# Control of the parameters and composition of molecular and cluster beams by means of IR lasers

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Abstract. The widespread use of molecular and cluster beams in research and practice makes it necessary and relevant to develop methods to control their parameters and composition. Among the methods already developed, those based on using lasers play a considerable role. In this paper, we present results of research on the use of infrared (IR) lasers to control the parameters and composition of molecular and molecular cluster beams. We describe the methods and present research results on neutral molecular beam acceleration due to the vibrational excitation of molecules at the nozzle outlet. We review experimental results on high-energy molecule production and the generation of molecular radicals in secondary pulsed molecular beams obtained by forming a pressure shock in front of a solid surface interacting with an intense pulsed gasdynamically cooled molecular flow, with molecules excited by the laser directly at the secondary beam source. Molecular beam kinetic energies of one to several electron volts have been achieved by this method. The optimum conditions for obtaining high-energy molecules are found. Methods for determining the composition and content of pulsed molecular cluster beams are considered, as are results on the IR laser control of the composition and

Received 27 June 2017, revised 21 September 2017 Uspekhi Fizicheskikh Nauk **188** (7) 689–719 (2018) DOI: https://doi.org/10.3367/UFNr.2017.10.038269 Translated by M N Sapozhnikov; edited by A M Semikhatov content of molecular cluster beams using the resonance vibrational excitation of molecules and clusters by laser radiation in the zone of gasdynamic nozzle outlet expansion. Other methods, including laser-based ones, for controlling the velocity of beam atoms and molecules are briefly discussed.

**Keywords:** atom, molecule, cluster, nanoparticle, molecular and cluster beam, method for detecting molecular and cluster beams, laser-based control of the parameters and composition of molecular and cluster beams

## 1. Introduction

Today, molecular and cluster beams are widely used in research and practical applications (see, e.g., monographs and collections of research papers [1–19] and reviews [20–53]). Among them are high-energy molecular beams [21, 37, 54–72], in which the kinetic energy of molecules (atoms) considerably exceeds their thermal energy at room temperature ( $E_{\rm kin} \leq 0.025 \text{ eV}$ ), and low-energy molecular beams [39, 40, 69–79], in which the kinetic energy of particles is considerably lower than their thermal energy at  $T \approx 300 \text{ K}$ .

The intense beams ( $\geq 10^{18} - 10^{20}$  molecules/sr s) of accelerated molecules with a kinetic energy ranging from one to a few electronvolts are required in various fields of fundamental and applied investigations for studying chemical reactions with energy barriers, elastic and inelastic collisions, the interaction of molecules with surfaces, and simulations of the near-Earth orbital space [21, 54–61]. Low-energy molecular beams are required for studying chemical

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reactions without barriers, in spectroscopy, cold chemistry, precision measurements with laser, magnetic, and optical traps, etc. [39, 40, 69–79].

Cluster beams are extensively used to study the interaction of radiation with matter, in particular, under extremal conditions and also in various practical applications [8, 9, 230, 28-34, 37, 44, 47, 80-158]. The excitation of clusters by ultrahigh-power ultrashort laser pulses [80-97] allows producing highly ionized atoms and high-energy ions, observing Coulomb and hydrodynamic explosions of clusters [80-97], and obtaining X-rays [98-109] and neutrons [110-118]. Highenergy clusters and cluster ions are used for studying their interaction with surfaces [8, 9, 21, 29-31, 33, 47], the initiation of chemical reactions [119–128], the deposition of films [9, 29, 30, 33, 129-144], and surface processing [145-158]. Interest in clusters and cluster beams greatly increased due to the rapid development of nanotechnology [159-162]. Laser-induced intracluster physicochemical processes were recently extensively investigated in molecular van der Waals clusters [24, 28, 42, 48, 163-193]. Their spectra and structure were studied in [18, 22, 23, 28, 41, 42, 45, 49–52, 163–169], temperature in [31, 36, 43, 173–176, 178], and intracluster dynamics in [22, 233, 41-43, 45, 48, 164-168, 181, 183, 186, 187, 192]. The fragmentation of clusters upon intense resonance excitation of molecules in clusters by IR laser pulses was studied in [48, 172, 180, 181, 183, 186, 187, 190, 192, 193]. Selective processes involving cluster and molecular beams were studied in [25, 27, 170, 184, 185, 188, 191, 193]. Cluster beams also attract interest in and of themselves by their properties and the processes in which they participate [8, 10-17, 29, 31-35, 44, 46, 192].

Because molecular and cluster beams are widely used in both research and practical applications, the development of methods to control their parameters and composition is an important and urgent issue. This review presents the results of studies on controlling the parameters and composition of molecular and molecular cluster beams by IR lasers. We restricted ourself to the consideration and analysis of methods for obtaining high-energy neutral molecular beams (with the kinetic energy from  $\approx 0.1$  to 5 eV) and controlling their parameters, leaving aside the analysis of many papers on obtaining and controlling low-energy molecular and atomic beams. However, we also briefly consider the methods used to obtain and control the parameters of both high-energy and low-energy atomic and molecular beams.

The most widespread method for obtaining intense molecular and cluster beams is their separation by skimmers from gasdynamically cooled jets obtained with the help of continuous or pulsed nozzles [4–8, 26, 29, 34, 50–52]. The main characteristics of molecular beams are the intensity, velocity, and width of the velocity distribution of molecules or atoms in the beam (the gas cooling degree). The important characteristics of cluster beams are the composition and content of clusters in the beam. The analysis of the methods and results of studies on controlling these parameters of molecular and cluster beams is the aim of this review.

We note two recent reviews by the author [188, 192], in which processes in clusters vibrationally excited by IR lasers were also discussed. In this connection, we emphasize that this review differs from [188, 192]. In [188], we considered problems related to the development of low-energy methods of molecular laser isotope separation involving molecular and cluster beams, based on isotope-selective vibrational excitations of molecules and small van der Waals clusters by IR lasers. In [192], we considered and analyzed methods of spectroscopy of clusters and atomic–molecular complexes based on their IR vibrational predissociation, as well as methods for studying the intracluster dynamics. These methods involve measuring the intramolecular and intracluster relaxation times for energy absorbed by clusters and the fragmentation times of clusters vibrationally excited by highpower ultrashort IR laser pulses. In this review, we address totally different questions from those discussed in [188, 192], namely, the methods and results of controlling parameters and the composition and content of initial molecular and cluster beams themselves. This review therefore substantially differs from [182, 192] by its subject, presented results, contents, and the essence of the problems considered.

This review is organized as follows. In Section 2, we briefly describe methods for obtaining accelerated molecular beams and controlling their parameters using nozzle heating, aerodynamic acceleration, the formation of discharges of different types in a source, and resonance excitation of molecules by CW IR lasers. The fundamentals of methods and the results of earlier studies are considered. A method for obtaining accelerated and decelerated molecular beams with the help of a rotating beam source is described. We analyze precision laser methods to control the motion of atoms and molecules, including their acceleration and deceleration, by using dipole and ponderomotive forces, gradient fields, and periodic potentials (optical gratings) produced by intense ultrashort laser pulses.

In Section 3, we consider a method for obtaining accelerated molecular beams using multiphoton IR excitation of molecules in the gas expansion region directly at the nozzle exit. The fundamentals of the method and its realization in experiments are described. The experimental setup is considered and the results of producing accelerated molecular beams are analyzed. The optimal conditions for obtaining accelerated molecular beams are found. It is shown that this method allows obtaining molecular beams with kinetic energies ranging from 0.01–0.02 eV to 1.0–1.2 eV.

Section 4 is devoted to the detailed description and analysis of a method for obtaining high-energy molecules in secondary pulsed molecular beams produced in the interaction of intense pulsed gasdynamically cooled molecular beams (flows) with solid surfaces. A method for obtaining intense secondary pulsed molecular beams is described. The results of studies on producing accelerated and decelerated molecules in secondary beams are analyzed. The optimal conditions for obtaining high-energy molecules in secondary pulsed molecular beams, it is possible to obtain high-energy molecules with the kinetic energy ranging from 0.01–0.02 eV to 1.5–3.0 eV, as well as accelerated molecular radicals.

In Section 5, methods for determining the composition of cluster beams are considered. A new method is described in detail in which the composition and content of neutral pulsed cluster beams are analyzed by the ion signals of cluster fragments reflecting the time-of-flight spectra of clusters in beams. This method can be used to determine the composition and content of neutral van der Waals molecular and atomic-molecular clusters in beams, both homogeneous and mixed. The potential of the method is demonstrated by the example of beams with mixed  $(SF_6)_mAr_n$  clusters (where  $1 \le m \le 4$  and  $0 \le n \le 9$  are the respective numbers of molecules in atoms and clusters) of different sizes.

Section 6 is devoted to the description and analysis of experimental studies on controlling the composition and content of molecular cluster beams using the resonance vibrational excitation of molecules and clusters by IR lasers near the nozzle exit, resulting in the suppression of clustering of molecules and dissociation of small clusters in the beam. Studies were performed with SF<sub>6</sub> and CF<sub>3</sub>I molecular gases diluted in argon or xenon and excited by CW CO<sub>2</sub> lasers. The experimental setup and method are described. The results of studies on the suppression of clustering of molecules and the dissociation of clusters are presented. The conditions that provide the most efficient control of molecular clustering and cluster dissociation in beams are found.

Finally, Section 7 presents the main results of studies discussed in the review and the most important advances and prospects, in the author's opinion.

# 2. Methods for obtaining accelerated molecular beams and controlling their parameters

### 2.1 Fundamentals of the methods.

### **Results of earlier studies**

The range of particle energies from approximately one to a few electronvolts is difficult to utilize, and today no universal methods exist for obtaining molecular (atomic) beams with kinetic energies in this range. There are several strategies to solve this problem [6–8, 54–61]. They can be classified according to the process used for controlling the energy of atoms or molecules. Some methods are based on electrostatic process using the neutralization of accelerated ion beams [54]. Other methods use the thermodynamic process based on the separation of molecular (atomic) beams from supersonic jets with the help of skimmers.

In the first case, the kinetic energy of molecules is controlled by selecting a voltage across accelerating electrodes placed in the way of charged particles of the beam. In other cases, the energy (velocity) of beam particles is controlled by varying the gas temperature  $T_0$  before expansion through a nozzle. The velocity of beam particles is related to the temperature  $T_0$  as [4–8, 56, 57]

$$\frac{1}{2}mv^{2} = \frac{\gamma}{\gamma - 1}k_{\rm B}(T_{0} - T_{\parallel}), \qquad (2.1)$$

where v is the steady-state flow velocity, m is the molecule (atom) mass,  $\gamma = c_p/c_V$  is the ratio of specific heats of the expanding gas (adiabatic exponent),  $k_B$  is the Boltzmann constant, and  $T_{\parallel}$  is the steady-state temperature of molecules or atoms in the beam. It follows from (2.1) that at room temperature of a gas in a source, the energy of molecules in the beam, depending on the value of the adiabatic exponent  $\gamma$ , is approximately from  $\approx 50-60$  meV (for a monatomic gas) to  $\approx 150-200$  meV (for a gas of polyatomic molecules).

Thus, at room temperature of a gas in a source, the kinetic energy of molecules in the beam cannot be increased, except when the gas under study is diluted in a lighter carrier gas (H<sub>2</sub>, He, CH<sub>4</sub>, ...) [194, 195]. This method, called the aerodynamic acceleration technique, is not efficient enough when the mass ratio of the gas under study and the carrier gas is small. This technique can be combined with nozzle heating to  $T_0 \approx 3000$  K. The methods using nozzle heating to high temperatures are

not universal because chemical reactions, dissociation of molecules, and damage of materials can occur at high temperatures.

