 275, 282–284]. This frequency (2143 cm⁻¹ for a free CO molecule [285]) falls into the region with no other vibrational frequencies. The shift of this vibrational frequency upon the binding of CO molecules to the metal is a sensitive indicator of the type of such an interaction.

Let us consider the results of experimental IR photodissociation of $Co(CO)_n^+$ and $Co(CO)_n^+Ar_m$ complexes reported in Ref. [275] allowing the determination of the coordination number of the $Co(CO)_n^+$ complex and the number of its ligand shells. If the number of ligand molecules in a complex is higher than the coordination number, the internal ligands are bound to metal ions much more strongly than the external ones. The binding energy of the external CO ligands, bound to the internal ones, can be estimated from a comparison with the binding energy of (CO)₂ dimers equaling, according to calculations, $D_0 = 93 \text{ cm}^{-1}$ [286]. The binding energy of external CO molecules in a complex must be in all probability higher than this value, because ligands in the inner shell are polarized as a result of interaction with the metal ion, which must increase the energy of their binding to the external ligands. However, it may be supposed that their binding energy is lower than the IR-photon energy needed to



Figure 8. (a) Mass spectra of the $Co(CO)_n^+$ complex photofragmentation showing fragmentation channels as a result of IR-induced excitation near valent C–O vibrations. Negative peaks correspond to the reduction in mass-selected parent ions resulting from their photofragmentation, and positive ones to the presence of smaller in mass fragments which are formed under these conditions. In each case, a parent ion loses a CO molecule [275]. (b) IR photodissociation spectra of large $Co(CO)_n^+$ complexes detectable by virtue of CO detachment. Two major spectral bands are produced by the $Co(CO)_5^+$ ion core, and 2165–2168-cm⁻¹ bands by external CO molecules unbound from metal [275].

excite C–O bonds (2143 cm⁻¹). Accordingly, vibrational excitation of the C–O bonds in mass-selected large complexes containing 7–9 ligands causes effective photodissociation and the loss of external CO molecules [275, 282].

Results of a so-called breakdown experiment are presented in Fig. 8a in which a series of mass-spectrometer tracks illustrates the fragmentation of $\text{Co}(\text{CO})_n^+$ complexes with n = 5-9 [275, 282]. These data obtained by computerassisted treatment of the measured mass spectra include parent ions undergoing fragmentation (negative peaks) and resultant fragments (positive peaks). The complex with n = 5is characterized by relatively low fragmentation efficiency and loses only one CO ligand. All larger complexes lose one or more ligands, with $\text{Co}(\text{CO})_5^+$ being the smallest fragment in all the cases. This final point in the process of complex fragmentation attributable to the elimination of external weakly bound CO molecules indicates that the strongly bound perfectly coordinated $\text{Co}(\text{CO})_5^+$ ion forms the central nucleus of the complex. The structure of an 18-electron $\text{Co}(\text{CO})_5^+$ complex is analogous to the structure of an isoelectron neutral Fe(CO)₅ complex [275, 282].

The absence of fragmentation (stability) of $\text{Co}(\text{CO})_n^+$ complexes with n < 5 is due to the high energy of binding between internal ligands and the metal ion (1.80, 1.58, 0.85, and 0.78 eV for the detachment of the last CO ligand from complexes with n = 1-4, respectively [287]). The dissociation energy of complexes with n = 5 is estimated at 0.78 eV. Its weak dissociation (Fig. 8a) seems to be due to multiphoton absorption.

The frequency dependences of fragmentation of the above $Co(CO)_n^+$ complexes (IR photofragmentation spectra) are illustrated in Fig. 8b. The low fragmentation efficiency accounts for a small peak in the spectrum of the complex with n = 5. All larger clusters undergo much stronger fragmentation and produce intense spectra. Each of the spectra for n = 6-9 exhibits two intense bands with the centers near the vibrational C–O stretch frequency in a free molecule. A much weaker spectral band emerges at 2168 cm⁻¹ for a complex with n = 6; it is also present, even if somewhat shifted, in the spectrum formed during fragmentation of larger clusters. Two intense bands are attributed to IR-active absorption bands of the central $Co(CO)_5^+$ ion [282]; the band in the 2165–2168 cm⁻¹ frequency range refers to the absorption band of external CO molecules.

As is mentioned in the foregoing, $Co(CO)_n^+$ complexes with n < 5 do not contain weakly bound ligands, which accounts for their inefficient fragmentation under the effect of vibrational excitation of C-O bonds. These complexes were tagged by argon atoms to enable investigation of their photodissociation spectra [275, 282], allowing the corresponding $Co(CO)_n Ar_m^+$ ions to be obtained and their IR photodissociation spectra to be measured upon detachment of weakly bound argon atoms from the complexes (Fig. 9). The measured spectra give evidence that in a complex with n = 1 the argon atom was strongly bound, and a complex containing a single argon atom, $Co(CO)_1^+Ar_1$, resisted fragmentation. With this in mind, this complex was tagged by two argon atoms, one of which was detached in the course of experiment. The $Co(CO)_n^+$ complexes with n > 1 singly tagged with an argon atom underwent fragmentation as a result of Ar atom detachment.

Linear complexes with n = 1-2 exhibit one IR-active vibration of the C–O bond with a frequency slightly shifted to the high-frequency side of the spectrum with respect to the vibrational frequency in a free molecule. A complex with n = 3 has a C_{2v} symmetry structure with two overlapping IRactive bands. All the measured spectra of small Co(CO)⁺_n complexes proved to be in excellent agreement with theoretically predicted spectra of the lowest-energy structures [275, 282]. The spectrum of the Co(CO)⁺₅Ar complex shown at the



Figure 9. (Color online.) IR photodissociation spectra of small $Co(CO)_n^+Ar_m$ complexes detectable due to Ar atom detachment. The number of molecules and atoms in a cluster is marked in parentheses. The red dashed line denotes vibrational frequency of free CO molecules in the gaseous phase. The insets show the structure of the respective $Co(CO)_n^+$ complexes deduced based on the density functional theory [275].

top of Fig. 9 exhibits the same two bands as the spectra of complexes with $n \ge 6$; however, $Co(CO)_5^+Ar$ has no ligand in the outer shell, which accounts for the absence of a band in the vicinity of 2168 cm⁻¹ in its spectrum.

To conclude this section, it is worthwhile to note that the results of the above research demonstrate that IR photodissociation spectroscopy and photofragment spectroscopy provide a powerful tool for gaining new insights into the nature of molecular clusters and complexes.

5.3 Application of IR vibrational predissociation of van der Waals molecules for isotope separation

The authors of earlier studies on IR photodissociation spectra of van der Waals complexes emphasized the possibility of isotope-selective dissociation of clusters under the influence of IR irradiation [230, 231, 288–290]. Yuan T Lee, a Nobel Prize laureate in Chemistry 1986, has patented a method for isotope-selective IR vibrational predissociation of van der Waals complexes as a new isotope separation technique [288]. It was later evaluated by many authors as a tool for isotopeselective dissociation of clusters [231, 288–296] and used in research on spectroscopy and the dynamics of weakly bound molecular van der Waals complexes [297–303] (see also reviews [32, 223–225, 304] and references cited therein).

Spectroscopic investigations of small molecular van der Waals complexes [223–225, 290, 297–299] have demonstrated that absorption spectra of dimers and small clusters (both homogeneous and heterogeneous) can sometimes be much narrower than those of unclustered (free) molecules and appear as rather narrow bands localized near vibrational frequencies of monomeric intracluster molecules [231, 297, 299]. This opens up the possibility of selectively exciting and dissociating clusters (especially dimers) containing the isotopomers of interest and thereby separating isotopes. Cluster dissociation by this method due to a contribution from recoil processes is accompanied by fragment (monomer) escape from the beam.

In the laboratory coordinate system, the targeted molecules (dissociation products) propagate within a relatively large solid angle determined by their mass and velocity, while the nontargeted ones remain in the near-axis area of the cluster beam. Detection of a molecular/cluster beam with the aid of a mass spectrometer or a pyroelectric sensor reveals a depletion of excitable (targeted) molecules.

The applicability of IR vibrational predissociation of van der Waals molecules to isotope separation was evaluated in Refs [291–294] using $(SF_6)_n Ar_m$ complexes (where $1 \le n \le 3$, $1 \le m \le 9$). These complexes formed in a free jet upon the expansion of an SF₆-argon atom mixture through a 0.1-mm nozzle at an SF_6 partial pressure 0.5%. The studies have demonstrated isotope selectivity of the complex dissociation process. In a natural mixture of SF₆ isotopomers in argon irradiated with a 20-W continuous wave CO₂-laser [291, 294], the enrichment coefficients for ${}^{i}SF_{6}$ (i = 32, 34) exceeded $K_{\rm enr} \approx 1.2$ [291]. The value of $K_{\rm enr} \approx 1.2$ means that the concentration of ³⁴SF₆ molecules in a mixture of molecules after laser irradiation (in products) was roughly 1.2 times that in the natural mixture of isotopomers [304]. The enrichment factors were shown to depend on the laser radiation frequency. A beam can be either rich in or depleted of isotopomers by varying the radiation wavelength.

To efficiently separate isotopes by IR vibrational predissociation of van der Waals clusters in a free jet, the beam must contain a large enough fraction of these particles. In principle, this condition can be fulfilled by maintaining high pressure p_0 and low temperature T_0 over the nozzle. But clusters [in this case, $(SF_6)_n Ar_m$] become increasingly more widely distributed by size as their number increases. All these clusters have different IR absorption spectra [223, 291, 297, 298], which accounts for a very complicated dependence of isotope enrichment on the radiation wavelength: $({}^{i}SF_{6})_{n}Ar_{m}$ clusters of different sizes can dissociate at each of the given wavelengths, thereby contributing to beam enrichment or depletion of concrete isotopomers. The possibility of applying IR vibrational predissociation of van der Waals clusters to the separation of uranium isotopes was considered in Ref. [296] (see also review [304]).

It should be noted that the method in question does not require high energy density to dissociate molecules, unlike the isotope-selective IR multiphoton dissociation technique [305, 306] characterized by relatively high energy capacity due to the high dissociation energy ($E_D \ge 3-5 \text{ eV}$) of molecules and requiring high energy density of laser radiation for molecular dissociation ($\Phi_{IR} \ge 4-5 \text{ J cm}^{-2}$). The method can be realized using continuous wave lasers and possibly in combination with a selective control of molecular clusterization in gasdynamically cooled jets and flows [291, 294, 304]. It provides an approach to the development of low-energy laser-assisted molecular isotope separation techniques (with the activation energy of the process $E_a \leq 0.5-1$ eV) [296, 304].

6. Fragmentation of molecular clusters by intense IR radiation

The fragmentation of molecular clusters by intense IR laser pulses was investigated in Refs [167-172]. In contrast to experiments considered in Section 5, the authors of these studies experimented with size-distributed clusters instead of size-matched ones. The mean size of clusters in beams varied from a few dozen to hundreds of molecules (atoms), depending on the objectives of concrete investigations designed to elucidate spectral and photophysical properties of the clusters [167, 168], the mechanisms and dynamics of their fragmentation, vibrational overexcitation [168,170], the role of energy input and relaxation channels in cluster fragmentation [169, 171, 172], the influence of the environment on this process [171, 172], and elaboration of theoretical models for the description of experimental results [167, 168, 170]. Other important objectives of the research included determining lifetimes of excited clusters versus their decay and observing nonstatistical dissociation and explosive disintegration of the clusters with the aid of short laser pulses [170].

The above-mentioned studies were carried out with the use of pulsed molecular/cluster beams. Cooled clusters were generated under conditions of supersonic expansion of a mixture of the molecules of interest with a carrier gas (Ar, Xe) at the nozzle outlet (see Section 2.1). Resonant vibrational excitation of intracluster molecules was induced by intense pulses from a CO₂-laser [167-169, 171, 172] or its second harmonic [169] or an optical parametric generator [170]. Clusters and fragmentation products were detected using resonance enhanced multiphoton ionization (REMPI) of the particles by UV laser radiation with a time-of-flight photoionization mass spectrometer (see Fig. 5). Most of the above studies [167-169, 171, 172] investigated fragmentation of iodine-containing molecular clusters, because the production of iodine molecular ions under the effect of UV multiphoton excitations [167, 168] facilitated the determination of cluster concentration in the beams.

6.1 Character and efficiency of IR fragmentation of homogeneous clusters

The character and efficiency of IR-induced fragmentation of homogeneous molecular clusters will be considered as exemplified by $(CF_3I)_n$ and $(IF_2CCOF)_n$ complexes (see Section 6.2). Laser UV ionization and IR photodissociation of $(CF_3I)_n$ clusters was studied in Refs [167, 168]. The clusters were generated in a gas mixture of CF_3I :Ar (1:15). Their mean size depended on gas pressure over the nozzle and varied from n = 50 to n = 120 at 3–4.6 atm [167].

It was established that UV multiphoton ionization of these clusters using an excimer XeCl-laser ($\lambda = 308$ nm) with intensity $I_{\rm UV} \ge 1.2 \times 10^8$ W cm⁻² caused their fragmentation, with the formation of I₂⁺ and I⁺ ions, the molecular I₂⁺ ions being precursors of I⁺ ions. Based on the data obtained in these studies, the authors arrived at the conclusion that the I₂⁺ ion is the primary product of the photochemical reactions inside a cluster undergoing UV multiphoton ionization, whereas the atomic I⁺ ion results from UV photodissocia-



Figure 10. IR photofragmentation of $(CF_3I)_n$ clusters. Dependences of ionic signal $S(I_2^+)$ on energy density of pumping CO₂-laser radiation at different CF₃I gas pressures above the nozzle (i.e., for different cluster sizes). Experimental data are marked with different symbols. The curves represent results of approximation of experimental data by function (6.1) [167].

tion of the molecular I_2^+ ion. Formation of the I_2^+ molecular ion peak under UV multiphoton ionization of iodine-containing molecular clusters makes possible the study of their fragmentation using this ion peak as a marker [167–169, 171, 172].

An evaluation of the dependences of the character and effectiveness of cluster IR dissociation on energy density and frequency of CO₂-laser radiation (at a pulse length of about 10^{-7} s) exciting a v₁ (1075 cm⁻¹ [307]) vibration of cluster-forming CF₃I molecules, as well as the analysis of IR absorption spectra (IR photodissociation) of the clusters, showed that (CF₃I)_n clusters effectively dissociate at IR radiation energy densities Φ_{IR} much lower than the threshold densities necessary for IR multiphoton dissociation of CF₃I molecules themselves (around 0.3–0.4 J cm⁻² [305, 308, 309]). For example, at $\Phi_{IR} = 40$ mJ cm⁻², practically all the clusters, including the largest ones, undergo fragmentation (Fig. 10, curve *I*). The experimental dependences of the ionic signal $S(I_2^+)$ on Φ_{IR} are fairly well described by the exponential function

$$S(I_2^+) = S_0 \exp(-k_0 \Phi_{\rm IR}).$$
(6.1)

The respective fitting curves calculated from relation (6.1) are presented together with the experimental data in Fig. 10. The rate constant of cluster dissociation for all three dependences is $k_0 = 104 \pm 10$ cm² J⁻¹. However, for the largest clusters (curve 1 in Fig. 10), the initial part of the experimental dependence deviates from the exponential law. The deviation is attributable to the dissociation lag observed in Ref. [169] in association with cluster fragmentation by IR radiation (see Section 6.2). For $n \leq 80$, relation (6.1) is fulfilled over the entire range of Φ_{IR} variations. The cluster photodissociation spectrum is much wider than the IR absorption spectrum of CF₃I molecules in a cooled molecular beam [167] and the (CF₃I)₂-dimer photodissociation spectrum. The exponential character of the dependence $S(I_2^+; \Phi_{IR})$ (6.1) suggests that cluster fragmentation is actually a size-diminishing process due to gradual evaporation of cluster's constituent molecules [167]. A similar character of IR photodissociation was



Figure 11. Dependences of flying-apart velocity $V_{M\perp}$ of free CF₃I molecules flying out from excited $(CF_3I)_n$ clusters (a) and cluster dissociation yield β (b) on pumping IR pulse energy density. The value of β was found from the experimental dependence of fragmentation probability of $(CF_3I)_n$ clusters on excitation energy density, analogous to the dependences shown in Fig. 10. (c) Temperature T_{tr} of CF₃I molecules flying apart at different β values. Clusters were generated by expansion of a CF₃I/Ar mixture (1:5) under a total above-nozzle pressure of 1.15 atm. Mean cluster size in the beam is $n \approx 110$ [168].

observed in experiment [235] utilizing the size-selected molecular clusters.

Paper [168] reports on adapting the technique of a free CF_3I molecule detection by the CF_3^+ ion fragment and the time-of-flight method (see Fig. 5) for the measurement of the formation rate constant of the $(CF_3I)_n$ cluster (with a mean size of $n \approx 110$) dissociation products — CF_3I molecules — at various cluster fragmentation degrees (Fig. 11a, b), as well as of their translational temperature T_{tr} (Fig. 11c) reaching approximately 215 K. This also allowed estimating the temperature of disintegratable $(CF_3I)_n$ clusters themselves.

The translational temperature of a particle escaping cluster is assumed to equal temperature T_{tr} of the transition state of a decaying cluster. The latter is somewhat lower than parent cluster temperature T_{cl} prior to decay, because part of its energy is spent on detaching the monomer. According to Ref. [168], the temperature of decaying clusters exceeds the translational temperature of monomers evaporating from them by 10–30%.

Results reported in Refs [167, 168] and their analysis in the framework of the evaporative ensemble model [23, 310] (see also Section 7.3) indicate that $(CF_3I)_n$ cluster decay under

given experimental conditions (excitation rate, IR pulse duration) can be regarded as a stationary or quasistationary process of sequential evaporation of CF_3I molecules accompanying energy absorption by the clusters in excess of the evaporation energy. This process is not associated with an appreciable overexcitation of the clusters. Their estimated lifetime relative to decay is less than 10^{-8} s.

6.2 Role of energy input channels in the process of cluster fragmentation

The role of energy input channels in the process of cluster fragmentation associated with their excitation by intense IR laser pulses was evaluated in Ref. [169] from the dissociation of $(IF_2CCOF)_n$ clusters under the effect of resonant excitation of their constituent IF₂CCOF molecules by 10^{-7} -s pulses. The design of the experiment was described in Section 4 (see Fig. 5). The $(IF_2CCOF)_n$ clusters were generated by means of supersonic expansion during an IF₂CCOF-argon gas mixture (1:5 pressure ratio) outflow from the nozzle, with the total above-nozzle pressure varying from 0.8 to 1.3 atm. Two different cluster excitation channels were used: one via C-F bond vibrations (9.3 µm), and the other via vibrations of the double C=O bonds (5.3 μ m) in chromophore IF₂CCOF molecules. The C-F bond vibrations were excited with a CO_2 -laser radiation, and C=O vibrations by the second harmonic of the same laser radiation, using a nonlinear AgGaSe₂ crystal. UV multiphoton ionization of the clusters was induced by the second harmonic of an excimer XeCl laser-pumped dye laser ($\lambda_{UV} = 232 \text{ nm}$).

IR photodissociation of clusters was investigated by measuring ionic signal I_2^+ proportional to the cluster concentration in the beam. The molecules were exposed to radiation in a mass-spectrometer ionizer, with the laser beam directed towards the cluster beam at a small angle (see Fig. 5). The dependence of the I_2^+ signal on IR radiation energy density Φ_{IR} , $S(I_2^+; \Phi_{IR})$, had two characteristic features (Fig. 12): (1) a dissociation lag, i.e., a cluster dissociationfree region of initial energy densities $0 \le \Phi_{IR} \le \Delta \Phi_{th} (\Delta \Phi_{th})$ for curve I is $\Phi_{01} = 0.02 \text{ J cm}^{-2}$), and (2) cluster dissociation



Figure 12. Fragmentation of $(IF_2CCOF)_n$ clusters by 9-µm (dependence *1*) and 5-µm (dependence *2*) IR radiation; $\lambda_{UV} = 232$ nm. Triangles and diamonds denote experimental dependences of the cluster fragmentation probability on pumping IR radiation energy density, and dashed curves are results of approximation of experimental data by exponential function (6.2) (see the text). Clusters were generated by expansion of an IF₂CCOF/Ar mixture (1:5) under a total above-nozzle pressure of 1.3 atm [169].

for $\Phi_{IR} \ge \Delta \Phi_{th}$ fairly well described by the exponential dependence

$$S(I_2^+; \Phi_{\rm IR}) \sim \exp\left[-k(\Phi_{\rm IR} - \Delta \Phi_{\rm th})\right].$$
 (6.2)

Coefficient k in relation (6.2), i.e., the measure of cluster dissociation efficiency, is $k_1 = 14.9 \text{ cm}^2 \text{ J}^{-1}$ for dependence *I* shown in Fig. 12. The presence of lag (threshold energy density) in $S(I_2^+; \Phi_{IR})$ dependences can be accounted for by the necessity to absorb an energy commensurate with the vaporization energy by a cluster awaiting fragmentation. The absorption brings the cluster to a dissociation threshold, after which its constituent molecules begin to evaporate. Threshold energy density $\Delta \Phi_{th}$ depends on the cluster size, composition, and starting temperature. It is this lag in dependence $S(I_2^+; \Phi_{IR})$ that appears to have been observed in an earlier study [167] of (CF₃I)_n clusters (see dependence *I* in Fig. 10).

Let us compare the results obtained by exciting different vibrational modes of $(IF_2CCOF)_n$ clusters. Dependence 1 in Fig. 12 was derived from cluster excitation through C-F bond vibrations under the effect of CO₂-laser radiation at a frequency of 1084.6 cm⁻¹, and dependence 2 through C=O bond vibrations and second-harmonic irradiation by the same laser at a frequency of 1877.38 cm⁻¹. In the case of dependence 2, threshold energy density was $\Phi_{02} =$ 0.027 J cm⁻² and parameter $k = k_{eff} = 7 \text{ cm}^2 \text{ J}^{-1}$. However, this difference was due to different cluster irradiation conditions [169]. In the case of dependence 1, the lateral size of the laser beam ($d_{1IR} = 6$ mm) exceeded that of the cluster beam ($d_{cl} = 2.44$ m); therefore, IR radiation energy density was homogeneous in the cluster excitation region [169]. In the case of dependence 2, the lateral size of the laser beam $(d_{2IR} = 1.24 \text{ mm})$ was smaller than that of the cluster beam; therefore, energy density values averaged over the spot area were used. The authors re-calculated dependence 2 for homogeneous energy density. The resulting dependence is represented by curve 3 in Fig. 12. For this curve, $\Phi_{02} =$ 0.027 J cm⁻² and parameter $k_{02} = 11.5$ cm² J⁻¹. These values are comparable to those for curve 1.