Other methods were developed for obtaining energy beams of hydrogen and oxygen atoms. The photolysis of HBr [196, 197] or HI [198, 199] was used to generate highenergy hydrogen atoms. The photolysis of molecules in these methods performed by pulsed lasers gives very low-intensity hydrogen atom flows. High-energy atomic beams can be obtained by combining the dissociation of molecules with gas heating by a discharge [55] ignited in the corresponding gas medium. Microwave [60, 200], radiofrequency [201], and arc [202, 203] discharges were used to generate oxygen atomic beams for studying chemical reactions. The kinetic energy of oxygen atoms thus obtained is  $\leq 0.8$  eV and controlling their energy is rather difficult.

High-energy atomic beams were generated in [56, 204– 207] using pulsed or continuous optical discharges [208, 209]. In the method using a continuous optical discharge, a plasma is ignited by a pulsed laser or an electric spark and is maintained by a CW CO<sub>2</sub> laser (Fig. 1) [57, 58]. The plasma is ignited inside a nozzle directly in front of the exit opening. This method was used in [56–58] to obtain atomic argon beams with kinetic energies up to 2.55 eV. By combining the nozzle heating with aerodynamic acceleration and using hydrogen as the carrier gas (with the pressure ratio  $p(Xe)/p(H_2) = 0.23/100$ ), the authors of [210] obtained continuous atomic xenon beams with kinetic energies up to  $\approx 30$  eV.

A considerable increase in the velocity of SF<sub>6</sub> molecules in a beam was observed in [211] upon their resonance irradiation by a CW CO<sub>2</sub> laser inside a nozzle capillary transparent to laser radiation directly in front of the exit opening. The kinetic energy of laser-excited molecules was  $\approx 0.21$  eV. In [212, 213], the acceleration of SF<sub>6</sub> molecules was observed (by 5–25%) in a continuous supersonic jet excited by a 5–20 W CW CO<sub>2</sub> laser (at the gas pressure  $\approx 2$  atm above the nozzle) in the collision region near the nozzle exit. In experiments [211–213], molecules in a beam were accelerated due to their vibrational laser excitation, which was partially transformed in collisions into the directional motion of molecules.

The method of aerodynamic acceleration in combination with nozzle heating was used in [214, 215] to accelerate neutral silicon cluster isomers  $Si_N$  (with N = 20-109) in a mixture with helium as the carrier gas. Silicon clusters were generated



Figure 1. Schematic of a free plasma jet maintained by an IR laser and an atomic-beam generator with a time-of-flight analyzer [56, 58].

by evaporating a silicon rod placed near the nozzle exit using a pulsed Nd:YAG laser. In this case, silicon cluster isomers of cylindrical and spherical shapes were produced. Because these isomers have different cross sections in collisions with helium atoms, the efficiency of their acceleration by atoms varies. As a result, clusters with different shapes have different final velocities in the beam and therefore different time-of-flight spectra. The relative content of isomers in the beam could be changed by varying the source temperature, which, in turn, resulted in a change in the time-of-flight spectra of clusters. By analyzing time-of-flight spectra, the authors determined the relative content of silicon cluster isomers in the beam and their aspect ratio, and studied the dependence of the aspect ratio on the cluster size. It was found in [214] that cylindrical isomers are metastable and their concentration in the beam decreases with increasing the source temperature.

# **2.2** Controlling the velocity of molecular beams with a rotating source

The original method for obtaining accelerated and decelerated molecular beams was proposed and developed in [69– 72]. The method uses a rapidly rotating beam source (Fig. 2a). The molecular beam source is placed near the cusp of a hollow rapidly rotating rotor, allowing the velocity distribution of the beam to be displaced forward or backward in a broad velocity range with respect to the distribution obtained with a stationary source (Figs 2b, c). It can be seen from Fig. 2a that the method for obtaining accelerated or decelerated molecular beams is based on the fact that in the laboratory frame, the velocity of molecules obtained with a source at rest increases or decreases approximately by the value of the peripheral velocity of the rotating beam source.

The velocity distribution of molecules in the molecular beam in the laboratory frame obtained in this way is [70, 72]

$$F(V) = C_{\rm N} V^2 (V - V_{\rm rot}) \exp\left[-\left(\frac{V - u_{\rm lab}}{\Delta v}\right)^2\right],\qquad(2.2)$$

where  $C_N$  is the normalization constant depending on the gas pressure above the nozzle and the setup parameters,  $V_{\text{rot}}$  is the peripheral velocity of the beam source (rotor),  $u_{\text{lab}} = u + V_{\text{rot}}$ is the flow velocity along the central axis of the beam in the laboratory frame, and u is the flow velocity with respect to the rotating nozzle exit. In the deceleration regime, the rotor rotates in the opposite direction with respect to the gas flow coming out from the nozzle ( $V_{\text{rot}} < 0$ ); in the acceleration regime, the rotor rotates in the flow direction ( $V_{\text{rot}} > 0$ ) (Fig. 2a). The flow velocity and the width of the velocity distribution of molecules in the beam (the gas cooling degree) are given by

$$u = \left(\frac{2k_{\rm B}T_0}{m}\right)^{1/2} \left(\frac{\gamma}{\gamma - 1}\right)^{1/2} \left(1 - \frac{T_{\parallel}}{T_0}\right)^{1/2}, \qquad (2.3)$$

$$\Delta v = \left(\frac{2k_{\rm B}T_{\parallel}}{m}\right)^{1/2}.\tag{2.4}$$

The steady-state local (sometimes called parallel or longitudinal) temperature  $T_{\parallel}$  of molecules in the beam corresponds to the forward motion of molecules with respect to the flow velocity and determines the width of the velocity distribution of molecules in the beam in accordance with (2.4).

The setup of this method is shown in Fig. 3. Table 1 presents the parameters of molecular beams produced by this



**Figure 2.** (a) Schematic of a rotating molecular beam source in the regime of generating decelerated beams (top view). (b) Time-of-flight spectra of supersonic atomic argon beams obtained in the beam acceleration  $(V_{\rm rot} = 186 \text{ m s}^{-1})$  and deceleration  $(V_{\rm rot} = -186 \text{ m s}^{-1})$  regimes. (c) The same spectra transformed into velocity distributions of particles. The nozzle diameter is d = 0.01 cm, the gas pressure above the nozzle is  $p_0 = 30$  Torr ( $p_0d = 0.3$  Torr cm). The dashed curve shows the velocity distribution of particles in a stationary beam [70].

method of 'rotating supersonic molecular beams' [70]. The accelerated and decelerated molecular beams of inert gases, oxygen,  $CH_3F$ , and  $SF_6$  have been obtained. The deceleration of  $O_2$  and  $CH_3F$  molecules was also performed in combina-

Atoms, molecules	$p_0 d$ , Torr cm	$V_{\rm rot},{ m m~s^{-1}}$	$u_{\rm lab},{ m m~s^{-1}}$	$E_{\rm lab}/k_{\rm B},{ m K}$	$\lambda_{\rm lab},{ m \AA}$	$\Delta v,  { m m \ s^{-1}}$	$T_{\parallel}, \mathrm{K}$		
Ar	1.12	-403	170	70	0.582	87	18		
Ar	1.02	0	518	645	0.191	75	14		
Ar	1.15	+403	974	2282	0.102	64	10		
Xe	1.03	-273	59	27	0.512	31	7.7		
Xe	1.04	0	295	686	0.102	34	9.1		
Xe	17.1	+403	720	4084	0.042	18	2.6		
$SF_6$	2.31	-310	55	27	0.493	80	57		
$SF_6$	0.224	0	307	828	0.088	94	77		
$SF_6$	16.6	+403	763	5112	0.036	68	41		
O <sub>2</sub> in Xe	1.53	0	299	172	0.414	39	2.9		
O <sub>2</sub> in Xe	1.83	-248	67	8.6	1.85	85	14		
CH <sub>3</sub> F in Xe	1.52	0	319	208	0.365	43	3.7		
CH <sub>3</sub> F in Xe	1.66	-248	91	17	1.28	94	18		
* The parameter $\lambda_{lab}$ corresponds to the de Broglie wavelength $\lambda_{B}$ in the laboratory frame.									

Table 1. Parameters\* for rotating supersonic jets [70].

tion with the aerodynamic method using heavy xenon carrier gas for deceleration. This method can provide a considerable acceleration or deceleration of atoms and molecules in the beam. For example, decelerated and accelerated atomic Xe beams with velocities  $40 \pm 5 \text{ m s}^{-1}$  and 720 m s<sup>-1</sup> [70, 72] and molecular SF<sub>6</sub> beams with velocities 55 and 763 m s<sup>-1</sup> were obtained [70].

An upgraded version of this source [71] can produce intense pulsed molecular beams with durations from 0.1 to 0.6 ms (depending on the rotor rotation velocity). The number of molecules in the beam is about  $10^{12}$  for the beam velocity  $\approx 35 \text{ m s}^{-1}$  and about  $10^{15}$  for the beam velocity 400 m s<sup>-1</sup>. This method can be used for decelerating or accelerating the beams of virtually any molecules in the gas phase. Beams with a controllable velocity are of interest for experimental studies of collisions between particles at low energies and chemical reactions with low barriers in molecular beams intersecting at a small angle (merging). For low velocities of particles in the beam, when the de Broglie wavelength  $\lambda_B$  becomes comparable to the distance between particles, quantum effects begin to reveal themselves in the interaction. It becomes possible to study their influence on the processes. (We recall that  $\lambda_{\rm B} = h/p = h/(mv)$ , where h is Planck's constant, p is the momentum, and m and v are the particle mass and velocity.)

The main disadvantage of this method is that only a small part of the gas escaping from the nozzle is used to obtain the beam, whereas most of the gas is scattered in a vacuum chamber, producing an undesirable background. Among other disadvantages, besides the complexity of the method, we note that such a source cannot produce molecular beams of semivolatile compounds, when, for example, laser evaporation of samples has to be used. The beam source under study can be used only for gases with a high vapor pressure under normal conditions.

# **2.3 Precision laser methods for accelerating and decelerating atoms and molecules**

Currently, precision laser methods for accelerating [74, 216–218] and decelerating [73–79] atomic and molecular beams are being extensively developed. Special attention has been devoted to the development of methods to decelerate atomic and molecular beams (see, e.g., [73, 76–79] and the references therein).

Low-energy atomic and molecular beams have been used for laser control of the motion of atoms and molecules in electric and magnetic fields (traps) [219–221], in particular, for developing laser methods for cooling and trapping atoms [222–224], producing Bose–Einstein condensates [226–227], atomic fountains [228, 229], and clocks [229–233].



**Figure 3.** Schematic of the experimental setup with a rotating beam source: (a) equipment for time-of-flight measurements (top view), (b) (side view) the rotor, elements of the gas supply and the rotor rotation mechanism, including components for its water cooling and dampers for suppressing vibrations [70].

We note that the 1997 Nobel Prize in Physics was awarded to S Chu, W Phillips, and C Cohen-Tannoudji "for development of methods to cool and trap atoms with laser light" [222–224], and the 2001 Nobel Prize in Physics was awarded to E A Cornell, W Ketterle, and C E Wieman "for the achievement of Bose–Einstein condensation in dilute gases of alkali atoms, and for early fundamental studies of the properties of the condensates" [226, 227].

Some of the precision laser methods for controlling the motion of atoms and molecules can also be used for accelerating these particles. The methods are based on using either ponderomotive forces produced by intense laser pulses interacting with atoms [217, 234], or pulsed gradient fields [235], dipole forces [236, 237 or periodic potentials (optical gratings) produced by two lasers [74, 216, 218].

Dipole forces induced by high-power nonresonance laser radiation were used to deflect  $CS_2$  [236, 237] and I<sub>2</sub> [237] molecules from a beam and accelerate and decelerate them. In these studies, a molecular beam intersected at the right angle with a focused laser beam. In this case, the transverse velocity of molecules in the beam changed. It was found that the change in the velocity was proportional to the gradient of the laser beam intensity, and an intense laser beam can therefore be used as a lens for molecular beam focusing.