These results were interpreted in the framework of the phenomenological model elaborated by the authors based on the data reported by Gspann [310, 311] and Klots [312, 313] (see also reviews [56, 314]) and on the evaporative ensemble concept regarding cluster dissociation as a quasistationary process of successive evaporation of molecules induced by heating clusters with resonant IR radiation. It follows from Refs [310–313] that the expression for the evaporation rate constant has the form

$$k_{\rm ev} = A \exp\left(-\frac{\Delta E}{k_{\rm B}T_{\rm cl}}\right),\tag{6.3}$$

where A is a constant, ΔE is the energy needed to evaporate a single particle, $T_{\rm cl}$ is the cluster temperature deducible from relation $k_{\rm B}T_{\rm cl} \approx \Delta E_{\rm ev}/G$, and G is the dimensionless Gspann parameter practically independent of the material: $G = 23.5 \pm 1.5$ [313]. In the case of $(\rm IF_2CCOF)_n$ clusters, $\Delta E = 0.36$ eV and estimated evaporation temperature $T_{\rm cl} \approx 190$ K. The initial cluster temperature in the beam of mean size n = 50 was $T_0 \approx 40$ K [169].

The excellent agreement between the model and experimental data enabled the authors to conclude that all intracluster relaxation processes, including monomolecular decay, occur for less than 10^{-7} s. Cluster IR dissociation is a stationary (or quasistationary) process of successive evaporation of molecules from the cluster. Nonstationary processes in cluster dynamics, including those allowing one to evaluate the role of energy input channels in cluster relaxation and fragmentation, can only be observed when they are excited by pico- and femtosecond laser pulses. Such processes are considered in greater detail in Section 7.

6.3 Influence of cluster environment

and energy relaxation channels on cluster fragmentation

Problems pertaining to the influence of environment and energy relaxation channels on cluster fragmentation have been addressed in Refs [171, 172] with reference to fragmentation of free homogeneous clusters $(CF_3I)_n$ in a molecular beam (mean number of molecules per cluster is $n \le 45$) and $(CF_3I)_n$ clusters residing inside or on the surface of larger Xe_m clusters with a mean number of atoms $m \ge 100$, which were subjected to IR laser radiation. Clusters $(CF_3I)_n$ of these three types were found to differ in resistance to fragmentation and as regards the dependence of the fragmentation probability on radiation energy. The methods employed in these studies and their results are briefly discussed below.

6.3.1 Certain details of experiments and methods. The experimental setup included a source of a pulsed molecular/ cluster beam, time-of-flight mass spectrometer, pulsed CO₂-laser, UV dye laser, and continuous wave CO₂-laser (see Fig. 5). Cluster beams were detected by the UV multiphoton ionization technique [171, 172]. The combination of UV multiphoton ionization and spectrometric beam cluster detection made possible diagnostics of the clusters and analyzing their fragmentation [167–169, 171, 172]. The following methods were employed to produce clusters.

(1) Homogeneous $(CF_3I)_n$ clusters were generated using an impurity-free CF₃I gas or gaseous CF₃I/Ar or CF₃I/Xe mixtures (1:15) above the nozzle to reduce the probability of producing mixed clusters and increase the output of homogeneous (pure) $(CF_3I)_n$ clusters. The carrier gases (Ar, Xe) were needed to achieve deeper cooling during gas expansion and enhance the efficiency of cluster generation for obtaining larger $(CF_3I)_n$ clusters. Their size was possible to control by varying gas pressure above the nozzle. In experiments with CF₃I/Ar mixtures (1:15) and total pressure $p_0 \leq 1$ atm, $(CF_3I)_n$ clusters of the mean size $n \leq 45$ were generated [167, 168]. Cluster excitation by UV laser radiation produced mass spectra dominated by I^+ and I_2^+ ion peaks. It was shown in Refs [167, 168] that the presence of the I_2^+ peak in the mass spectrum is a reliable indicator of the presence of $(CF_3I)_n$ clusters in the beam.

(2) $(CF_3I)_n$ clusters residing inside Xe_m clusters were produced utilizing a rather strongly diluted CF_3I/Xe mixture (1:100) above the nozzle. In this case, the probability of mixed clusters forming markedly increased and $(CF_3I)_nXe_m$ clusters prevailed. Their size was equally amenable to control by varying total above-nozzle pressure. Fragmentation of these clusters by UV radiation produced mass spectra exhibiting rather intense XeI⁺ ion peaks, besides I⁺ and I₂⁺ peaks. The intensity ratio of I₂⁺-to-XeI⁺ peaks (I₂⁺/XeI⁺) was roughly 1/1.

It is worthwhile to note that the condensation temperature $(\sim 100 \text{ K})$ of CF₃I molecules was much higher than that of Xe atoms ($\sim 80 \text{ K}$) [315]. Therefore, in the gas-dynamic cooling of the CF₃I/Xe mixture, CF₃I molecules were the first to aggregate into clusters, on which Xe atoms became con-

densed later. It can therefore be thought that $(CF_3I)_n$ clusters are localized inside Xe_m clusters. This conjecture is also confirmed by the fact that the binding energy of CF_3I molecules in $(CF_3I)_n$ clusters (about 0.36 eV [169]) is much higher than that of Xe atoms in Xe_m clusters (~ 0.16 eV [316]); particles with a higher binding energy, as a rule, occur in the center of a cluster with a lower binding energy of particles [53, 317, 318].

(3) $(CF_3I)_n$ clusters on the surface of Xe_m clusters were generated as a xenon cluster beam passed through a cloud of CF₃I gas preliminarily forced into the analyzer chamber (the region behind the skimmers). The CF₃I cloud was formed by injecting the gas into the chamber through the second pulsed nozzle. Under the proper conditions, the gas became completely thermalized within 15 ms after the injection and a quasistationary pressure of CF₃I molecules was established in the chamber; thereafter, a cluster beam was introduced into the chamber. CF₃I pressure in the cloud varied from 1.5×10^{-4} to 6×10^{-3} Torr, depending on the experimental conditions. The cloud lifetime amounted to a few dozen milliseconds. Xe_m clusters trapped CF₃I molecules as they were passing through the cloud, thus giving rise to heterogeneous $(CF_3I)_n Xe_m$ clusters. Because large clusters of noble gases have a solid structure [23, 319], it can be thought that CF₃I molecules trapped by Xe_m clusters remained on their surface. Subsequent diffusion of CF3I molecules and surface xenon atoms over the Xe_m cluster surface resulted in the formation of $(CF_3I)_n$ clusters. Their fragmentation under the effect of UV radiation gave rise to mass spectra exhibiting intense XeI⁺ ion peaks, besides I⁺ and I₂⁺ peaks. The ratio between intensities of I_2^+ and XeI⁺ peaks (I_2^+/XeI^+) was roughly 1/2.

As regards Xe_m cluster generation, the formation probability of these clusters and their mean size were estimated based on the Hagena parameter [see relation (2.1)]. Under the chosen experimental conditions ($d = 800 \ \mu\text{m}$, $\alpha = 45^{\circ}$, $T_0 = 295 \ \text{K}$, Xe pressure over the nozzle $p_0 = 1 \ \text{atm}$), the Hagena parameter was $\Gamma^* \approx 2700$. It was shown in experiment [320] that, with the employment of a pulsed nozzle analogous to that in Refs [171, 172], effective Xe clusterization occurred at a pressure $p_0 \ge 0.2 \ \text{atm}$. At $\Gamma^* \approx 2700$, the mean size of xenon clusters was $m \ge 100$ [320].

IR-induced fragmentation of clusters was performed in Refs [171, 172] with the aid of a tunable pulsed CO_2 -laser $(\tau_p \approx 150 \text{ ns})$ or a continuous wave laser. In the former case, the clusters were excited in the chamber of a mass spectrometer at the intersection area of the cluster beam with the UV laser beam and the mass spectrometer axis (see Fig. 5). Laser radiation was directed towards the cluster beam at a small angle to it. An appropriate system ensured synchronization of all pulses. In the study with the use of the continuous wave CO_2 -laser, the clusters were excited between the nozzle and the skimmer normally to the beam axis (see Fig. 5); the position of the laser beam could be scanned along and crosswise to this axis. The laser power was roughly 8 W, and its beam exhibited a Gaussian distribution over the cross section. Laser radiation was focused with a lens (f = 12 cm) onto a spot 0.43 mm in diameter. Laser energy flux density was determined from the relation

$$\Phi_{\rm IR} \left[{\rm J \ cm^{-2}} \right] = \frac{2RW}{\pi R^2 U} = \frac{2W}{\pi R U} \,, \tag{6.4}$$

where W is the laser power, πR^2 is the beam cross section, 2R/U is the time of particle travel through the beam, and



Figure 13. Time-of-flight mass spectra obtained by detecting a beam of Xe_m clusters (1), CF₃I molecules in the preliminarily created gas cloud (2), a beam of heterogeneous (CF₃I)_nXe_m clusters formed during the passage of an Xe_m cluster beam through a gas CF₃I cloud (3), and a beam of mixed (CF₃I)_nXe_m clusters formed by gas-dynamic cooling of a gas CF₃I/Xe mixture (1/100) (4) [171, 172].

 $U \approx 430 \text{ m s}^{-1}$ is the particle's directional movement speed. Energy flux density at a characteristic IR radiation power of 8 W was $\Phi_{\text{IR}} = 5.5 \text{ mJ cm}^{-2}$.

6.3.2 Results of the studies. Figure 13 presents mass spectra obtained by detecting an Xem cluster beam of CF₃I molecules in a preliminarily created gas cloud, a beam of heterogeneous $(CF_3I)_n Xe_m$ clusters formed during passage of Xe_m clusters through a CF₃I gas cloud, and a beam of homogeneous $(CF_3I)_n$ clusters generated with the use of a CF_3I/Ar gas mixture (1:15). The mass spectrum of the Xe_m cluster beam contained no ion peaks except background ones, because xenon atoms and clusters failed to be ionized at the chosen UV radiation wavelength. The I^+ , CF_3^+ , and CF^+ ion peaks were detected in a cloud of free CF₃I molecules, whereas an I_2^+ ion peak was absent, the cloud containing no $(CF_3I)_n$ clusters. Detection of an Xe cluster beam after its passage through the CF₃I gas cloud revealed intense I_2^+ and XeI⁺ peaks in addition to I^+ , CF_3^+ , and CF^+ peaks (Fig. 14). These observations give evidence that CF₃I molecules not only are trapped by Xe_m clusters but also form their own clusters $(CF_3I)_n$ on the Xe_m surface. Detection of homogeneous $(CF_3I)_n$ clusters has demonstrated intense I⁺ and I⁺₂ ion peaks in the mass spectrum. Mechanisms of I^+ and I_2^+ ion production during UV fragmentation of $(CH_3I)_n$ and $(CF_3I)_n$ clusters have been thoroughly investigated in Refs [321] and [322], respectively.

Figure 15 illustrates the dependences of I_2^+ and $I_2^+ + XeI^+$ ion signals on energy flux density of IR laser radiation in the case of excitation of homogeneous $(CF_3I)_n$ clusters in a beam, as well as $(CF_3I)_n$ clusters located in the bulk and on the surface of Xe_m clusters. Dependences 3 and 4 corresponding to the latter case were obtained for heterogeneous $(CF_3I)_nXe_m$ clusters of different sizes and compositions. The above-nozzle pressures of Xe and CF_3I gases were 1.0 and 1.3 atm, respectively, for dependence 3, compared with 2.0 and 0.6 atm for dependence 4. Thus, in the latter case (dependence 4 in contrast to dependence 3), $(CF_3I)_n$ clusters of a smaller size formed on the surface of larger Xe_m clusters.