The experimental setup is presented in Fig. 4a [236]. A pulsed CS<sub>2</sub> molecular beam was produced during the expansion of the  $CS_2$  gas at a pressure of approximately 25 Torr either without a carrier or with neon as the carrier gas at a total pressure of 1 atm through a nozzle 250 µm in diameter; the beam was detected with a time-of-flight mass spectrometer mounted perpendicular to the beam axis. The nozzle operated at a frequency of 10 Hz. The molecular beam intersected at a distance of about 8 cm from the nozzle at 90° with a focused beam from a 1.06  $\mu$ m,  $E_p \approx 10$  mJ Nd:YAG laser emitting 14 ns pulses (full width at half maximum (FWHM)) with the pulse repetition rate f = 10 Hz [236, 237] or a CO<sub>2</sub> laser ( $\lambda = 10.6 \ \mu m$ ,  $p \approx 600 \ mJ$ ,  $f = 10 \ Hz$ ,  $\tau_p = 70$  ns) [237]. Laser radiation was focused with a parabolic mirror onto a Gaussian spot  $\omega_0 = 7 \ \mu m$  in size in the waist in the region of intersection with the molecular beam. The peak intensity in the focus was  $I_0 \sim$  $9 \times 10^{11}$  W cm<sup>-2</sup> for the 10 mJ pulse.

In the experiments in [236, 237], a change in the transverse velocity of molecules in the beam was measured (along the time-of-flight spectrometer axis y (Fig. 4a)). Neutral molecules were detected by ionizing them by a tightly focused 625 nm femtosecond laser beam, and the time-of-flight distribution of  $CS_2^+$  ions was measured in the space between the interaction region and the multichannel plate of the mass spectrometer detector. We can see from Fig. 4b that by changing the geometry of molecular beam irradiation by a focused beam from an Nd:YAG laser, it is possible either to accelerate or to decelerate molecules, as well as to focus them.

The method is based on inducing a dipole moment in molecules of the beam entering the focal region of the Nd:YAG laser. This causes the Stark shift U of the ground state of the molecule [238]:

$$U(x, y, z, t) = -\frac{1}{4} \alpha E^2(x, y, z, t), \qquad (2.5)$$

where E(x, y, z, t) is the pulse envelope depending on space and time and  $\alpha$  is the molecular polarizability. With the static polarizabilities of CS<sub>2</sub> and I<sub>2</sub> molecules, the authors of [236, 237] used relation (2.5) to estimate the laser-produced Stark



**Figure 4.** (a) Experimental setup (in the vacuum chamber part) for the laser deflection of  $CS_2$  molecules. The view in the direction of the IR laser beam deflecting  $CS_2$  molecules (along the *z* axis). MCP detector is a microchannel plate detector. (b) A part of the time-of-flight spectrum showing the time of arrival of  $CS_2^+$  ions at the detector from the nondeflected (solid curve) and deflected (dotted and dashed curves) beams. The relative locations of the foci of the IR laser deflecting molecules and the ionizing laser are shown. The difference between the arrival times of deflected molecules of the beam and molecules with zero transverse velocity allows determining the transverse velocity of molecules in the beam. The horizontal scales show the time of arrival of molecules at the detector and their transverse velocity  $V_y$  [236, 237].

potentials at the laser focus center for the intensity  $I = 9 \times 10^{11}$  W cm<sup>-2</sup> and  $U_0 = 10$  and 12 meV for CS<sub>2</sub> and I<sub>2</sub> molecules, respectively. The Stark potentials calculated by the authors from their experimental measurements of the acceleration and deceleration of CS<sub>2</sub> and I<sub>2</sub> molecules [237] were  $U_0(CS_2) = 7$  meV and  $U_0(I_2) = 6.6$  meV, in good agreement with estimates taking inaccuracies in the determination of laser field parameters into account. The transverse velocity of CS<sub>2</sub> molecules in the beam (without a carrier gas) was initially about 0.7 m s<sup>-1</sup>, and after the action of the laser deflecting particles reached  $\approx 11$  m s<sup>-1</sup>; in other words, molecules were accelerated (and decelerated) by approximately 10 m s<sup>-1</sup> (Fig. 4b) by a 14 ns pulse [236].

These papers have demonstrated the possibility of controlling the transverse velocity of molecules in a beam and focusing molecular beams. The method can be applied to virtually all molecules and atoms. At the same time, as follows from these papers, this method can be used to control the velocity of low-energy atomic and molecular beams and to obtain accelerated or decelerated very-lowintensity beams.

The acceleration of neutral atoms by ponderomotive forces in the strong field of short laser pulses was studied in [217, 234]. Experiments in [217] and theoretical calculations in [234] were performed with helium atoms. Studies [217] were performed with an effusive atomic beam (pressure in the source was  $\approx 3.75 \times 10^{-7}$  Torr). Atoms were excited to the metastable He\* state by 40-120 fs, 600 µJ-1.8 mJ femtosecond pulses from a Ti:sapphire laser with the intensities  $2.8 \times 10^{15}$ - $8.3 \times 10^{15}$  W cm<sup>-2</sup>. Electronically excited helium atoms (with an energy of about 20 eV) were detected with a position-sensitive microchannel plate (MCP) [239]. It was found in [217] that ponderomotive forces cause a superstrong acceleration of neutral atoms to a value exceeding Earth's gravitational acceleration g by approximately  $10^{14}$  times. It is probably the largest acceleration of neutral atoms observed in an external field. Helium atoms were accelerated in [217] perpendicular to the laser beam direction, while in [234] they were accelerated both in the laser beam propagation direction and in the opposite direction.

The method is based on the fact that a charged particle in a laser field is subjected to the action of the ponderomotive force

$$F_{\rm p} = -\frac{q}{4m\omega^2} \,\nabla |E_0|^2 \,, \tag{2.6}$$

where *m* and *q* are the particle mass and charge,  $E(r, t) = E_0(r, t) \exp(i\omega t)$  is the electric field,  $\omega$  is the field frequency, and  $E_0(r, t)$  is the slowly varying field amplitude. It follows that the ion nucleus and electrons are subjected during the laser pulse to the action of a ponderomotive force depending on the mass, which causes their motion. This means, in turn, that the ponderomotive force acts on the center of mass of the atom, producing its acceleration.

The physical mechanism producing the acceleration of neutral atoms in a strong focused laser field is as follows. Neutral atoms are excited by a laser with a certain intensity to states that lie high (Rydberg states). Highly excited electrons weakly bound with the ion core experience socalled laser-induced quivering. The quivering quasi-free electrons are subjected to the action of the ponderomotive force during the laser pulse due to the intensity gradient in the focused laser beam. The excited Rydberg atom is therefore dragged by excited electrons due to Coulomb interaction forces between electrons and the ion core. As a result, neutral atoms are strongly accelerated in the direction perpendicular to the laser beam, as was demonstrated in [217] (Fig. 5). The excited helium atoms with the initial transverse velocity in the beam  $\leq 2 \text{ m s}^{-1}$  acquire the velocity  $\approx 55~m~s^{-1}$  under the action of 120 fs pulses. The accelerations of helium atoms excited by pulses with different durations lie in the range  $(4.5-6.0) \times 10^{14} \text{ m s}^{-2}$  [217].

The motion of neutral atoms and molecules, including their acceleration, was controlled in [74, 216, 218, 235] by using deep optical potentials (optical gratings) produced by two very intense counterpropagating laser beams. In this method, two laser beams counterpropagating at a small angle produce an optical grating (a periodic sequence of potential wells) to accelerate atoms and molecules. The atoms or molecules are initially in a cloud in a magnetooptical trap [218] or in a molecular beam [74, 216, 235].

The force acting on a particle in the potential produced by laser beams is proportional to the gradient of the optical



**Figure 5.** (Color online.) Deflection of neutral He atoms after interaction with a focused laser beam. (a) The distribution of excited He<sup>\*</sup> atoms on a detector (the color scale reflects the number of atoms). The laser beam direction is shown by the arrow. (b) Cross section of the distribution of atoms along the laser beam direction (along the *z* axis) for  $r_D = 0$  mm (black curve), the projection of the entire distribution on the *z* axis (red dashed curve), and the laser radiation intensity along the *z* axis in units of the laser peak intensity  $I_0 = 6.9 \times 10^{15}$  W cm<sup>-2</sup> (blue curve). (c) Cross sections of the atomic distribution for z = 0 (red curve) and z = -2.7 mm (black curve). The black curve shows the velocity distribution of excited neutral atoms in the position in which ponderomotive forces do not act on atoms, and therefore demonstrates the 'natural' velocity dispersion of atoms in the beam, whereas the red curve demonstrates the increase in the velocity of atoms caused by ponderomotive forces [217].

field appearing due to the interference of two intense almost counterpropagating laser beams (Fig. 6a). Laser beams in [74, 218] produced the one-dimensional periodic potential

$$U(z,t) = -\frac{2\alpha}{\varepsilon_0 c} \sqrt{I_1(t) I_2(t)} \cos^2\left[\frac{1}{2}(kz - \Delta\omega t)\right], \quad (2.7)$$

where  $\alpha$  is the effective polarizability of a particle,  $\varepsilon_0$  is the permittivity of free space, c is the speed of light,  $k = (4\pi \sin \phi)/\lambda$  is the wave number of the grating,  $\lambda$  is the wavelength of light used,  $\phi$  is the half-angle between the two beams,  $\Delta \omega = \omega_2 - \omega_1$  is the difference between the angular frequencies of two lasers, and  $I_{1,2}(t)$  is the intensities of laser beams. Because the angular frequencies are different, an optical grating moving at the velocity  $v_L = \Delta \omega/k$  is produced. The motion of the grating and the particles localized in the potential well can be controlled by varying  $\Delta \omega$ . In particle acceleration experiments (with argon atoms [218]), the grating was initially in the stationary state, and then the difference between laser frequencies was rapidly increased (chirped).

This method was used in [218] to accelerate argon atoms initially located in a bounded cloud in a magneto-optical trap (Figs 6b, c). Depending on the intensity of lasers used and the frequency-difference chirping process (linear or nonlinear), a small portion of argon atoms from the cloud acquired a velocity in the range 75–190 m s<sup>-1</sup>. In [74, 216], this method



**Figure 6.** (a) Schematic of an accelerator and diagnostics. Two intense laser beams are focused, intersect at  $172.5^{\circ}$ , and overlap with metastable argon atoms located in a magneto-optical trap (the mechanism of acceleration and deceleration of atoms is described in the text). The ionized (for time-of-flight measurements) atoms in the beam were detected with a microchannel EMCCD plate (Electron Multiplying Charge Coupled Device) [218]. (b) Fluorescence images of the acceleration of argon atoms due to resonance laser excitation at a wavelength of 811.53 nm. Argon atoms are initially (before acceleration, at 0  $\mu$ s) located in the form of a cloud in a magnetooptic trap. Successive time-delayed images show accelerated atoms. (c) Images of accelerated argon atoms obtained for a 75  $\mu$ s delay with the use of a potential that is four times deeper than that in Fig. 6b [218]. (d) The velocity distribution function of NO molecules perturbed by the action of optical gratings. Shown are the velocities of gratings with respect to the molecular beam velocity. For comparison, the calculated perturbed velocity distributions of molecules are presented [74].

was used to accelerate cold (1.8 K) NO molecules in a beam. The initial velocity of molecules 400 m s<sup>-1</sup> was increased by more than 50 m s<sup>-1</sup>. It was shown that when the velocity of the laser-induced grating was smaller than the molecular beam velocity, some of the molecules in the beam were decelerated (Fig. 6d). It was found in [216] that the depth of the optical grating potential increased with increasing the intensity of laser beams, and therefore the potential trap can capture and accelerate a larger part of the gas particles. The analysis performed in [216] shows that the velocity of particles in a trap can be increased from values typical for room temperature to 10–100 km s<sup>-1</sup> over a length as small as a few hundred micrometers.

In [235], this method was used to modify the velocity distribution of H<sub>2</sub> molecules in the beam. An optical grating was produced by 532 nm second-harmonic pulses from an Nd:YAG laser. The initial velocity of molecules in the beam, equal to 563 m s<sup>-1</sup>, was increased by  $202 \pm 61$  m s<sup>-1</sup>. The dependence of the change in the velocity on the optical gradient force produced by the lasers was studied.

We note that precision methods considered above are quite interesting for controlling the motion of atoms and molecules and manipulating low-intensity atomic and molecular beams. In Sections 3 and 4, we discuss methods for generating high-energy molecular beams, which can be used in research and in practical applications.

## **3.** Acceleration of intense molecular beams and jets under vibrational excitation of molecules by an IR laser at the nozzle exit

#### 3.1 Fundamentals of the method

The method for accelerating intense neutral molecular beams (supersonic jets), which was proposed and studied in [62–64], consists of the following. Molecules flowing out from a nozzle into a vacuum chamber are excited by high-power resonance IR laser radiation in the gasdynamic expansion region directly at the nozzle exit, where the concentration of molecules and therefore their collision rate are rather high. The multiphoton absorption by molecules in a strong IR field [25, 27, 240] results in a significant increase in their internal (mainly vibrational) energy. At the same time, due to rapid vibrational– translational (V–T) relaxation during the gas expansion in the vacuum, efficient energy transfer occurs from vibrational to translational degrees of freedom, resulting in the acceleration of molecules, including molecules not absorbing IR radiation. Therefore, the IR laser-induced acceleration of molecules in a beam can be schematically represented as

$$\mathbf{M}(v_0) + nhv \longrightarrow \mathbf{M}^*(v_0) \xrightarrow{\mathbf{V}-\mathbf{\Gamma}} \mathbf{M}(v_{\mathbf{L}}), \qquad (3.1)$$

where M and M<sup>\*</sup> are the respective ground-state and vibrationally excited molecules,  $v_0$  and  $v_L$  are the respective velocities of ground-state and laser-pulse-excited molecules, and *nhv* is the laser pulse energy absorbed by a molecule.

Because the concentration of molecules in the irradiation region in these experiments is rather high (the gas pressure directly at the nozzle exit is  $\approx 10-100$  Torr), both multiphoton excitation and V-T relaxation occur efficiently, resulting in a considerable increase in the velocity of molecules in the beam.

#### 3.2 Experimental realization of the method

Figure 7 shows a schematic of the experiment in [241, 242]. A molecular beam was obtained using a 'current loop' pulsed nozzle 0.75 mm in diameter with the FWHM opening time  $\approx 60 \ \mu s$  [243]. The gas pressure above the nozzle could be varied from  $\approx 0.2$  to 5 atm. The slit in the duraluminum nozzle had a cone shape 15 mm in length, with the total cone angle of 60°. A vacuum chamber in which the molecular beam was formed was evacuated to a pressure of  $1 \times 10^{-6}$  Torr. The nozzle operated at the frequency of 0.2 Hz. The molecular beam was separated from the jet using a conic diaphragm (skimmer) with a hole 1.5 mm in diameter mounted at a distance of 50 mm from the nozzle cut.

Molecules were excited by a tunable pulsed  $CO_2$  laser emitting 3 J pulses [241, 242]. Laser radiation was directed inside the cone to the region of gas escape from the nozzle. To avoid an optical breakdown inside the nozzle cone, the laser energy was decreased to approximately 0.1 J by separating a single transverse mode and additionally attenuating radiation. Laser radiation was directed into a gasdynamic expansion region without focusing.

The molecular beam was detected in [241, 242] with a movable pyroelectric detector [244] with a time resolution  $\approx 3-5 \,\mu$ m. In this way, the time-of-flight spectra of molecules were obtained at different points on the beam axis [242], and the most probable velocity of molecules in the beam was directly measured (at the maximum of the time-of-flight distribution). The detector measured the energy of molecules propagating inside a solid angle determined by the size (4 × 4 mm<sup>2</sup>) of the active element of the detector and the distance  $x_0x_2$  (see Fig. 7) from the nozzle slit to the detector.



Figure 7. Schematic of an experimental setup for generating pulsed molecular beams by IR laser vibrational excitation of molecules at the nozzle exit [62, 64].

Without preliminary excitation of molecules, the detector signal is proportional to the quantity [241, 242]

$$S_0 \sim nv \left( E_a + E + \frac{mv^2}{2} \right) \sim nv E_0 , \qquad (3.2)$$

where *n* the number density of molecules on the detector surface, *v* and *m* are the molecule velocity and mass, *E* is the molecule energy (the sum of the vibrational, rotational, and 'local' translational energies), and  $E_a$  is the absorption heat per molecule. Under vibrational excitation of molecules by a laser pulse, the signal is proportional to the quantity

$$S_{\rm L} \sim nv(E_0 + E_{\rm ab}), \qquad (3.3)$$

where  $E_{ab}$  is the laser pulse energy absorbed by a molecule and  $E_0 = E_a + E + mv^2/2$ . The additional signal induced in the detector compared to that from unexcited molecules is the measure of the laser pulse energy absorbed by molecules under their vibrational excitation [241, 242].

The experimental time-of-flight distributions of 'cold' and vibrationally excited molecules were used to determine the translational, rotational, and vibrational temperatures of molecules in the beam [241, 242]. The time-of-flight spectra of molecules were analyzed by using the standard expression (with two parameters) for the number density distribution of molecules over velocities in a supersonic molecular beam [4, 245],

$$n(v) \sim \left(\frac{v}{u}\right)^2 \exp\left[-\frac{(v-u)^2}{\alpha^2}\right],$$
 (3.4)

where *u* is the mean velocity of molecules in the beam, and  $\alpha = (2k_{\rm B}T_{\parallel}/m)^{1/2}$  is the most probable velocity of molecules in the frame comoving with the beam. The energy balance of molecules before and after their flowing out of the nozzle was also taken into account. Thus, this method was used for measuring both kinetic and internal energies of molecules in the beam [241, 242].

Under excitation of a molecule in a beam at large enough distances from the nozzle ( $x \ge 50$  mm), where collisions and therefore the V–T relaxation is virtually absent, the velocity of excited molecules does not differ from that of unexcited molecules [241, 242]. If molecules are excited in the gas-dynamic expansion region, where the collision rate is high, the absorbed energy is completely or partially transferred to the translational degrees of freedom due to the V–T relaxation, resulting in the acceleration of molecules.

#### 3.3 Results of studies

In the experiments in [62–64], the time-of-flight spectra of molecules in a beam were measured at different distances from the nozzle, and the most probable velocities of molecules were determined in nonaccelerated and accelerated beams. Studies were performed with SF<sub>6</sub>, CF<sub>3</sub>I, NH<sub>3</sub>, and CF<sub>2</sub>HCl molecules, both with and without carrier gases (H<sub>2</sub>, D<sub>2</sub>, N<sub>2</sub>, Ar, CH<sub>4</sub>). Detector signals (the time-of-flight spectra of SF<sub>6</sub> molecules) without laser acceleration are presented in Fig. 8a, and with laser acceleration, in Figs 8b, c. The molecules were excited by the 944.2 cm<sup>-1</sup> 10P(20) line of a CO<sub>2</sub> laser that was resonant with the  $v_3$  vibration of the molecule [241, 246]. In the case in Fig. 8b, the delay between pulses triggering the nozzle and the CO<sub>2</sub> laser ( $\tau_d = 120 \ \mu$ s) was selected so as to accelerate all the molecules in the beam. In the case in Fig. 8c,

~	Pressure in the nozzle, atm	Mean flow ve	elocity, m s <sup>-1</sup>	Kinetic energy	CO <sub>2</sub>	
Gas composition		$v_0$	$v_{\rm L}$	$E_{ m kin}^0$	$E_{\rm kin}^{\rm L}$	laser line
$SF_6$	4.0	470	815	0.17	0.51	10P(20)
$SF_6$	1.5	455	800	0.16	0.50	10P(20)
$SF_6 + H_2(1:10)$	2.0	1220	1530	1.15	1.80	10P(20)
$SF_6 + D_2(1:10)$	1.1	1170	1450	1.05	1.60	10P(20)
$SF_6 + N_2(1:12.5)$	1.0	790	890	0.48	0.61	10P(20)
$SF_6 + Ar(1:15)$	1.3	650	750	0.32	0.42	10P(20)
$SF_6 + CH_4(1:10)$	1.0	980	1165	0.74	1.05	10P(20)
$CF_3I$	1.0	415	845	0.18	0.74	9R(12)
$CF_{3}I + CH_{4}(1:15)$	1.3	815	1065	0.70	1.19	9R(16)
CF <sub>2</sub> HCl	1.0	600	720	0.16	0.24	9R(30)
$NH_3 + CH_4(1:1.5)$	1.2	1040	1420	0.09	0.18	9R(30)

Table 2. Results on laser-induced acceleration of molecular beams [63, 64].



**Figure 8.** Time-of-flight spectra of SF<sub>6</sub> molecules without laser acceleration (a), upon laser acceleration (b) of all molecules in the beam, and (c) only molecules escaping from the nozzle at the first moment. The distance from the nozzle to the detector was 25 cm. The SF<sub>6</sub> pressure over the nozzle was 4 atm. The 944.2-cm<sup>-1</sup> 10P(20) CO<sub>2</sub> laser energy was 0.1 J (b) and 0.05 J (c) [63, 64].

the delay was reduced ( $\tau_d = 60 \ \mu s$ ) to accelerate only molecules flowing out from the nozzle at the first instant, other molecules remaining nonaccelerated. When, on the contrary, the delay was increased ( $\tau_d = 180 \ \mu s$ ) and a laser pulse exited molecules flowing out from the nozzle at the last instant, the accelerated molecules kept ahead of the nonaccelerated molecules.

The most probable velocity of SF<sub>6</sub> molecules in the absence of laser acceleration was  $v_0 = 470 \text{ m s}^{-1}$ , corresponding to the kinetic energy  $E_{\text{kin}}^0 \approx 0.17 \text{ eV}$ , while the velocity of accelerated molecules was  $v_{\text{L}} = (815 \pm 15) \text{ m s}^{-1}$ , corresponding to the kinetic energy  $E_{\text{kin}}^{\text{L}} \approx 0.51 \text{ eV}$ . In combination with the aerodynamic acceleration of SF<sub>6</sub> molecules in a

mixture with methane (for the pressure ratio SF<sub>6</sub>: CH<sub>4</sub>=1:10 and the total gas pressure above the nozzle  $p_{\Sigma} = 1$  atm), the velocities  $v_0 = 1000 \text{ m s}^{-1}$  and  $v_{L} = 1200 \text{ m s}^{-1}$  were obtained, which corresponds to the kinetic energy of SF<sub>6</sub> molecules  $E_{\text{kin}}^{\text{L}} \approx 1.0 \text{ eV}$ .

In similar experiments with CF<sub>3</sub>I molecules in [63, 64] (the above-nozzle pressure  $p_0 = 1$  atm and the molecules excited by the 1073.3 cm<sup>-1</sup> 9R(12) CO<sub>2</sub> laser line), the velocity of molecules without laser excitation was  $v_0 = (415 \pm 10)$  m s<sup>-1</sup>  $(E_{kin}^0 \approx 0.18 \text{ eV})$ , and with acceleration,  $v_L = (845 \pm 15)$  m s<sup>-1</sup>, corresponding to the kinetic energy  $E_{kin}^L \approx 0.74$  eV. In combination with the aerodynamic acceleration of CF<sub>3</sub>I in a mixture with methane (CF<sub>3</sub>I:CH<sub>4</sub> = 1:15,  $p_{\Sigma} = 1.3$  atm), the most probable velocity of molecules without laser acceleration was  $v_0 = (815 \pm 15)$  m s<sup>-1</sup>, and with laser acceleration,  $v_L = (1065 \pm 20)$  m s<sup>-1</sup>, which corresponds to the kinetic energy of CF<sub>3</sub>I molecules  $E_{kin}^L \approx 1.2$  eV.