There is a clear-cut difference in the character of the above dependences and between energy flux densities at which IR



Figure 14. Part of the time-of-flight mass spectrum taken in the region of ion peaks I_2^+ and XeI⁺ (within the range of mass numbers m/z = 254-263) in the case of detecting a $(CF_3I)_n Xe_m$ cluster beam formed during the passage of an Xe_m cluster beam through a CF₃I cloud. Vertical straight lines show positions of the respective mass peaks. The Gaussian curves show the I_2^+ ion peak and XeI⁺ ion peaks in accordance with percent composition of Xe isotopes [171, 172].



Figure 15. Dependences of I_2^+ and $I_2^+ + XeI^+$ ion signals on IR laser radiation energy density in the case of fragmentation of homogeneous $(CF_3I)_n$ clusters in a beam (curve *I*), $(CF_3I)_n$ clusters localized inside xenon clusters (curve 2), and $(CF_3I)_n$ clusters on the surface of xenon clusters (curves 3 and 4). Sequences of numbers show the slopes of the respective sections of the dependences. The UV ionizing radiation energy for dependences *I*–4 is 270, 220, 95, and 109 µJ, respectively [171, 172].

fragmentation of clusters occurs. Homogeneous $(CF_3I)_n$ clusters undergo efficient fragmentation at relatively low energy flux densities of laser radiation ($\Phi_{IR} \le 25 \text{ mJ cm}^{-2}$), whereas higher energy flux densities ($\Phi_{IR} \approx 75 \text{ mJ cm}^{-2}$) are needed for fragmentation of $(CF_3I)_n$ clusters inside Xe_m clusters; they must be even higher ($\Phi_{IR} \approx 150 \text{ mJ cm}^{-2}$) to ensure fragmentation of $(CF_3I)_n$ clusters on the surface of Xe_m clusters. In the case of heterogeneous $(CF_3I)_n$ Xe_m clusters formed during the passage of Xe_m clusters through a CF_3I cloud under low pressure, i.e., when small $(CF_3I)_n$ clusters formed on the surface of relatively large Xe_m clusters, no fragmentation of $(CF_3I)_n$ clusters (attenuation of the ionic signal) could be observed at energy flux densities up to about 250 mJ cm⁻² (see Fig. 15, curve 4).

In the framework of the model propounded in Ref. [169], cluster fragmentation caused by IR laser excitation can be described as a quasistationary process of molecular evaporation at temperature T_{ev} depending on the balance between the



Figure 16. Dependences of I_2^+ ion signal on IR laser radiation energy flux density in the case of fragmentation of homogeneous $(CF_3I)_n$ clusters of different sizes at gas pressures $p_0(CF_3I/Ar = 1/15)$ above the nozzle equal to 1 atm (1) and 0.5 atm (2). Ionizing UV radiation energy is 270 µJ [172].

energy absorbed by the cluster and the energy spent to successively detach molecules from it. The efficiency of fragmentation may be characterized by the steepness of the ionic signal vs IR radiation energy flux density curve decay, viz. $S(I_2^+; \Phi_{IR})$. In certain cases, this dependence can be approximated by the (6.2)-like exponential function, while the rate constant of molecular evaporation from a cluster is defined by relation (6.3). At a given cluster temperature, constant k_{ev} increases with decreasing energy of particle evaporation from a cluster (ΔE).

The results (see Fig. 15) indicate that, for both homogeneous and heterogeneous clusters (notwithstanding the significant differences between them), the slope of the curve formed by plotting cluster fragmentation efficiency versus energy flux density Φ_{IR} gradually increases. In homogeneous clusters, this effect is largely due to a decrease in cluster size during evaporation and the related reduction in the binding energy of intercluster molecules [23, 314, 323], as confirmed by the data presented in Fig. 16 (the dependence of ionic signals $S(I_2^+)$ on IR radiation energy flux density for homogeneous $(CF_3I)_n$ clusters of different sizes obtained at different above-nozzle pressures). For dependences 1 and 2, gas pressure $p_0(CF_3I/Ar = 1/15)$ over the nozzle was 1 and 0.5 atm, respectively. In the latter case, much smaller clusters than in the former were generated, as follows from a comparison of ionic signals $S(I_2^+)$ in the absence of IR excitation of the clusters. It can be seen from Fig. 16 that the approximation of the cluster signal in the form $S(I_2^+) \sim$ $\exp(-k\Phi_{IR})$ yields the exponent $k = 27 \text{ cm}^2 \text{ J}^{-1}$ in dependence 1 (at small decays); it is much higher in dependence 2 $(k = 70 \text{ cm}^2 \text{ J}^{-1}).$

It is equally clear from Fig. 16 that if experimental values of ionic signals obtained with smaller clusters (described by curve 2) are shifted parallel towards higher energy flux densities (by approximately 0.022 J cm^{-2}), they fairly well coincide with experimental results for larger clusters described by curve *1* that have already undergone fragmentation into smaller ones. In other words, the fragmentation efficiency correlates perfectly well with cluster size, which means that small clusters disintegrate faster, because the binding energy of their molecules lowers with decreasing cluster size [23, 314, 323].

Unlike the model description of homogeneous molecular clusters, that of laser IR fragmentation of heterogeneous

clusters based on the experimental results obtained in Refs [171, 172] appears doubtful, because a model has to take account of many unknown parameters, such as IR absorption cross sections, binding energy of intracluster atoms and molecules, and exact cluster structure and composition. All these parameters change with variations of cluster size during fragmentation. Moreover, the model-based description of the mixed cluster fragmentation requires that not only the number of CF_3I molecules evaporated from the heterogeneous clusters but also the number of evaporated Xe atoms be known. However, the number of evaporated Xe atoms was not measured in the experiments being considered.

In heterogeneous clusters like $(CF_3I)_n Xe_m$, there are several different values of the particle's binding energy (in the zeroorder approximation), viz., for the binding between CF3I molecules, between Xe atoms, and between CF₃I molecules and Xe atoms. As a result, IR excitation of clusters first causes particles with the lowest binding energy to evaporate (in this instance, Xe atoms) at characteristic temperature T_{ev} that is not high enough to ensure efficacious evaporation of CF3I molecules, the number of which in a cluster is determined from the amplitude of signal $S(I_2^+ + XeI^+; \Phi_{IR})$. Evidently, a higher energy needs to be absorbed to detach a single CF₃I molecule from the cluster (taking account of the energy utilized to evaporate part of the Xe atoms) than in the case of homogeneous $(CF_3I)_n$ clusters. Accordingly, the signal behavior (at the initial section) is characterized by gently sloping dependences $S(I_2^+ + XeI^+; \Phi_{IR}) \propto \exp[-k(\Phi - \Phi_0)]$ (with a smaller parameter k).

However, the role of Xe atoms in the vaporization process diminishes as they evaporate; the same is true of evaporation energy removal. As a result, the temperature of cluster evaporation increases the same as the probability of CF₃I molecule evaporation. Fragmentation efficiency grows too and tends in the limit toward the fragmentation efficiency of homogeneous clusters. These changes are reflected in the signal behavior as the increased steepness of the $S(I_2^+ + XeI^+; \Phi_{IR})$ curve decay [higher $k(\Phi)$] with increasing energy flux density Φ_{IR} (see Fig. 15).

The behavior of the observed dependences is influenced, as in the case of UV-induced cluster fragmentation [173], by the initial cluster characteristics, such as the size, composition, m/n ratio, structure, and temperature, which, in turn, depend on the conditions of cluster formation. Such behavior of the dependences is quite apparent in experiments using medium-size clusters with the commensurable component ratio (see curves 2 and 3 in Fig. 15). A rise in the number of Xe atoms has to hamper fragmentation of $(CF_3I)_n$ clusters inside heterogeneous $(CF_3I)_nXe_m$ clusters, especially in the presence of excess Xe atoms. Thus, at IR radiation energy flux densities used in the experiments under consideration, small $(CF_3I)_n$ clusters on the surface of large Xe_m clusters (n < m) do not undergo fragmentation at all: the ionic signal does not diminish with increasing energy flux density (curve 4 in Fig. 15). As was mentioned earlier, it can be due to the fact that the energy absorbed by $(CF_3I)_n$ clusters in the bulk of heterogeneous $(CF_3I)_n Xe_m$ clusters is spent to evaporate Xe atoms whose binding energy in the cluster is lower than the energy of binding between CF₃I molecules and between CF₃I and Xe atoms [169, 316]. Therefore, the process does not reach the evaporation of CF₃I molecules at experimental energy flux densities.



Figure 17. Dependences of $S(I_2^+)$ ionic signal on IR radiation energy flux density in the case of fragmentation of homogeneous $(CF_3I)_n$ clusters by a continuous (dark dots, curve *I*) and pulsed (light dots, curve 2) CO₂ lasers. Light dots show results represented by curve 2 in Fig. 16. Gas pressure and composition $p_0(CF_3I/Ar = 1/15)$ above the nozzle are 0.5 atm in both cases [172].

The data obtained give evidence that the evaporation of Xe atoms (as weaker bound ones) induced by the excitation of heterogeneous clusters results in relaxation of the absorbed energy and, eventually, in a change to the dependence of ionic signals on IR radiation energy flux density, i.e., a more gentle dependence by virtue of higher cluster stability.

The above assumption of the quasistationary character of cluster decay owing to resonant excitation of intracluster molecules by IR laser radiation was confirmed by experiments with the exploitation of a continuous wave CO₂-laser [172]. Figure 17 plots dependences of the ionic signal $S(I_2^+)$ on IR radiation energy flux density in the case of fragmentation of homogeneous $(CF_3I)_n$ clusters under the effect of pulsed and continuous wave CO₂-laser radiation. The results obtained in both cases are in excellent agreement. They allow us to conclude that the fragmentation of $(CF_3I)_n$ clusters excited by IR pulses longer than 10^{-7} ns can be regarded as a quasistationary process of evaporation of their constituent atoms and molecules.

Efficient relaxation of the energy in heterogeneous clusters associated with evaporation of atoms (or molecules) having a low binding energy has been reported in many articles [50-53, 324-328]. For example, the authors of Ref. [326] observed cooling of heterogeneous Ar/CO₂ clusters in the course of evaporation of Ar atoms. They showed that a trapping of SF_6 molecules by CO_2 clusters occurred only when the clusters cooled as a result of evaporation of carrier gas atoms. Reference [327] reports a marked suppression of UV laser fragmentation of heterogeneous water clusters generated upon the expansion of a mixture of water molecules with carrier gases (in comparison with UV-induced fragmentation of clusters generated without a carrier gas) and the formation of 'nonprotonated' cluster ions resulting from rapid cooling of water cluster ions due to evaporation of carrier gas atoms bound to them. As is known, it is the evaporation of atoms that contributes to the stabilization of the temperature of superfluid helium nanodroplets trapping molecules [50-53]. The evaporation of weakly bound atoms from heterogeneous atomic-molecular clusters is an effective energy relaxation channel, as shown in experiments on the disintegration of weakly bound clusters

of argon, nitrogen, krypton, and xenon trapping highly vibrationally excited SF_6 molecules in crossed beams [324, 325].

7. Dynamics of molecular cluster fragmentation

7.1 A few remarks

Investigations into intracluster dynamics (relaxation of the absorbed energy upon excitation of clusters and their fragmentation [174, 175]) are a very important area of research on weak intermolecular interactions. The processes of vibrational energy relaxation in molecules and clusters are key issues as regards chemical reactions in condensed media and gases. These investigations are closely related to the problem of intramolecular vibrational relaxation (IVR-1) or intramolecular vibrational redistribution (IVR) in free molecules, dealt with in numerous publications (see, for instance, monographs [329, 330], reviews [331–336], and articles [337–339]).