Results of the laser acceleration of molecular beams are presented in Table 2. We note that the efficiency of the IR laser-induced acceleration of molecules depends on the absorbed laser energy and the V–T relaxation rate. This method is the most efficient for accelerating polyatomic molecules, because multiphoton IR absorption [25, 27, 240] provides the storage of a greater amount of energy in the internal degrees of freedom of the molecules. In addition, as the absorbed energy is increased, the V–T relaxation rate of molecules considerably increases. For example, for SF<sub>6</sub>,  $p\tau_{V-T} \approx 122 \mu$ s Torr in a weak IR field and  $p\tau_{V-T} \approx$ 22 µs Torr in the CO<sub>2</sub> laser radiation field with the energy density  $\Phi_{IR} \approx 0.5 \text{ J cm}^{-2}$  [249].

The results in Table 2 show that the  $SF_6$  and  $CF_3I$ molecules are accelerated quite efficiently, even without a carrier gas. This is related to multiphoton absorption by these molecules [240, 241, 248] and a considerable increase in the V-T relaxation rate for highly excited molecules [249]. The CF<sub>2</sub>HCl molecules are not accelerated efficiently enough because the excitation frequency of a CO<sub>2</sub> laser is strongly detuned (by more than  $30 \text{ cm}^{-1}$ ) from the maximum of the absorption band of molecules [250], which greatly reduces the excitation efficiency. In the case of small molecules (for example, NH<sub>3</sub>), for which multiphoton absorption is absent, the laser acceleration efficiency mainly depends on the V-T and rotational relaxation rates. The latter is important for involving a large fraction of molecules in the interaction with the laser pulse. The rapid rotational relaxation and cyclic interaction of molecules with laser radiation (rapid V-T relaxation) can ensure the efficient acceleration of molecules.

The dependences of the kinetic energy of molecules on the exciting laser pulse energy and frequency were studied in [62–64]. Figure 9 shows the dependences of the kinetic energy of SF<sub>6</sub> molecules in the beam on the energy of the exciting 10P(16) CO<sub>2</sub> laser line coinciding with the Q branch of the  $v_3 = 1 \leftarrow v_3 = 0$  vibrational transition in SF<sub>6</sub> molecules at the frequency  $v_3$  [241, 246]. Curve *I* shows the total kinetic energy of molecules in the beam, and curve *2* shows the laser-induced energy. For comparison, curve *3* also presents the dependence [251] of the energy absorbed by SF<sub>6</sub> molecules on the laser pulse energy density for pumping SF<sub>6</sub> in a cell at room temperature and a pressure of 0.15 Torr.

Some difference in the behavior of curves 2 and 3 is explained as follows. The energy  $E_{ab}$  absorbed by a molecule can be represented as the fraction q of excited molecules times the mean excitation level  $\varepsilon_q$  ( $E_{ab} = q\varepsilon_q$ ) [252]. Because in the case under study the concentration of molecules in the excitation region is sufficiently high and the rotational relaxation time is shorter than the laser pulse duration,  $q \approx 1$  [252]. Therefore, in this case, as the pump energy is increased, only the level of vibrational excitation of molecules increases. At the same time, in the case of curve 3, as the pump energy density is increased, both the fraction of excited molecules and the mean excitation level increase. Because of this, curve 2 in Fig. 9 is flatter than curve 3.

The laser-induced kinetic energy  $E_{kin}^{L}$  behaves like the energy absorbed by SF<sub>6</sub> molecules [241]. Therefore, we can assume that for higher exciting-pulse energy densities (which can be easily obtained with a nozzle without a cone [242]) and higher gas pressures above the nozzle, molecular beams with kinetic energies exceeding 1 eV can be obtained. Indeed, the dissociation energy of most of the molecules lies in the range 2–5 eV. Therefore, even disregarding the cyclic interaction, molecules can absorb a laser pulse energy comparable to the dissociation energy. With the cyclic interaction, which occurs when the V–T relaxation time is much shorter than the exciting laser pulse duration ( $\tau_{V-T} \ll \tau_p$ ), taken into account, the total energy absorbed by molecules can considerably exceed the dissociation energy.



**Figure 9.** Dependence of the kinetic energy of accelerated SF<sub>6</sub> molecules on the exciting CO<sub>2</sub> laser pulse energy: (1) total kinetic energy of SF<sub>6</sub> molecules in the beam; (2) laser-induced kinetic energy. The SF<sub>6</sub> pressures above the nozzle was 2.5 atm. The 947.8 cm<sup>-1</sup> 10P(16) laser line was used. For comparison, the energy absorbed by SF<sub>6</sub> molecules is shown as a function of the exciting pulse energy density (curve 3, the upper abscissa and the right ordinate), which was obtained in [251] at  $T \approx 300$  K and the SF<sub>6</sub> pressure in a cell equal to 0.15 Torr [64].



**Figure 10.** Dependence of the laser-induced kinetic energy of SF<sub>6</sub> molecules in the beam on the exciting radiation frequency [64]. For comparison, the dependences on the mean number  $\langle n \rangle$  of photons absorbed per molecule [253] (the SF<sub>6</sub> pressures was 0.45 Torr) and on the dissociation yield  $\beta$  of SF<sub>6</sub> molecules [254] (at the pressure 0.2 Torr and the exciting pulse energy density  $\Phi_{IR} \approx 3 \text{ J cm}^{-2}$ ) are shown. The lowest curve is the linear absorption spectrum for the  $v_3$  vibration of SF<sub>6</sub> at room temperature, taken from [255].

Figure 10 shows the dependence of the laser-induced kinetic energy of SF<sub>6</sub> molecules on the excitation frequency obtained for the laser pulse energy  $E_p = 0.12$  J and the pressure  $p_0 = 2.5$  atm above the nozzle [64]. For comparison, this figure also presents the dependence of the average number  $\langle n \rangle$  of photons absorbed by a molecule on the laser frequency for the energy density  $\Phi_{IR} \approx 0.12$  J cm<sup>-2</sup> and the SF<sub>6</sub> pressure p = 0.45 Torr [253], the frequency dependence of the dissociation yield  $\beta$  for  $\Phi_{IR} \approx 3$  J cm<sup>-2</sup> and p = 0.2 Torr [254], and the linear absorption spectrum of the vibration of SF<sub>6</sub> molecules at room temperature [255].

It was found in [64] (Fig. 10) that the dependence  $E_{kin}^{L}(v)$  is wider than the dependences  $\langle n \rangle (v)$  and  $\beta (v)$  and is significantly shifted to the red with respect to the linear absorption spectrum. This is due to the higher pressure of SF<sub>6</sub> in the case under study and therefore due to the stronger manifestation of the vibrational anharmonicity. At high pressures, the higher vibrational molecular states are efficiently excited, resulting in the red spectral shift. In this case, the V–T relaxation rate [249] also increases, thereby increasing the efficiency of laser-induced acceleration of molecules.

The local maximum of the dependence  $E_{kin}^{L}(v)$  in the 930 cm<sup>-1</sup> region is caused by the absorption band of  ${}^{34}SF_6$  molecules in this frequency region [256]. The content of  ${}^{34}SF_6$  molecules in the natural SF<sub>6</sub> mixture is about 4.2%. The  $v_3$  vibrational absorption band is shifted by approximately 17 cm<sup>-1</sup> to the red with respect to the  $v_3$  vibrational absorption band of  ${}^{32}SF_6$  molecules [256]. The efficient acceleration of SF<sub>6</sub> molecules in the beam was also observed in [64] under their excitation to the 990 cm<sup>-1</sup>  $v_2 + v_6$  absorption band [257, 258]. The intensity of this band is approximately two orders of magnitude lower than that of the  $v_3$  vibrational band [258].

We estimate the intensity of accelerated  $SF_6$  molecular beams obtained in [62–64], noting that accelerated beams are less intense than nonaccelerated ones because the perpendicular velocity of molecules in accelerated beams is also higher. The intensity of nonaccelerated molecular beams can be estimated if the total number N of molecules escaping from the nozzle per pulse and the time-of-flight distribution of molecules in the beam are known. In the case of  $SF_6$  molecules, as is shown in [241],  $N \approx 10^{17}$  at the gas pressure above the nozzle  $p_0 = 5$  atm (see Section 4, Fig. 12a). The FWHM of the time-of-flight distribution of SF<sub>6</sub> molecules in the beam at a distance of 25 cm from the nozzle (on the detector surface) was  $\approx 150 \,\mu\text{s}$  (Fig. 8a). Assuming that all the molecules flowing out from the nozzle propagate within a solid angle determined by the nozzle cone angle (d $\omega \approx 1$  sr), the peak intensity of the nonaccelerated molecular SF<sub>6</sub> beam at a distance of x = 25 cm from the nozzle is estimated as  $\approx 10^{21} \text{ sr}^{-1} \text{ s}^{-1}$ . The intensity of the accelerated SF<sub>6</sub> beam is somewhat lower [259]. These intensities are rather high, especially for accelerated molecular beams [6–8].

Thus, it was shown in [62-64] that the vibrational excitation of molecules by resonance IR laser radiation in the gasdynamic expansion region at the nozzle exit can be used to obtain intense accelerated molecular beams with the kinetic energy ranging from 0.1-0.2 eV to 1-1.2 eV. The main disadvantage of this method is that high excitation energy densities cannot be reached because of the optical breakdown occurring near the nozzle exit. In addition, the method cannot efficiently accelerate all molecules in the beam.

# 4. Production of high-energy molecules in secondary molecular beams

It follows from the discussion in Sections 2 and 3 that highenergy molecular beams can be efficiently produced by exciting molecules by high-power IR laser radiation inside a pulsed beam source itself, i.e., before the gas flows out from the nozzle. This was first done using the method of formation of a secondary pulsed molecular beam proposed in [65, 66]. As a result, intense beams of accelerated SF<sub>6</sub> and CF<sub>3</sub>I molecules with kinetic energies up to 2.0-3.0 eV were obtained [66]. It was shown in [67, 68, 260] that by using high-power IR laser radiation and secondary molecular beams, accelerated molecular radicals can also be obtained. We briefly consider the method of generating intense secondary pulsed molecular beams and the results obtained with them [65–68, 260].

## 4.1 Method for forming

### secondary pulsed molecular beams

The method for obtaining secondary pulsed molecular beams [65, 66] consisted of the following (Fig. 11). An intense  $(\ge 10^{21} \text{ sr}^{-1} \text{ s}^{-1})$  wide-aperture (divergence  $\omega \approx 0.05 \text{ sr}$ ) molecular beam (flow) was incident on a solid surface — a metal substrate with a hole at the center. A polished duraluminium substrate 7.5 mm in thickness was used, which was placed at the distance  $x \approx 60$  mm from the nozzle. The hole had the form of a diverging cone with the input diameter  $d_{\text{in}} \approx 2$  mm and the output diameter  $d_{\text{out}} \approx 5$  mm. The walls of the hole were polished.