Investigations into the intramolecular dynamics of free molecules are motivated to a long extent by the desire of researchers to realize intramolecular selectivity, i.e., the possibility of selectively exciting the distinguished vibrational mode or a group of modes and the subsequent nonstatistical decay of the molecule. It is known [305, 306] that the excitation of molecules by powerful $10^{-8} - 10^{-7}$ s IR laser pulses makes it possible to achieve a high degree of *intermolecular* selectivity to be used for laser-assisted isotope separation and other directed photophysical and photochemical processes. The ultimate dream of researchers developing selective methods of interaction between radiation and substances remains the realization of *intramolecular* selectivity.

Intramolecular or mode selectivity opens up new opportunities for both basic research (molecular dynamics, biology, and gene engineering) and the development of innovative technologies. A major limitation hampering the realization of vibrational mode-selective multiphoton excitation of molecules is rapid intramolecular vibrational energy redistribution [175, 329, 331, 336] taking place in an isolated polyatomic molecule. In this process, the vibrational energy is redistributed from excited vibrational mode, after exceeding a certain threshold value (the so-called stochastization energy $E_{\rm st} \approx 3000-7000 \text{ cm}^{-1}$), between other molecular vibrational modes for a characteristic time of $10^{-13}-10^{-11}$ s, which results in the loss of initial mode selectivity of laser excitation. This accounts for the statistical character of subsequent monomolecular reactions.

The advent of powerful femtosecond laser sources of radiation in the mid-infrared range (4–10 μ m) yielding energy flux density $\Phi_{IR} \ge 0.1$ J cm⁻² [162–164] makes it possible not only to overcome the limitation on IVR in terms of the time parameter but also to achieve a high level of excitation in molecules sufficient for them to reach the reaction barrier [340, 341].

The situation is more complicated as regards molecular clusters, because the process of vibrational energy relaxation (redistribution) implies consideration of not only vibrational modes of excitable intracluster chromophore molecules but also vibrational modes of other molecules contained in the cluster, as well as its van der Waals modes. This accounts for multistep and even multilayer redistribution of the vibrational energy in clusters [342]. Energy relaxation in a cluster can be either a sequential or a simultaneous process. The study of cluster dynamics implies consideration of *intramolecular* vibrational relaxation (IVR-1), i.e., energy relaxation inside an excitable molecule, intermolecular or *intracluster* energy relaxation (intracluster vibrational relaxation, IVR-2), i.e., vibrational energy relaxation inside a cluster, and vibrational cluster *predissociation* (VP). The first two processes are sometimes regarded as a single one; then, intramolecular vibrational relaxation rates (times) in a cluster (meaning *intracluster* vibrational relaxation rates) and vibrational predissociation rates are measured as in the case of free polyatomic molecules (see below).

The authors of early experiments most frequently measured times (rates) of cluster vibrational predissociation. These times were also estimated from spectral measurements of fluorescence line (band) widths or the widths of cluster IR predissociation spectra (see Section 5.1).

The primary objective of the studies on these processes in clusters is to measure rate constants (times) of IVR-1, IVR-2, and VP, evaluating the possibility of realizing the site-selectivity in cluster excitation, elucidating the dependence of intracluster vibrational energy relaxation and vibrational predissociation on various parameters of clusters themselves and exciting radiation. In the framework of this goal, the experimenters studied the dependences of rate constants of IVR-1, IVR-2, and VP on the excitation energy, excitable mode, cluster structure and intracluster bond strength, proton-donor and proton-acceptor nature of intracluster molecules, density of states in van der Waals modes and their stored energy, cluster decay channels, and decay product composition and state.

7.2 Dynamics of molecular cluster fragmentation in the electron excited state

Direct measurements of intracluster vibrational energy relaxation and vibrational predissociation times in polyatomic van der Waals complexes were made both using clusters in the electronically excited state S_1 [243, 343, 344] and in the ground electronic state S_0 [345–351]. In the former case, Franck–Condon factors made possible the excitation of a large number of electronic-vibrational (vibron) modes of the state S_1 . Energy transfer processes were studied either by detecting laser-induced fluorescence (LIF) from starting clusters and end products [243, 342–344] or by resonance enhanced multiphoton ionization (REMPI) of clusters and fragments by UV laser radiation [49, 170, 345–356]. In the latter case, two-photon (the so-called 1+1 REMPI or RE2PI) ionization schemes via the S_1 state were used most frequently.

To recall, the LIF technique was also employed in a few studies [243, 342, 350–355] to clarify the structure, vibrational frequencies, binding energies, and time ratios of different IVR cluster channels, as well as fragments formed during vibrational predissociation of clusters. It was shown that intracluster energy relaxation and vibrational predissociation processes are in many cases nonstatistical, and only a few states are involved in decays, despite the large number of energetically excited levels.

Intracluster vibrational energy relaxation times appear to have been measured for the first time in Ref. [243] for dimethyltetrazine $(DMT)_2$ dimers (see Section 5.1). Clusters were generated in the course of supersonic expansion of a mixture of DMT vapors at 22–40 °C with helium and a pressure of 2–5 atm at the exit from the slot nozzle



Figure 18. Time-resolved fluorescence recorded after excitation of the $\overline{16a^2}$ level of the electron excited state S₁ of an s-tetrasine–Ar complex and time dependences of emission from the initially excited state, the intermediate $\overline{16a^{1*}}$ state populated as a result of energy relaxation, and the excited 0^0 state of the fragments (tetrasine molecules). Solid curves — approximations of experimental data by the results of calculations based on the successive energy relaxation model [352].

 $(27 \times 270 \ \mu\text{m})$. Clusters and monomers were excited (transition to electronic state ${}^{1}\text{B}_{3u}$) by 10-ps pulses from an Ar⁺ laser-pumped wavelength-tunable dye laser. The rise times of fluorescence front from dimer levels populated as a result of energy redistribution and from laser-excited monomers were measured. The dimers exited by radiation at a wavelength of 572.2 nm passed into the $\overline{6a_{1}^{0}}$ state, and their fluorescence was observed at 583.4 nm. Monomers passed into the 0_{0}^{0} state at 571.4 nm, and their fluorescence from the $6a_{1}^{0}$ state was observed at 588.4 nm. Fluorescence from the dimers lagged behind that from the monomers due to energy relaxation in the dimers. The intracluster vibrational energy relaxation time for dimers was found to be 35 ± 10 ps [243].

Experiments reported in Refs [352–355] were designed to study the temporal evolution of s-tetrasine- $(Ar)_{1,2}$ (s-tetrasine = $H_2C_2N_4$) complexes (see the inset to Fig. 18) that passed as a result of excitation to the lower vibrational levels of state S₁. It was shown based on the resolved structure in the laser-induced fluorescence spectrum that an argon atom of the s-tetrasine-Ar₁ complex is located at the symmetry axis C₂ outside the tetrasine molecule plane. A van der Waals bond was 3.4 Å long. The cooled complexes obtained in a gasdynamic jet were excited by picosecond pulses of a dye laser pumped by an Ar⁺-laser. The spectral resolution of fluorescence was achieved with the use of a monochromator. Conditions for selective excitation of electronic-vibrational levels in clusters and selective detection of fluorescing products were determined from frequency shifts in the fluorescence spectra. Time profiles of fluorescence bands were detected with a resolution of about 25 ps.

To determine intracluster energy relaxation and cluster vibrational predissociation rates, three types of radiation were detected in experiments: (1) fluorescence from initially excited states, (2) fluorescence from other (initially nonexcited) states, and (3) fluorescence from dissociation fragments, i.e., from free s-tetrazine molecules in the S_1 state. The existence of radiation of the third type confirmed the occurrence of vibrational predissociation of the clusters. In the case of excitation of free s-tetrazine molecules, fluorescence could be observed only from excited states.

The time dependences of fluorescence of the above three types induced by excitation of the $\overline{16a^2}$ level of the cluster S_1 state are plotted in Fig. 18 [352]. The bars designate the levels of the argon-containing complex to distinguish them from the respective levels in free s-tetrazine. Relaxation was followed by fluorescence from the $\overline{16a^{1*}}$ state (the asterisk indicates that the radiant state involves a vibrational quantum in the van der Waals mode) and fluorescence of fragments from the s-tetrasine ground vibrational level for state S_1 (0⁰). Figure 18 clearly shows different rise times of fluorescence in the above three cases. It testifies to intracluster redistribution of the vibrational energy.

The above studies clarified the microscopic picture of competing vibrational movements, both parallel and sequential, inside clusters and allowed determining the rate constants of subsequent processes leading to cluster predissociation. Moreover, dissociation end products (s-tetrasine in state S_1) were identified, decay times of cluster excited states estimated, and concomitant intermediate cluster states observed [352]. Intracluster vibrational energy relaxation (IVR-2) and vibrational predissociation (VP) times were found to be 2.2 and 1.1 ns, respectively [352], i.e., of the same order of magnitude as free s-tetrasine decay times after it passed under the effect of excitation onto the same electronic-vibrational levels. Free s-tetrasine decay yields HCN and N2. However, the tetrasine decay channel is blocked in the case of an s-tetrasine-Ar complex, and its dissociation occurs via a competing channel with the lowest binding energy $(E_b \approx 281 \text{ cm}^{-1})$, i.e., with the detachment of the argon atom [355]. IR vibrational predissociation of the complex also takes place.

Experiments with s-tetrasine–Ar₁ and s-tetrasine–Ar₂ complexes in Ref. [355] gave evidence that energy relaxation and vibrational predissociation rates depend on excess vibrational energy ε_w in van der Waals modes. The value of ε_w was altered by varying the wavelength of the exciting laser radiation within the absorption band contour of a complex. The dissociation rate for either complex was around 10^9 s^{-1} [355]. Thus, for the s-tetrasine–Ar₁ complex at $\varepsilon_w = 0$ (direct optical excitation of the $\overline{16a^2}$ level), the rate constant $k_{\text{VP}} = 0.54 \times 10^9 \text{ s}^{-1}$; at $\varepsilon_w = 175 \text{ cm}^{-1}$ and $\varepsilon_w = 250 \text{ cm}^{-1}$, $k_{\text{VP}} = 2.3 \times 10^9 \text{ s}^{-1}$ and $k_{\text{VP}} = 0.95 \times 10^9 \text{ s}^{-1}$, respectively (excitation of the $\overline{6a_0^1}$ state). The authors of Ref. [355] ascribed the decline in the complex dissociation rate at $\varepsilon_w = 250 \text{ cm}^{-1}$, as opposed to that at $\varepsilon_w = 175 \text{ cm}^{-1}$, to the energy gap for relaxation transitions in the S₁ state of tetrasine.

Experiments [344, 356] were designed to study the vibrational dynamics of aniline–Ar, aniline–CH₄ [356], and aniline–N₂ [344] clusters (aniline = $C_6H_5NH_2$) in the vibrationally excited state S₁ with the aid of the laser-induced fluorescence technique. The intramolecular vibrational relaxation and vibrational predissociation rates were measured. The binding energies of the three complexes amounted

to 450, 515, and 480 cm⁻¹, respectively [356]. Densities ρ_w of van der Waals states in aniline complexes with Ar, N₂, and CH₄ were significantly different at a fixed excess of vibrational energy over cluster dissociation energy. The density of states in these clusters increased in accordance with the $\rho_w(\text{aniline}-\text{Ar}) < \rho_w(\text{aniline}-\text{N}_2) < \rho_w(\text{aniline}-\text{CH}_4)$ relation. At the cluster vibrational energy $E_{vib} = 700 \text{ cm}^{-1}$, $\rho_w(\text{aniline}-\text{CH}_4)$ is roughly three orders of magnitude greater than $\rho_w(\text{aniline}-\text{Ar})$.

It was revealed in Refs [344, 356] that the initially excited states in aniline–Ar clusters have relatively long (nanosecond) lifetimes, whereas the lifetimes of intermediate (transient) states are very short. In contrast, the initially excited states and intermediate vibrationally excited states in aniline-CH4 clusters exhibit short lifetimes (≤ 100 ps). These findings can be interpreted in qualitative terms in the framework of the sequential IVR/VP-mechanism [344, 356], which satisfies the following requirements: (1) probabilities of intramolecular vibrational energy relaxation from a chromophore to the van der Waals modes are given by Fermi's golden rule, and the density ρ_w of van der Waals vibrational states is the most important factor determining relative IVR rates; (2) IVR among van der Waals modes represents a very rapid process, and (3) vibrational predissociation rates can be calculated based on the Rice-Ramsperger-Kassel-Marcus (RRKM) statistical theory of monomolecular decay [357, 358]. The density of van der Waals states in aniline-CH₄ clusters being three orders of magnitude greater than that in aniline-Ar clusters, the model predicts that the slow IVR process in aniline-Ar clusters restricts the vibrational predissociation rate. In contrast, in aniline–CH₄ clusters, vibrational predissociation is a slow process ($\tau_{\rm VP} = 150$ ns) limiting the rate of energy relaxation. The IVR and VP rates for aniline-N2 clusters are intermediate between the respective rates for aniline–Ar and aniline–CH₄ clusters [344].

7.3 Intracluster dynamics in the ground electronic state

The authors of Refs [350, 351] studied in real time IR photodissociation of $(NO)_2$ clusters. The value of $(NO)_2$ dimers for time-resolved measurements lies in the fact that they exhibit in IR region active fundamental vibrations [symmetric N–O stretch vibrational modes v_1 (1869 cm⁻¹), and asymmetric N–O vibrational modes v_4 (1789 cm⁻¹)] characterized by strong absorption. Moreover, dissociation products of (NO)₂ clusters include NO fragments readily detectable by the laser-induced fluorescence technique. The equilibrium geometry of $(NO)_2$ dimers in the gaseous phase has a symmetrical trapezoidal structure C_{2v} . The length of the N-N bond is 2.236 Å, the ONN angle is 99.6°, and the length of the N–O bond is 1.161 Å [359]. The energy of the weak van der Waals bond is $E_b = 800 \pm 150 \text{ cm}^{-1}$ [360]. Because in the excitation of any of these vibrational modes, v_1 or v_4 , the energy put into a cluster is higher than the van der Waals bond energy, the cluster becomes metastable and eventually undergoes fragmentation. The decay is not accompanied by the formation of vibrationally excited NO products for the shortage of energy.

 $(NO)_2$ dimers were generated by supersonic expansion of an NO/He or NO/H₂ mixture in a pulsed molecular beam. They were excited by 2-ps IR laser pulses with energy $E_p = 0.5$ mJ emitted by two dye lasers pumped by a modelocked Nd:YAG laser and nonlinear crystals. Dissociation products (NO molecules) were excited by UV radiation at a wavelength of 226 nm (a mixture of second harmonic



Figure 19. Time-resolved emergence of NO fragments after excitation of (a) symmetric (v_1) and (b) asymmetric (v_4) valent vibrational modes of $(NO)_2$ clusters. Solid curves — approximations of experimental data by the results of calculations using relation (7.1). Note the 20-fold difference between times plotted on the abscissas [174, 351].

radiation from one of the dye lasers and fundamental harmonic from the Nd:YAG laser). The vibrational predissociation time of $(NO)_2$ clusters was determined by measuring the evolution of fluorescence intensity of NO fragments passing into the X³ $\Pi_{3/2}$ state, depending on the delay time τ_D between a cluster-exciting IR pulse and a fragment-probing UV pulse (Fig. 19). Fluorescence signals were approximated by an exponential function with the monomolecular decay rate $k_{uni} = 1/\tau_{VP}$:

$$S(\tau_{\rm D}) = S(\infty) \left[1 - \exp\left(-\frac{\tau_{\rm D}}{\tau_{\rm VP}}\right) \right].$$
(7.1)

It was shown that photodissociation from the lower-energy antisymmetric v_4 mode takes $\tau_{VP} = 39 \pm 8$ ps, whereas the higher-energy symmetric v_1 mode has a much longer lifetime $\tau_{VP} = 880 \pm 260$ ps.

The mechanism of $(NO)_2$ cluster dissociation is difficult to explain in terms of purely statistical theories. Such a great difference between decay rates reflects specific mode coupling in a vibrationally excited complex. According to Refs [350, 351], the relationship between the vibrational potential and the mode-dependent forces may be responsible for the observed dependence of vibrational predissociation time on the excitable mode. Results of experiments with $(NO)_2$ [350, 351] and $(HF)_2$ [237, 238] clusters suggest that the greater the shift of the excitable vibrational frequency in a cluster relative to that in a free molecule, the smaller the cluster predissociation time for exciting a given vibration. As shown in Ref. [234], there is a correlation for many clusters between the decay time and the frequency shift of the cluster IR-excitable mode with respect to the frequency in a free molecule. In this context, a classical example is the $(HF)_2$ dimer, for which broadenings of well-resolved rotational lines in the IR spectra related to vibrational predissociation of the dimer were measured [237, 238]. IR line widths give evidence that the excitation of stretching vibration of a hydrogen H–F bond (v₂, frequency shift –92 cm⁻¹) causes the dimer to disintegrate for 0.5 ns, whereas excitation of a free H–F bond (v₁, frequency shift –32 cm⁻¹) takes 12 ns to produce the same effect. These data indicate that the dependence of the interaction potential on the type of vibrational motion exerts considerable influence on the cluster vibrational predissociation time.

Many intracluster dynamics studies were conducted with clusters cooled in a supersonic molecular beam using timeresolved picosecond IR-UV pump-probe spectroscopy [49, 345-349]. A picosecond IR laser pulse excited vibrations of intracluster molecules, while the temporal evolution of the populations of excitable levels and those populated by energy redistribution was registered using the method of resonance enhanced multiphoton ionization (REMPI) by a picosecond UV pulse. Ionization of both clusters and resulting products was effected via the excited electronic state S_1 . In the majority of the above studies, the sources of IR radiation for the vibrational excitation of clusters were an optical parametric generator (OPG) based on two LiNbO3 crystals with an optical parametric amplifier (OPA) (the OPG/OPA system) pumped by a mode-locked Nd:YAG laser. UV radiation tunable in the 33,000-36,000-cm⁻¹ frequency range was generated using the OPG/OPA system pumped by an Nd:YAG laser with its subsequent transformation into the second harmonic. The widths of the spectra of IR and UV laser pulses were approximately 15-20 and 5-7 cm⁻¹, respectively, while the pulse lengths at half-height were around 12 ps in both cases [348, 349].

The authors of Refs [49, 345-348] investigated the dynamics of vibrational energy relaxation in phenol complexes with hydrogen bonds by means of picosecond spectroscopy. Reference [346] was focused, in particular, on sitedependent relaxation in the excitable part of a phenol dimer cluster. It was revealed that relaxation of the vibrational energy from phenol (a proton donor) is a faster process than that from a phenolic proton acceptor. The authors of Ref. [347] studied the dynamics of intracluster vibrational energy relaxation in phenol (C₆H₅OH) and partly deuteriumsubstituted phenol (C_6D_5OH) clusters in a variety of molecular solvents under vibrational excitation of O-H bonds in clusters. To elucidate the influence of hydrogen bond strength on energy redistribution, clusters of two types were used: (1) those with strong σ -type hydrogen bonds (phenol-dimethyl alcohol and phenol dimer clusters), and (2) those having weak π -type hydrogen bonds (phenolethylene clusters).

It was found that relaxation of the population of the excited level obeyed the exponential law with a single index. The relaxation rate increased with increasing strength of hydrogen bonds. At the same time, induced (transient) UV spectra from the vibrational levels populated as a result of energy redistribution undergo a different temporal evolution at different UV radiation frequencies. The analysis of temporal profiles of transient UV spectra provided a basis for a three-step scheme for the description of the energy flux from an excited level to the hydrogen bond dissociation

channel: (1) redistribution of the vibrational energy inside the phenol portion of the cluster and the formation of hot phenol; (2) redistribution of the energy from hot phenol between vibrational modes of all cluster molecules, and (3) cluster dissociation along the hydrogen bond.

The rate of the first step is highly dependent on the strength of hydrogen bonds, whereas that of the last two steps does not really depend on the bond strength. A comparison of the observed cluster dissociation rates with those calculated based on the statistical RRKM model of monomolecular decay [357, 358] demonstrated that cluster dissociation along the hydrogen bond occurs much faster than complete energy randomization.

Intramolecular and intracluster vibrational energy relaxation times and vibrational predissociation times were measured in phenol–ethylene clusters with hydrogen bonds $(C_6H_5OH-C_2H_4)$ in Refs [49, 348]. These clusters are peculiar in that their phenol serves as a donor and ethylene as an acceptor of proton. Hence, special attention is given to the channels and rates of intracluster vibrational energy redistribution and to the times of vibrational predissociation associated with excitation of both proton-donating and proton-accepting portions of the clusters. In the former case, IR radiation excited either O–H bonds (3580 cm⁻¹) or C–H bonds (3054 cm⁻¹) in phenol, and the C–H bonds (3104 cm⁻¹ and 2987 cm⁻¹) in ethylene in the latter case.

It turned out that the O-H vibrational excitation in a $C_6H_5OH-C_2H_4$ cluster gives rise to operating the following energy dissipation channel starting from the O-H bond:

$$Ph(OH)^* - C_2H_4 \rightarrow (PhOH)^* - C_2H_4$$

$$\rightarrow (PhOH - C_2H_4)^* \rightarrow PhOH + C_2H_4, \qquad (7.2)$$

where $Ph(OH)^*$, $(PhOH)^*$, and $(PhOH-C_2H_4)^*$ stand for IR-excited phenol, hot phenol, and a hot cluster, respectively. In the case of C-H vibrational excitation in ethylene, the following energy dissipation channel operates:

$$PhOH - (C_2H_4)^* \rightarrow (PhOH - C_2H_4)^* \rightarrow PhOH + C_2H_4.$$
(7.3)

It has been established that the energy of O-H and C-H bond vibrations is rapidly distributed over a phenol bath mode (for 10 ps from O-H bond vibrations) and for less than 5 ps from C-H bond vibrations) and thereafter undergoes redistribution over the entire cluster. On the other hand, the energy of C-H vibrational modes v_9 and v_{11} in ethylene is instantaneously distributed over the entire cluster. The existence of these two types of energy relaxation channels is due to strongly bound bath modes in the phenol part of the cluster, and their absence in the ethylene portion,

Table 1. Times of intramolecular redistribution of vibrational energy (τ_{IVR-1}), intracluster redistribution of vibrational energy (τ_{IVR-2}), and vibrational predissociation (τ_{VP}) for a phenol-d₀-ethylene cluster [49].