When the primary beam was incident on the substrate, a shock wave was formed in front of it [261–263], in which the gas density, pressure, and temperature were considerably higher than in the incident beam [264, 265]. According to estimates [260], the concentration of SF<sub>6</sub> molecules in the shock wave changed, depending on the primary beam intensity, from approximately  $10^{16}$  to  $5 \times 10^{17}$  cm<sup>-3</sup>. As long as the shock wave existed in front of the surface, gas flowed out from it through a hole in the substrate to the high-vacuum part of the chamber, resulting in the formation of a new, secondary pulsed molecular beam with parameters different from those of the primary beam. The secondary



**Figure 11.** Schematic of experiments on generating high-energy secondary pulsed molecular beams upon vibrational excitation of molecules by intense IR laser pulses directly in the beam source itself. The formation of a secondary molecular beam with the help of a substrate with a hole in the form of a diverging cone [66, 260].

molecular beam could also be obtained by using not a substrate with a conical hole but hollow converging truncated cones and convergent-divergent Laval cones. The intensity of secondary molecular beams produced with the help of cones considerably (by 5–7 times) exceeded the intensity of beams obtained using a substrate [66, 260]. When the primary beam interacted with the cone, a shock wave was formed inside the converging part of the cone.

The primary beam was obtained using the pulsed nozzle described in Section 3.2, but with a narrower and longer output cone to provide a higher intensity. The opening time was 50-80 µs (FWHM) depending on the gas composition and pressure above the nozzle. The gas pressure was varied in these experiments from  $\approx 0.1$  to 7 atm. The nozzle slit was made in the form of a cone 35 mm in length with the total solid angle of 15°. The number of molecules flowing out from the nozzle per pulse changed from  $\approx 3 \times 10^{15}$  to  $\approx 1.1 \times 10^{17}$  during the pulse [264, 265] (Fig. 12a). Such a nozzle design provided the production of high-intensity molecular beams (flows) (see Section 4.2) for generating intense secondary beams. Using a pyroelectric detector, the time-of-flight spectra of molecules were measured at various distances from the sources of the primary and secondary molecular beams. These spectra were used to measure the beam velocity and the velocity dispersion of molecules in beams (see Section 4.2).

#### 4.2 Characteristics of secondary molecular beams

It was found in [65–68, 260] that for relatively high-intensity primary molecular beams ( $\ge 10^{20} \text{ sr}^{-1} \text{ s}^{-1}$ ), the secondarybeam intensity becomes comparable to that of the unperturbed primary beam. Figure 12b shows the dependences of the primary-beam intensity (curve *I*) and secondary-beam intensity (curves *2* and *3*) on the SF<sub>6</sub> pressure above the nozzle. In the case of curve *2*, the secondary beam was formed using a convergent cone ( $d_{in} = 11 \text{ mm}$ ,  $d_{out} = 2.8 \text{ mm}$ , the total length 32 mm), and in the case of curve *3*, using a convergent–divergent Laval cone ( $d_{in} = 14 \text{ mm}$ ,  $d_0 = 2 \text{ mm}$ ,  $d_{out} = 7 \text{ mm}$ , the total length 40 mm, the length of the converging part 30 mm). The distance from the nozzle to the detector was 143 mm and from the cone waist to the detector, 79 mm. It can be seen that at the SF<sub>6</sub> pressure above the

	Pressure above		Primary beam		Secondary beam		
Gas composition	the nozzle, atm	$v_1$ , m s <sup>-1</sup>	$\Delta v_1, \mathrm{m}\mathrm{s}^{-1}$	$v_1/\Delta v_1$	$v_2, \mathrm{m~s^{-1}}$	$\Delta v_2,\mathrm{m~s^{-1}}$	$v_2/\Delta v_2$
$SF_6$	5.0	560	62	9.1	476	82	5.8
$SF_{6}/H_{2}(1/10)$	3.2	1130	97	11.6	1090	156	7.0
$SF_{6}/He(1/10)$	3.0	940	85	11.1	1000	230	4.4
$SF_{6}/CH_{4}(1/10)$	3.1	870	99	8.8	835	128	6.5
CF <sub>3</sub> I	4.6	417	53	7.9	406	57	7.1

Table 3. Measured parameters of primary and secondary molecular beams [67, 260].



**Figure 12.** (a) Dependence of the total number  $N_b$  of molecules flowing out from the nozzle per pulse at the SF<sub>6</sub> pressure above the nozzle for voltages  $U_{noz} = 3.0 \text{ kV}$  (curve 1) and  $U_{noz} = 3.2 \text{ kV}$  (curve 2) applied to the nozzle [260]. (b) Dependences of the intensity of the unperturbed primary molecular beam (curve 1) and secondary molecular beams (curves 2 and 3) on the SF<sub>6</sub> pressure above the nozzle,  $U_{noz} = 3.2 \text{ kV}$ . The distance between the nozzle and detector was 143 mm. Secondary beams were formed using cones. The parameters of cones and experimental conditions are presented in the text [260].

nozzle  $p \ge 1.0$  atm, the pyroelectric signal induced by the secondary molecular beam in the detector (curve 3) exceeds the signal from the primary beam (curve 1).

The parameters of the primary and secondary beams measured in [67, 260] are presented in Table 3. The durations and rates of the primary and secondary molecular beams were found to be insignificantly different [66, 67, 260]. But the velocity dispersions of molecules differ greatly. The velocity dispersion in the secondary beam was 20–40% greater than in the primary beam. It follows from Table 3 that the velocity dispersion in the secondary molecular beam, as in the primary beam, is not very large either, which means that the gas was quite significantly cooled (the Mach number was  $M_2 \approx v_2/\Delta v_2 \approx 5$ ).

Thus, it is shown in [65–67, 260] that using a shock wave produced in front of a solid surface, intense pulsed molecular beams with parameters close to those of primary beams can be obtained.

# 4.3 Generation of high-energy molecules in secondary beams

Using secondary pulsed molecular beams, it is easy to excite molecules by a laser directly in the beam source itself (see Fig. 11). Another advantage of secondary molecular beams is that considerably higher energy densities can be used to excite molecules, which allows producing high-energy molecular and molecular radical beams [65–68, 260]. When high-energy beams were obtained using a setup with a cone, the convergent part of the cone was replaced with a truncated tetrahedral hollow pyramid made of thin NaCl plates transparent to  $CO_2$  laser radiation. Molecules were then excited inside the pyramid directly in front of the secondary nozzle exit.

The IR-laser-induced acceleration of molecules in secondary molecular beams can be schematically represented by relation (3.1).

Molecules were excited by a laser in a shock wave directly in front of the secondary nozzle exit (see Fig. 11). The laser beam was directed parallel to the surface. The parameters of the secondary molecular beam and the production of highenergy molecules in it were studied in experiments. The dependences of the velocity (kinetic energy) of molecules in the beams on the energy density, the exciting radiation frequency, and the carrier gas were studied for  $SF_6$  and  $CF_3I$  molecular beams.

Because the concentration of molecules in the shock wave in front of the surface was high [the pressure was  $\approx 1-10$  Torr (see below)], multiphoton excitation of molecules and V-T relaxation were efficient in these experiments. This resulted in a considerable increase in the velocity of molecules in secondary beams. Gas heating in the shock wave due to deceleration (see below) also facilitated the increase in the velocity of molecules in secondary beams.

Figure 13a shows the dependence of the secondary SF<sub>6</sub> molecular beam velocity on the laser energy density under excitation of molecules in the secondary beam source [inside a hollow truncated pyramid made of NaCl plates and attached to the front wall of the substrate with a cone hole (see Fig. 11)]. The 938.7 cm<sup>-1</sup> 10P(26) laser line was resonant with the  $v_3 = 948$  cm<sup>-1</sup> vibration of SF<sub>6</sub> molecules [246]. The average velocity of molecules without laser excitation was  $v_0 = 460$  m s<sup>-1</sup>, and that with laser excitation reached  $v_L > 1400$  m s<sup>-1</sup>.

Figure 13b shows the dependence of the kinetic energy of  $SF_6$  molecules in the secondary molecular beam on the  $CO_2$  laser excitation frequency at the  $SF_6$  pressure above the nozzle equal to 5.8 atm and the laser energy density

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Gas composition	Pressure above the nozzle, atm	CO <sub>2</sub> laser line	Energy density, J cm <sup>2</sup>	Mean velocity of molecules in the beam, m s <sup>-1</sup>		Kinetic energy of molecules, eV	
				$v_0$	$v_{\rm L}$	$E_{\rm kin}^0$	$E_{\rm kin}^{\rm L}$
$SF_6$	6.2	10P(26)	3.7	460	1400	0.163	1.5
$SF_{6}/H_{2}(1/10)$	3.1	10P(20)	3.5	1176	1875	1.06	2.7
$SF_{6}/He(1/10)$	6.0	10P(20)	3.7	1050	1810	0.85	2.5
SF <sub>6</sub> /CH <sub>4</sub> (1/10)	5.0	10P(24)	3.7	1020	1835	0.8	2.6
CF <sub>3</sub> I	4.6	9 <b>R</b> (10)	1.8	417	1065	0.18	1.2

Table 4. Results of experiments on the acceleration of  $SF_6$  and  $CF_3I$  molecules in a secondary molecular beam [67, 260].



**Figure 13.** (a) Dependence of the velocity of the secondary molecular SF<sub>6</sub> beam on the laser radiation energy density. Molecules were excited by the 938.7 cm<sup>-1</sup> 10P(26) laser line. The SF<sub>6</sub> pressure over the nozzle was 5.8 atm,  $U_{noz} = 3.2$  kV [66, 260]. (b) Dependence of the kinetic energy of SF<sub>6</sub> molecules in the secondary molecular beam on the laser excitation frequency. The excitation energy density was  $\Phi_{IR} = 3.9$  J cm<sup>-2</sup> [67, 260].

≈ 3.9 J cm<sup>-2</sup>. The mean kinetic energy of molecules without laser excitation was  $E_{kin}^0$  ≈ 0.163 eV. For comparison, in the lower part of Fig. 13b, the linear absorption spectrum for the  $v_3$  vibration of SF<sub>6</sub> is shown [255]. The spectrum obtained is similar to the one in Fig. 10. The maximum acceleration was observed under excitation of molecules by 10P(22) – 10P(26) laser lines in the 940 cm<sup>-1</sup> range. A small maximum at 931 cm<sup>-1</sup> is related to excitation of the  $v_3$  vibration of <sup>34</sup>SF<sub>6</sub> molecules at ≈ 930.5 cm<sup>-1</sup> [256].

Results on the acceleration of SF<sub>6</sub> and CF<sub>3</sub>I molecules in secondary beams are presented in Table 4. Molecular SF<sub>6</sub> beams were obtained with the kinetic energy  $E_{\rm kin}^{\rm L} \approx$ 1.5 eV ( $v_{\rm L} \approx 1400 \text{ m s}^{-1}$ ) without the carrier gas and with  $E_{\rm kin}^{\rm L} \approx 2.5-2.7$  eV with He, CH<sub>4</sub>, and H<sub>2</sub> carrier gases, and also CF<sub>3</sub>I molecular beams with  $E_{\rm kin}^{\rm L} \approx 1.2$  eV. These values considerably exceed the corresponding values obtained in [63, 64] for molecules excited at the nozzle exit (see Section 3.3).

The parameters of the molecular flow incident on the surface measured in experiments and gasdynamic relations were used in [67, 241, 260] to estimate the concentration and temperature of SF<sub>6</sub> molecules in a direct shock wave in front of the surface under the experimental conditions considered. It was shown that for SF<sub>6</sub> pressures above the nozzle in the range from 3 to 5 atm, the concentration of molecules in the shock wave was from  $\approx 9.6 \times 10^{16}$  cm<sup>-3</sup> to  $\approx 5 \times 10^{17}$  cm<sup>-3</sup> (pressure up to 28.6 Torr), while the increase in the gas temperature due to acceleration was  $\Delta T \approx 635$  K.

The fraction of the absorbed energy spent to the acceleration of molecules was estimated from the measurements of the laser pulse energy absorbed by SF<sub>6</sub> molecules [241, 266] and SF<sub>6</sub> acceleration measurements [67, 241, 260]. It was found in [67, 241, 260], for example, that under excitation by the 10P(16) laser line with the energy density  $\Phi_{IR} \approx 3.5-4 \text{ J cm}^{-2}$ , about 45% of the absorbed laser energy was spent to accelerating molecules.

# 4.4 Generation of accelerated radicals in secondary beams

The production of accelerated radicals in a secondary beam was studied for the multiphoton dissociation of CF<sub>3</sub>I molecules in a secondary beam source by detecting CF<sub>3</sub> radicals [67, 68, 260]. The secondary beam was produced with the help of a substrate with a conic hole and a hollow truncated pyramid attached in front to the substrate. The pyramid was made of NaCl plates transparent to laser radiation. The CF<sub>3</sub>I molecules in the shock wave were excited by a 1073.3 cm<sup>-1</sup> 9R(12) laser line resonant with the  $v_1$  vibration of CF<sub>3</sub>I [247]. This frequency coincides with the maximum of the spectral dependence of the IR multiphoton CF<sub>3</sub>I dissociation yield in a gasdynamically cooled molecular flow [266, 267]. For the excitation energy density  $\Phi_{IR} \approx 3 \text{ J cm}^{-2}$ , the CF<sub>3</sub>I dissociation yield was  $\geq 80\%$ [248, 268]. The time-of-flight spectra of CF<sub>3</sub> radicals and accelerated and nonaccelerated CF<sub>3</sub>I molecules are shown in Fig. 14.

The time-of-flight spectrum of CF<sub>3</sub> radicals was recorded by exciting molecules at the initial instant of shock wave formation. At long delay times between the primary molecular beam pulse and the laser pulse, the time-of-flight spectra of CF<sub>3</sub> radicals and accelerated CF<sub>3</sub>I molecules overlapped, thereby preventing the detection of CF<sub>3</sub> radicals by this method. We note that the products of the multiphoton IR dissociation of CF<sub>3</sub>I molecules are only CF<sub>3</sub> radicals and iodine atoms, due to the rather large differences among the masses of the CF<sub>3</sub> radical, the CF<sub>3</sub>I molecule, and the iodine atom, and it was therefore possible to record the time-offlight spectrum of CF<sub>3</sub> radicals.



**Figure 14.** Oscillogram showing the time-of-flight spectra of CF<sub>3</sub> radicals (peak 2) and accelerated and nonaccelerated CF<sub>3</sub>I molecules (peaks 3 and 4, respectively) in a secondary molecular beam. Peak *I* is the scattered exciting laser pulse. The CF<sub>3</sub>I molecules in a shock wave were excited by the 1073.3 cm<sup>-1</sup> 9R(12) laser line [67, 260].

The velocity and the width of the velocity distribution of radicals in the secondary beam were measured to be  $v_2 \approx 800 \text{ m s}^{-1}$  and  $\Delta v_2 \approx 120 \text{ m s}^{-1}$  (the Mach number was  $M_2 \approx v_2/\Delta v_2 \approx 6.7$ ). Hence, an intense beam of cooled CF<sub>3</sub> radicals with the kinetic energy  $E_{\text{kin}} \approx 0.25 \text{ eV}$  was obtained in these experiments. The CF<sub>3</sub> radicals were accelerated in the secondary beam due to an increase in the gas temperature caused by deceleration and also due to the V–T relaxation of excited molecules that did not dissociate because of a lack of energy.

It was found in [65–68, 260] that the multiphoton IR excitation of molecules in a shock wave formed in front of the surface, which is used as the source of a secondary beam, can produce intense pulsed molecular beams with controllable kinetic energy, as well as accelerated cold radical beams.

We note in the conclusion of this section that the shockwave method of generating secondary pulsed molecular beams can also be used to obtain intense pulsed low-energy molecular and atomic beams [269-271]. Secondary beams are then produced in nozzles in the form of liquid-nitrogencooled ( $T_0 \approx 80$  K) multichannel plates or cones, inside which a cold shock wave is generated by the incident molecular beam, which is a source of the secondary beam. This method was used in [269-271] to generate intense molecular and atomic He, H<sub>2</sub>, N<sub>2</sub>, Kr, and CH<sub>4</sub> beams with kinetic energies  $\leq 10$  meV and H<sub>2</sub> and He beams with respective kinetic energies  $\leq 0.3$  and  $\leq 0.6$  meV. As a carrier gas, krypton was used in experiments with pressure ratios  $p_0(\mathrm{H}_2)/p_0(\mathrm{Kr})$  and  $p_0(\mathrm{He})/p_0(\mathrm{Kr}) = 1/5$ . The possibility of heating secondary nozzles to high temperatures  $T_0 \ge 400-450$  K and continuously changing their temperature allows generating both high-energy and low-energy secondary beams with controllable parameters [269–271].

### 5. Determining the composition and content of molecular cluster beams

### 5.1 Background

In all the methods for obtaining clusters, in particular, in gasdynamic jets, a size distribution of the clusters is generated [6–8, 11, 34]. This is explained by the statistical nature of the cluster formation process. The size distribution obtained is

logarithmically normal [8, 272–274], Gaussian in the coordinate system with the logarithmic abscissa. The half-width of the asymmetric distribution approximates the average cluster size. In experimental studies of cluster properties and processes involving them, it is desirable to know the composition and content of cluster beams and to be able to control these parameters. However, determining the composition and content of cluster beams is a rather complicated task.

Cluster beams are usually detected with mass spectrometers. At the same time, the size-selective detection of clusters by ionization followed by their separation in a mass spectrometer is impossible or very complicated because of the fragmentation process [275]. A strong fragmentation during ionization in a mass spectrometer is especially typical for systems with van der Waals, hydrogen, and ionic bonds, where the interaction potentials for neutral and ionized particles are considerably displaced with respect to each other. As a result, ionization leads to the population of highly excited vibrational states, which causes the fragmentation (evaporation) of clusters [34, 275].

The composition of cluster beams can be determined by size-selection methods [192]. A few such methods exist. In some of them, the size separation of clusters is performed before their detection, whereas in others it is effected during their detection in a mass spectrometer. These methods include the separation of clusters of a certain size from the beam using a transmission quadrupole mass spectrometer [276, 277], the size selection of clusters by diffraction from an atomic beam [278, 279], the deposition of molecular chromophores with a low ionization energy ( $\leq 7-8 \text{ eV}$ ) on the clusters [280–282], and doping clusters by atoms with low ionization energies [283]. In the last case, sodium atoms are used ( $E_i = 5.14 \text{ eV}$ ).

Clusters with molecular chromophores deposited on them are ionized due to resonance two-photon two-frequency excitation if laser wavelengths are selected such that ionization occurs without cluster fragmentation. This method requires the presence of corresponding electronic transitions in the molecular chromophore. Clusters doped with sodium atoms are ionized by a photon of resonance laser radiation. Upon excitation of clusters to a state close to the ionization threshold of the sodium atom, it is possible to observe the ionization of clusters, actually without their fragmentation [283], which allows determining the real composition of the cluster beam from the mass spectrum [192].

All the methods mentioned above are successfully used in experiments with cluster beams [192], despite being quite complicated in practice. Therefore, the development of alternative methods to determine the composition and content of cluster beams is an important and urgent problem. Recently, a new method was proposed in [189] for determining the composition and content of neutral pulsed molecular cluster beams by the ion signals of cluster fragments.

# 5.2 Fundamentals of the method and its realization in experiments

The method proposed in [189] is based on the analysis of ion signals of cluster fragments reflecting the time-of-flight spectra of clusters in beams. The ion signals are formed during the beam flight through the ionization region of a quadrupole mass spectrometer (QMS) containing ion products produced in the fragmentation of different-size clusters ionized in the mass spectrometer. These ion products contribute to the product to which the mass filter of the mass spectrometer is tuned. The potential of this method is demonstrated by cluster beams containing mixed  $(SF_6)_mAr_n$ clusters ( $1 \le m \le 4, 0 \le n \le 9$ ) of various sizes and compositions. It was found that resonance excitation of molecules and clusters in a beam by a CW CO<sub>2</sub> laser considerably increases the sensitivity of this method.

The experimental setup (Fig. 15a) contains a pulsed source of molecular cluster beams (with a hole 0.16 mm in diameter), a QMS, and three vacuum chambers evacuated separately by turbomolecular pumps (a camera with the molecular/cluster beam source evacuated to a pressure  $\leq 10^{-5}$  Torr, a reaction chamber, and a QMS chamber evacuated to  $(2-3) \times 10^{-7}$  Torr. The beam source chamber is separated from the reaction chamber by a skimmer (with the hole diameter 0.49 mm) located at a distance of 50 mm from the nozzle. The QMS chamber is separated from the reaction chamber is separated from the reaction chamber is separated from the separated from the separated from the separated from the reaction chamber is separated from the separated from the

Clusters were generated in [189] during the gasdynamic expansion of an  $SF_6 + Ar$  gas mixture at the nozzle exit. The duration of the nozzle opening pulse was 300 µs. To obtain clusters with different compositions and sizes,  $SF_6 + Ar$  gas mixtures with different  $SF_6/Ar$  pressure ratios 1/20, 1/80, and 1/200 above the nozzle were used at different total pressures.

The setup also contains a tunable CW  $CO_2$  laser, a pulse synchronization system, and a data acquisition and processing system. The mass spectrometer can operate in two modes: the mode of measuring the survey spectrum of ion fragments produced at a specified moment of time and the time-of-flight mode, where the QMS was tuned to a certain mass and the time evolution of the ion signal was measured upon the arrival of particles at the QMS ionization chamber.



Figure 15. (a) Schematic of an experimental setup for determining the composition and content of pulsed molecular cluster beams. Distances from the nozzle to the entrance hole of the skimmer, diaphragm, and ionizer of the mass spectrometer are indicated in millimeters. The oval in the ionizer shows the ionization region [189]. (b) Typical mass spectrum of a cluster beam obtained with an SF<sub>6</sub> + Ar mixture with a pressure ratio of 1/200 [189].

The time of flight of a neutral cluster with mass M from the source to the detector is  $L/U_M$ , and the signal appearance time can be expressed as

$$\tau_M = \frac{L}{U_M} + t_{\rm NZ} + t_{\rm MS} \,, \tag{5.1}$$

where *L* is the distance from the nozzle to the mass spectrometer ionizer,  $U_M$  is the velocity of clusters of mass *M* in the beam, and  $t_{NZ} + t_{MS}$  is the delay due to the operation of the pulsed nozzle and QMS. Because of the rather large distance L = 570 mm from the nozzle to the mass spectrometer ionizer and small values  $t_{NZ} \approx 150$  µs and  $t_{MS} \approx 20$  µs, the main contribution in (5.1) is made by the first term in the right-hand side, i.e., by the time of flight of neutral particles of a certain size from the nozzle to the QMS ionizer (1.3–3.0 µs). Obviously, the experimental values of  $\tau_M$  can be used for determining the corresponding velocities:

$$U_M = \frac{L}{\tau_M - t_{\rm NZ} - t_{\rm MS}} \,. \tag{5.2}$$

Under appropriately chosen experimental conditions (the flight length L, the mass M of particles, the time resolution of the mass spectrometer, etc.), the time-of-flight spectrum exhibits a structure (see Section 5.3) determined by different arrival times of particles contributing to the ion signal being measured. The spectrum reveals a discrete set of arrival times  $\tau_M$  and the corresponding set of velocities  $U_M$ . It is shown in [189] how this set of velocities can be assigned to a discrete set of masses of clusters of different sizes to determine the composition of particles in the initial cluster beam.