Excitable mode	Frequency, cm ⁻¹	τ _{IVR-1} , ps	τ _{IVR-2} , ps	τ _{VP} , ps		
Phenol O-H bond Ethylene C-H bond (v9) Phenol C-H bond	3580 3104 3054	10 ± 2 $- *$ $\leqslant 5$	$\begin{array}{c} 20\pm 4\\ 62\pm 8\\ 20\pm 3\end{array}$	$90 \pm 10 \\ 100 \pm 10 \\ 120 \pm 20$		
* Experimental data suggest that the excitation of the valent vibration of the ethylene $C-H$ bond instantaneously induces the first stage of energy relaxation in the entire cluster.						

while vibrational predissociation times in the case of excitation of the above modes do not differ so much, viz., 90 ps and 120 ps when O-H and C-H bonds are excited, respectively (Table 1).

The possibility of realizing site-selectivity of cluster excitation was evaluated in paper [349] designed to study vibrational energy relaxation after picosecond time-resolved excitation of Fermi-polyad vibration of C-H bonds in a benzene dimer Bz₂ and trimer Bz₃. In the case of the Bz₂ dimer, site-selectivity of excitation was achieved in a T-shaped structure utilizing an isotopically substituted heterodimer hd, where $h = C_6H_6$, and $d = C_6D_6$. The result was compared with that obtained for an hh homodimer. In the hd heterodimer, the two isomers, h(stem)d(top) and h(top)d(stem), demonstrate a quite apparent site-dependent intracluster redistribution of the vibrational energy. The IVR time of the h(stem)d(top) portion fell in the range of 140– 170 ps or roughly 2.5 times shorter than that of the h(top)d(stem) portion (370–400 ps).

Bath modes are responsible for a broad electronic transition in transient UV spectra that gradually disappears on a nanosecond time scale. The transient spectrum has various time profiles at different wavelengths, described by the three-step vibrational energy relaxation model, including the processes of intramolecular and intracluster vibrational relaxation and vibrational predissociation: initial state \rightarrow bath-1 (intramolecular relaxation) \rightarrow bath-2 (intermolecular or intracluster relaxation) \rightarrow fragments. Moreover, this model fairly well describes time profiles of the fragment formation, i.e., benzene. Bz₃ trimers are also characterized by three-step relaxation of the vibrational energy, even if energy relaxation at each step takes less time than in Bz₂ dimers (Table 2) [349].

The dependence of intracluster dynamics on excitation energy was investigated in Ref. [345] with reference to its influence on vibrational energy relaxation times in complexes composed of natural and deuterated phenol and water molecules.

Table 2. Vibrational energy relaxation times in a benzene dimer and trimer after IR-induced excitation of Fermi polyads (bands a, b, and c) of CH valent vibration [349].

Relaxation time	Band a		Band b		Band c		
	hd	hh	hd	hh	hd	hh	hdd
τ_1 , ps Stem Top	* *	* *	$\begin{array}{c} 140\pm10\\ 370\pm20 \end{array}$	$\begin{array}{c} 120\pm10\\ 360\pm20 \end{array}$	$\begin{array}{c} 160\pm10\\ 400\pm20 \end{array}$	$\begin{array}{c} 140\pm10\\ 420\pm30\end{array}$	50 ± 10 **
τ_2 , ps			200-	- 700			$300\pm100~^{**}$
$\tau_{\rm VP},{\rm ps}$			2000-	- 6000			1000 ± 200 **
* Time dependences of decay are undetectable. ** Data derived from time dependences of dd^+ ion signal.							



Figure 20. (a) Schematic energy level diagram in the three-step energy relaxation model for a phenol- d_0 – H_2O complex and its IR-absorption spectrum in the OH valent vibration region. (b) Schematic energy level diagram in the model of three-step energy relaxation for a phenol- d_1 – D_2O complex and its IR-absorption spectrum in the OD valent vibration region [345].

Figure 20 presents schematically energy levels and vibrational energy relaxation for a hydrogen-containing system ($C_6H_5OH-H_2O$, phenol- d_0-H_2O) and a deuterated $(C_6H_5OD - D_2O, \text{ phenol-d}_1 - D_2O)$ system. The insets to the left part of the figure show the vibrational spectra of phenol O-H stretch at a frequency near 3525 cm^{-1} , and the same spectra of phenol O–D stretch near 2600 cm⁻¹. Real-time studies of energy redistribution from phenol vibrational modes OH/OD were carried out using IR-UV pump-probe spectroscopy. The potential energy of the complexes along the hydrogen bond coordinate and IR-excited energy levels are schematically depicted in Fig. 21. Populations of energy levels excited by IR laser pulses and populated as a result of energy redistribution were detected by the method of resonant two-photon ionization (R2PI) of complexes via the excited electronic state S1 (see Fig. 20). Time dependences of UV absorption at different radiation wavelengths, induced upon vibrational excitation of the complexes, were deduced from ion yields (Fig. 22) that were also used to determine intramolecular (IVR-1) and intracluster (IVR-2) vibrational energy relaxation times, as well as vibrational predissociation times of complexes.



Figure 21. Potential energy of phenol- d_0 -H₂O and phenol- d_1 -D₂O complexes along the hydrogen bond coordinate [345].

The data obtained were analyzed taking account of the three-step energy relaxation model and compared with calculated results of two theoretical approaches: the anharmonic force field, and the RRKM model. The results proved to be consistent with experimental observations (Tables 3 and 4) and confirmed the importance of couplings between

Table 3. Fitting parameters for the descri	ption of signals observed in IR	pumping-UV probing of	phenol-water complexes [345].
	p		

Complex	Valent mode	Frequency, cm ⁻¹	Excess energy, cm ⁻¹	IVR-1: τ_1 , ps	IVR-2 : <i>τ</i> ₂ , ps	VP: τ_3 , ps
Phenol-d ₀ -H ₂ O	v _{OH}	3525	1525	4	6	40
$Phenol-d_1-D_2O$	V _{OD}	2600	600	12	24	100

Table 4. Calculated density $\rho(E)$ of vibrational states, total number of vibrational and rotational states of fragments *W*, predicted dissociation times τ_{RRKM} , and observed vibrational predissociation times τ_3 [345].

Complex	$\rho(E) \times 10^5$, cm	$W(E-E_{\rm D}) imes 10^5$	$\tau_{\rm RRKM}$, ps	Experiment, τ_3 , ps
Phenol-d ₀ -H ₂ O	1.85	4.8	100	40
$Phenol-d_1 - D_2O$	0.786	1.91	330	100

vibrational modes determining the dissociation rate constant in phenol-water complexes in which dissociation occurs after complete energy randomization. Anharmonic force field-based calculations done in Ref. [345] gave evidence that the number of interconnected levels in the case of an O-H bond is greater than in the case of an O-D bond, in agreement with experimental findings. The lifetime of a complex versus hydrogen bond dissociation can be interpreted in terms of the RRKM theory. The RRKM model also describes the difference between the lifetimes of two complexes.



Figure 22. (Color online.) Temporal evolution of phenol- d_1 – D_2O complex absorption spectra at four various UV radiation frequencies: (a) OD₁⁰ band, and (b–d) bath states. Circles—experimentally obtained ionic signals in the pump–probe regime. Red and blue curves demonstrate changes in the level populations in bath-1 and bath-2 states, respectively (see the text) [345].

According to the RRKM theory [357, 358], the dissociation rate constant is expressed in the form

$$k(E) = \frac{1}{h} \frac{W(E - E_{\rm D})}{\rho(E)} , \qquad (7.4)$$

where $\rho(E)$ is the density of vibrational states in OH/OD modes at the complex energy E, h is the Planck constant, E_D is the energy of hydrogen bond dissociation in the complex, and $W(E - E_D)$ is the total number of quantum states of the complex in the transient state with excess energy $E - E_D$ (see Fig. 21). Complex predissociation times measured experimentally and calculated based on the RRKM theory are in excellent agreement [345] (see Tables 3 and 4).

The recent paper [170] reports on results of the first experimental on-line observation of molecular cluster dissociation under the effect of resonant femtosecond IR radiation. Let us consider them in greater detail. The study was carried out with the use of iron pentacarbonyl, $(Fe(CO)_5)_n$, clusters. The Fe(CO)₅ molecules are known to strongly absorb at a wavelength of 5 µm, which is due to valent vibrations (v₆ and v₁₀ modes) of C=O bonds. $(Fe(CO)_5)_n$ clusters were generated by gas-dynamic expansion of an Fe(CO)₅–argon mixture (Fe(CO)₅/Ar pressure ratio 1:50) at the exit from the pulsed nozzle. The mean cluster size in the beam was $250 \le \overline{n} \le 300$ [169,170].

A Ti:sapphire laser (Spectra-Physics) with a pulse repetition rate of 1 kHz, radiation wavelength $\lambda = 800$ nm, and pulse length $\tau_p = 50$ fs was used in experiments. Laser radiation was divided into two channels. One was intended to pump an optical parametric generator with an amplifier, which induced IR pulses for the vibrational excitation of the clusters. Radiation frequency in the other channel was doubled with a nonlinear crystal; it served to detect clusters and their fragments by UV multiphoton ionization with the aid of a photoionization mass spectrometer. IR pulses with a frequency of around 2000 cm⁻¹ and an energy up to $17 \,\mu J$ were obtained along with roughly 100-fs UV pulses $(\lambda = 400 \text{ nm})$. Experiments of two types [170] were conducted using IR pulses with the spectrum full width at halfheight (FWHM) equal to $\approx 105 \text{ cm}^{-1}$ and $\approx 185 \text{ cm}^{-1}$. IR pulse lengths were approximately 220 and 160 fs.

Multiphoton ionization of $Fe(CO)_5$ molecules by femtosecond pulses at a wavelength of $\lambda = 400$ nm produced a molecular ion peak in the mass spectrum (Fig. 23a), making possible the detection of free molecules in the beam.

The typical mass spectrum of ionic products formed upon $(Fe(CO)_5)_n$ cluster ionization by femtosecond radiation at $\lambda = 400$ nm is presented in Fig. 23b. The spectrum exhibits a



Figure 23. (a) Time-of-flight mass spectrum of an $Fe(CO)_5$ molecular beam (beam pulse length 200 µs); M^+ is the molecular ion. (b) Mass spectrum of a cluster beam (pulse length 300 µs); the signal is magnified 5 times for visual clarity. (c) Time-of-flight mass spectrum of a cluster beam in the IR-UV pump-probe regime. The delay time between pump and probe pulses is 1.4 ns [170].

'comb' of peaks formed by ions with masses surpassing the $Fe(CO)_5^+$ molecular ion mass. These ion peaks correspond to cluster fragments. They have the $Fe_x(CO)_y$ structure and reside as far apart from one another as the value corresponding to the mass of a single CO ligand (28 amu). The presence of these peaks in the spectrum permits the clusters in a beam to be distinguished against the monomers background. Cluster ionization at this wavelength gives rise to only a small number of molecular $Fe(CO)_5^+$ ions in the mass spectrum, which makes possible the detection of molecules formed upon cluster disintegration under the effect of IR radiation.

A mass spectrum obtained by irradiation of $(Fe(CO)_5)_n$ clusters with a femtosecond IR-pulse that vibrationally excites molecules in a cluster and with a UV pulse is presented in Fig. 23c. Energy density in the IR pulse $\Phi_{IR} = 32 \text{ mJ cm}^{-2}$; the time lag between IR and UV pulses is 1.4 ps. Cluster ion peaks diminish appreciably while molecular ion peaks, including the parent $Fe(CO)_5^+$ ion peak, increase. Strengthening of the signal from monomers serves as a reliable marker in studies of cluster decay.

Kinetic curves illustrating the yield of $Fe(CO)_5^+$ molecular ions depending on the time lag between pump and probe pulses and reflecting the appearance of free molecules as a result of cluster decay induced by femtosecond IR radiation



Figure 24. (Color online.) Dependence of $Fe(CO)_5^+$ molecular ion yield on the time lag between pump and probe pulses in the case of $(Fe(CO)_5)_n$ cluster excitation by an IR pulse with a spectrum width of 105 cm⁻¹ and energy density $\Phi_{IR} = 32$ mJ cm⁻² (red circles) and IR pulse with a spectrum width of 185 cm⁻¹ and energy density $\Phi_{IR} = 25$ mJ cm⁻² (blue circles); the signal is magnified 3 times for visual clarity. Solid curves results of calculations in terms of the two-step energy relaxation model (see the text) [170].

are presented in Fig. 24. These data were obtained in two series of experiments with IR pulses of various spectral widths. It was shown that narrower-band radiation (red circles in Fig. 24) causes a rapid enhancement of the signal at time delays starting from $\tau_{\rm D} \approx 400$ ps that rapidly leads to saturation in times over 1 ns. Only the initial stage of signal amplification is reached when broader-band radiation (blue circles in Fig. 24) is applied. A characteristic feature of the curves thus obtained is a certain 'induction time', suggesting that cluster fragmentation yielding free molecules is preceded by relaxation processes on a characteristic time scale of about 10^{-10} s. When clusters are excited by broaderspectrum IR radiation, the 'induction time' is longer than in the case of their excitation by narrower-spectrum radiation. The authors of Ref. [170] ascribe this situation to the difference between amounts of energy absorbed by the clusters, arising from the difference in spectral widths of IR pulses and energy densities ($\Phi_{IR} = 32$ and 25 mJ cm⁻² for pulses with a spectral width of 105 and 185 cm⁻¹, respectively).

The analysis of the data obtained enabled the authors of paper [170] to conclude that fragmentation of $(Fe(CO)_5)_n$ clusters excited by femtosecond IR laser pulses can be regarded as a process of sequential evaporation of their molecules due to cluster heating associated with intramolecular and intracluster (intermolecular) relaxation of the energy absorbed from the initially IR-excited cluster molecules. Based on this inference, the authors of Ref. [170] developed a model that fairly well describes the experimental behavior of the Fe(CO)_5^+ molecular ion signal, depending on the time lag between pump and probe pulses.

Model [170] postulates that the magnitude of the $Fe(CO)_5^+$ ion signal is a function of the mean cluster size \bar{n} , its starting temperature T_0 (these two parameters, in turn, depend on the cluster formation conditions), energy ΔE needed to successively evaporate molecules from the cluster, its effective IR absorption cross section, and energy relaxation rate constants. The internal energy of a cluster composed of *n* molecules is expressed in the general form as

$$E_{\rm cl}(T,n) = (3n-6) k_{\rm B}T + n E_{\rm vib}(T) , \qquad (7.5)$$

where the first term on the right-hand side denotes the vibrational energy of intracluster molecules, the second term shows the internal vibrational energy of *n* individual molecules, and *T* is the cluster temperature in the near-equilibrium state. The value of $E_{\rm vib}$ was calculated from the known vibrational frequencies of an Fe(CO)₅ molecule. The IR radiation energy absorbed by the cluster was found from the relation

$$E_{\rm abs} = n\sigma \Phi_{\rm IR} \,, \tag{7.6}$$

where *n* is the cluster size, and σ is the absorption cross section of a single molecule. Cluster dissociation rate constants k_{diss} were calculated based on the concept of an 'evaporation ensemble' formed by the clusters cooling as a result of particle evaporation (see Refs [310–313] and also [314]).

It follows from the above studies that dissociation (evaporation) rate constants are given by (6.3)-like relations. The pre-exponential constant *A* depending on the cluster size and entering formula (6.3) can be found from the relation $A(n) = 3 \times 10^{13} n^{2/3} \exp(6.0/n^{1/3})$ [312] ($A = 3.13 \times 10^{15} \text{ s}^{-1}$ for n = 260). In general, ΔE is also a function of the cluster size: $\Delta E(n) = \Delta E f(n)$. However, the expression for f(n) has an appreciable influence on ΔE only for small clusters [314, 323]; therefore, the ΔE value in model [170] was assumed to be constant.

The energy stored in $C \equiv O$ bond vibrations passes during relaxation into intermolecular vibrations of a cluster, which increases its temperature in accordance with formula (7.5). A rise in cluster temperature leads, in turn, to an increase in the dissociation rate constant k_{diss} , depending on the energy E_{abs} absorbed by the cluster and energy relaxation rate constants. Cluster temperature grows monotonically till k_{diss}^{-1} becomes equal to the time elapsed from the moment of IR- excitation onset. At this moment, the first molecule evaporates from the cluster. Each subsequent molecule takes away energy ΔE and thereby contributes to cooling the cluster. Its new temperature T' is determined from the energy balance equation

$$E_{\rm cl}(T',n) = E_{\rm cl}(T,n-1) + E_{\rm mol}(T) + \Delta E, \qquad (7.7)$$

where $E_{\text{mol}}(T) = (7/2)k_{\text{B}}T + E_{\text{vib}}(T)$ is the energy of an evaporated molecule. The further evolution of cluster temperature on a nanosecond time scale depends on the competition between relaxation-related heating and cooling by successive evaporation of molecules.

Based on the above relations, the authors of Ref. [170] used the rate equation approximation to describe the intracluster relaxation processes. They considered one- and two-step energy relaxation models (Fig. 25a). In the two-step model, the energy of $C \equiv O$ bond vibrations first spreads among low-frequency modes of $Fe(CO)_5$ molecules (bath-1) with a rate constant k_1 . Then, the intermolecular redistribution of the energy occurs (bath-2) with a rate constant k_2 . Finally, clusters residing in the bath-2 mode dissociate with a rate constant k_{diss} . The one-step relaxation model assumes that the energy of $C \equiv O$ bond vibrations is instantaneously distributed among all internal and intermolecular vibrational modes of a cluster (bath-2) with the rate constant k'.

The authors of Ref. [170] could not accurately determine the relaxation rates k_1 and k_2 , because they failed to experimentally observe the evolution of populations of Fe(CO)₅ low-frequency modes (bath-1 in Fig. 24a). Therefore, they assumed k_1 and k_2 to be equal for the purpose of



Figure 25. (Color online.) (a) Diagram of energy flow in an IR-excited $(Fe(CO)_5)_n$ cluster. Two schemes of energy relaxation into a single bath mode (with relaxation rate constant k') and successively into two bath modes (with relaxation rate constants k_1 and k_2). (b) Normalized time profiles describing vibrational energy redistribution and dissociation output of $(Fe(CO)_5)_n$ clusters. Results of calculations for two- and one-step vibrational energy relaxation models are shown by solid and dashed lines, respectively. Experimental data obtained using an IR pulse with the spectral width of 105 cm⁻¹ (red circles) are normalized to the maximum calculated signal amplitude [170].

model calculations, although such an assumption does not follow from experiment. Experimental results are well described by both the one-step relaxation model with time $(k')^{-1} = 600$ ps and the two-step model with times $k_1^{-1} = k_2^{-1} = 280$ ps. Nevertheless, simulation of the two-step energy relaxation mechanism yielded better agreement with experimental data (Fig. 25b). The time of 280 ps is consistent with the relaxation time for Fe(CO)₅ molecules in a solvent, where relaxation evolves as a two-step process, too. The energy of $C \equiv O$ bond vibrations is first redistributed among lowfrequency molecular modes for approximately 150 ps and only afterwards relaxes in the solvent [361].

8. Conclusions

The main achievement and the most important result of the studies considered are the elucidation of the physical nature and measurement of absorbed energy relaxation times during IR laser-induced excitation of complex quantum systems, such as clusters composed of polyatomic molecules linked by van der Waals bonds. Equally important are the results of investigations into cluster structure and composition. The above studies revealed many characteristics of IR photodissociation and photofragmentation of molecular clusters and atomic-molecular complexes, as well as energy relaxation channels and times, and cluster decay times and channels. The dependence of these characteristics on the parameters of exciting laser radiation (wavelength, duration, pulse energy), energy input and relaxation channels, structure, composition, and environment of the clusters was demonstrated.

The available methods for cluster beam generation (generation in gas-dynamic jets, laser-assisted generation of molecular complexes containing metal atoms, cluster doping with atoms and molecules) make it possible to obtain homogeneous and heterogeneous molecular clusters and atomic-molecular complexes of different sizes, structures, and elemental compositions. Methods for size-selecting clusters (mass spectrometry, cluster diffraction by atoms, doping clusters with low-ionization energy atoms and molecules) are used to form or selectively detect clusters of a desired size in the cluster beam with a broad size distribution. This opens up good prospects for the investigation of laserinduced size-dependent intracluster processes.

It has been shown that IR laser photodissociation and photofragmentation of molecular clusters and atomic-molecular complexes provide powerful tools for the spectroscopic study of interaction between radiation and matter at the atomic-molecular level. Copious valuable information on the structure, composition, and dynamics of molecular clusters and complexes, bond strengths, energy relaxation channels, stable configurations, coordination numbers, fragmentation channels, and environmental impacts has been obtained by these methods. The photodissociation and photofragmentation spectra of numerous molecular clusters and atomic-molecular complexes were investigated, as well as energy distributions of the fragments formed. IR photodissociation spectroscopy allowed phase transitions in large molecular water clusters to be observed.

Molecular cluster fragmentation induced by 100-ns laser pulses has been shown to proceed as a statistical process independent of the energy input channel. The statistical character of cluster decay has been confirmed in experiments on cluster excitation by continuous and pulsed IR radiation. The fragmentation rate highly depends on cluster structure and environment. Cluster excitation by pico- and femtosecond laser pulses results in energy distribution first inside the excitable molecules and thereafter over the entire cluster. Data have been obtained on both the intramolecular and intracluster vibrational energy relaxation rates and cluster fragmentation dynamics.

It has been shown that the relaxation of vibrational energy in molecular clusters occurs as a many-step process, while the process of dissociation is characterized by an exponential dependence on excitation energy density and well described in the framework of the evaporation ensemble model. Cluster fragmentation can be regarded as a process of successive evaporation of molecules from a laser-heated cluster. In most cases, cluster decay is fairly well described by the statistical theory of monomolecular disintegration. At the same time, experiments have also demonstrated the possibility of nonstatistical more rapid cluster fragmentation and the possibility of realizing site-selectivity in cluster excitation. Of great interest in this context are experiments on site-selectivity in clusters having a few van der Waals bonds with different energies (e.g., in trimers consisting of different molecules).

There is evidence that free [for example, $(CF_3I)_n$] clusters and clusters located inside or on the surface of large inert gas clusters (Xe_m) show a different resistance to fragmentation by IR radiation and a different dependences of probability of fragmentation on IR radiation energy flux density. The strongest dependence of the probability of fragmentation on energy density and the cluster fragmentation at low energy densities have been documented for free clusters. A weaker dependence was observed for clusters localized inside inert gas clusters and even weaker dependence for those on the surface of inert gas clusters. The main cause behind higher stability (less efficient IR-induced fragmentation) of the clusters inside and on the surface of noble gas clusters is the existence of an effective absorbed energy relaxation channel in the form of evaporation of gas atoms. The difference between the above dependences may also be due to the different energy content of individual cluster types related to their size, temperature, and geometric structure.

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