#### 5.3 Results of studies

Figure 15b shows the typical mass spectrum of a cluster beam obtained for the  $SF_6 + Ar$  mixture with a pressure ratio of 1/200. The mass spectrum clearly demonstrates the  $Ar_2^+$  and  $Ar_3^+$  ions fragmented from argon clusters and some other products indicating the presence of mixed  $(SF_6)_mAr_n$  clusters in the beam. In particular, the  $SF_5Ar_2^+$ ,  $SF_5Ar_3^+$ , and other fragmentation ions are observed. The  $SF_5^+$  peak is the most intense. This peak contains contributions from cluster ionization fragments and the ionization of nonclustered  $SF_6$  monomers present in the beam.

The mass spectrum exhibits a peak with the mass number m/z corresponding to the  ${}^{32}SF_6{}^{32}SF_5^+$  ion fragment (m/z = 273) produced upon ionization of the ( ${}^{32}SF_6$ )<sub>2</sub> dimer. At the same time, this mass also contains contributions from fragments of larger  $(SF_6)_m Ar_n$  clusters with m > 2. However, these clusters could not be detected directly because of the limited range of detected masses  $(m/z \leq 300)$ used in the QMS [189]. In addition, we note that even a mass spectrometer with a larger range of detected masses does not allow an accurate determination of the composition of the initial cluster beam because, as mentioned above, large clusters were decomposed during detection into fragments upon the electron-beam ionization in the mass spectrometer. As a result, the distribution of fragments produced does not reflect the real distribution of neutral clusters in the beam. The method proposed in [189] can be used to determine the cluster beam composition in the cluster size range indicated above and to estimate the relative content of corresponding neutral clusters in the beam.

Figure 16a (curve *I*) shows the time-of-flight spectrum of the  ${}^{32}\text{SF}_{6}{}^{32}\text{SF}_{5}^{+}$  cluster ion fragments obtained by detecting a cluster beam generated upon the expansion of



**Figure 16.** (a) Time-of-flight spectrum of the  ${}^{32}\text{SF}_6^+$  fragmentation ion. Curves *I* and *2* are the respective spectra obtained before and after irradiation of the molecular beam by a 932.96 cm<sup>-1</sup> 10P(32) CO<sub>2</sub> laser line. Measurements were performed with an SF<sub>6</sub>/Ar = 1/200 mixture, the total gas pressure above the nozzle was  $p_{\Sigma} = 1.83$  atm, the laser beam diameter was  $\approx 0.4$  mm, and the radiation energy density was  $\Phi_{IR} \approx 1.8$  mJ cm<sup>-2</sup> [189]. (b) The difference time-of-flight spectrum of the  ${}^{32}\text{SF}_6^{32}\text{SF}_5^+$ fragmentation ion (curve 2, dots). Curve I ( $\otimes$ ) is the time-of-flight spectrum of the same ion without laser irradiation of the beam. Solid curves 3 are mass peaks in the Gaussian approximation. The positions of peaks of the ( ${}^{32}\text{SF}_6^{32}\text{SF}_5^+$ ) ion signal for ( ${}^{32}\text{SF}_6$ )<sub>2</sub>Ar<sub>n</sub> clusters are denoted by 2 - n. Other conditions are as in Fig. 16a.

the SF<sub>6</sub>/Ar = 1/200 mixture at the total gas pressure above the nozzle  $p_{\Sigma} = 1.83$  atm. We can see that the time-of-fight spectrum is clearly structured. Analysis showed (see below) that this structure appears because the time-of-flight spectrum of a given ion fragment is a combination of the time-offlight spectra of all the neutral clusters with the (SF<sub>6</sub>)<sub>m</sub>Ar<sub>n</sub> composition ( $m \ge 2$ ,  $n \ge 0$ ) in the beam that make such a fragment upon ionization in the mass spectrometer. The vertical dashed line in Fig. 16a indicates where the  ${}^{32}$ SF<sub>6</sub> ${}^{32}$ SF<sub>5</sub><sup>+</sup> ion signal is mainly determined by the pure (SF<sub>6</sub>)<sub>2</sub> dimer.

The contrast of the observed structure and therefore the sensitivity of this method can be considerably increased by exposing the forming cluster beam to resonance IR radiation from a CW  $CO_2$  laser and representing the data obtained by the difference time-of-flight spectrum,

$$S_{\rm diff}(t) = S_0(t) - S_{\rm las}(t),$$
 (5.3)

where  $S_0(t)$  is the time-of-flight spectrum of the  ${}^{32}SF_5^+$  ion fragment in the absence of laser excitation of the beam and  $S_{\text{las}}(t)$  is the time-of-flight spectrum of this fragment

upon laser excitation. The exposure of the beam to sufficiently intense CW laser irradiation at the nozzle exit (in the gasdynamic expansion region where clusters are formed) reduces the  ${}^{32}SF_{5}{}^{32}SF_{5}{}^{+}$  ion signal, and the structure of the time-of-flight spectrum somewhat changes because of changes in the cluster beam composition and content. The composition and content of the beam exposed to laser irradiation change either due to the dissociation of resonantly excited clusters (when the beam is irradiated far from the nozzle, where the formation of clusters has ended already) or due to suppression of clustering caused by resonance excitation of  ${}^{32}SF_6$  molecules (when the beam is irradiated near the nozzle exit, where clusters are formed) [188, 212, 284].

In the experiments, the laser beam passed at a distance of 1.45 mm from the nozzle, where the clustering of  $SF_6$  molecules had already occurred to a considerable extent. Particles were excited by the 932.96 cm<sup>-1</sup> 10P(32) laser line, which was resonant with the absorption band of the  $({}^{32}SF_6)_2$  and  $({}^{32}SF_6)_mAr_n$  clusters [284]. The result of irradiation is presented in Fig. 16a (curve 2). We can see that because of the partial selective dissociation of these clusters, irradiation reduces the signal amplitude and somewhat changes its shape due to a change in the cluster beam composition.

The difference spectrum  $S_{\text{diff}}(t)$  obtained from Fig. 16a is presented in Fig. 16b (curve 2). For comparison, the initial time-of-flight spectrum of nonirradiated particles is also shown (curve 1). It can be seen that the difference spectrum exhibits a distinct  $({}^{32}\text{SF}_6)_2$  dimer peak (the 'earliest' peak) and successive peaks of mixed clusters  $({}^{32}\text{SF}_6)_2\text{Ar}_n$  with n = 1-5, which are well approximated by a set of corresponding Gaussian peaks (solid curves 3 in Fig. 16b). Thus, these data clearly demonstrate the possibility of using this method for measuring the composition of SF<sub>6</sub> clusters consisting of a strongly diluted state (SF<sub>6</sub>/Ar = 1/200) mainly of  $({}^{32}\text{SF}_6)_2\text{Ar}_n$  particles (where  $0 \le n \le 5$ ). In addition, a small number of  $({}^{32}\text{SF}_6)_3$  and  $({}^{32}\text{SF}_6)_3\text{Ar}$  clusters were generated [189].

The composition and size of clusters in the beam were also studied in [189] in  $SF_6 + Ar$  mixtures with  $SF_6/Ar$  pressure ratios over the nozzle equal to 1/20 and 1/80 at 2 atm of the total gas pressure above the nozzle in both cases. The difference time-of-flight spectra of clusters in the beams were analyzed. It was found in [189] that in the case of a weakly diluted  $SF_6/Ar$  mixture, the homogeneous  $(SF_6)_m$ and mixed  $(SF_6)_m Ar_n$  clusters were mainly generated with a small number of argon atoms. In the case of a strongly diluted  $SF_6/Ar$  mixture, the mixed  $(SF_6)_mAr_n$  clusters with one or two SF<sub>6</sub> molecules, many argon atoms, and argon clusters were generated. Thus, as the partial pressure of the carrier Ar gas in the initial mixture was increased, clusters with a smaller number of molecules and a greater number of carrier-gas atoms were generated. The size of the clusters produced in the beam depended on the total gas pressure above the nozzle and increased with increasing pressure.

The results in [189] also give a qualitative estimate of the relative content of clusters in the beams. In principle, if the dependence of the ionization cross section on the cluster size and the instrumental function of a QMS are known, the content of particles found in the beam can be found quantitatively. This method can be used for determining the composition and content of both homogeneous and mixed clusters in the beam. This opens up new possibilities for studying the properties of clusters and their interactions

with particles or radiation, in particular, laser-induced chemical reactions in clusters and selective processes with cluster and molecular beams [179, 184, 185, 188].

# 6. Controlling the composition and content of cluster beams by IR lasers

### 6.1 Fundamentals of the method and objects of study

In this section, we consider experimental studies on controlling the composition and content of molecular cluster beams by controlling the clustering process during gas expansion at the nozzle exit with the help of IR lasers [193, 212, 213, 284– 287]. Studies were performed with  $SF_6$  and  $CF_3I$  molecular cluster beams irradiated by CW  $CO_2$  lasers.

The laser control of clustering involves the preliminary (before the clustering onset) vibrational excitation of molecules, in particular, of a specified kind upon gasdynamic expansion at the nozzle exit. As a result, during the subsequent condensation, the stored vibrational energy suppresses the clustering of excited molecules. In addition, by appropriately choosing the location for irradiation of particles on the jet axis in the region in front of the skimmer (see Section 6.2), the dissociation of small clusters — dimers that are seeds for large clusters — can be performed, which can also be used to control the clustering of molecules. In this case, it is necessary to provide the predominant formation of dimers in the absence of large clusters (for example, by choosing suitable gas expansion conditions).

The method for controlling the clustering process is based on the resonance vibrational excitation of molecules or clusters in a beam by an IR laser at the nozzle exit. Depending on the distance to the particle excitation region from the nozzle 'cross-cut', laser irradiation of the beam either suppresses the clustering of resonantly excited molecules (when the beam is irradiated near the nozzle exit, where the clusters are formed) or causes the dissociation of small clusters (when the beam is irradiated far from the nozzle, where clusters are growing).

The suppression of molecular clustering and dissociation of clusters in beams were studied by measuring the integrated intensities of ion peaks of cluster fragments with a quadrupole [212, 213, 284–287] or a time-of-flight [193] mass spectrometer. The suppression efficiency of molecular clustering and cluster dissociation was shown to be strongly dependent on the laser radiation power, the gas pressure above the nozzle, the nozzle design, and the distance between the radiation region and the nozzle slit. The parameters were found that ensured the most efficient control of molecular clustering and cluster dissociation in beams.

The possibility of controlling clustering by IR lasers was demonstrated with the example of SF<sub>6</sub> molecule mixtures with argon in [212, 213, 284–288]. These studies were performed using CO<sub>2</sub> laser-induced selective suppression of clustering of SF<sub>6</sub> molecules and dissociation of these molecular clusters in gasdynamic jets in mixtures with argon for separating sulfur isotopes. The SF<sub>6</sub> molecule was chosen for studies because its structure and spectroscopic properties are the closest to those of the UF<sub>6</sub> molecule. The spectroscopic properties of SF<sub>6</sub> molecules and its clusters are well studied [212, 284, 289, 290]. In addition, the multiphoton excitation and dissociation of SF<sub>6</sub> molecules by intense IR laser radiation, in particular, in molecular beams and jets, have been investigated in detail [27, 240, 241, 266].



**Figure 17.** Decrease in the SF<sub>6</sub>SF<sub>5</sub><sup>+</sup> ion signal under irradiation of  ${}^{32}$ SF<sub>6</sub> monomers in the collisional region of the jet, measured depending on the distance from the irradiated region to the nozzle at laser powers of 1.25, 6, and 24 W. Molecules were irradiated by the 10.552 µm 10P(16) laser line. The gas pressure and temperature above the nozzle were  $p_0 = 1.7$  atm and  $T_0 = 222$  K [212].

It was shown in [212, 287] that the formation of  $(SF_6)_2$ clusters was strongly suppressed when SF<sub>6</sub> monomers were exposed to a resonance laser radiation with a power of several watts in the collisional region at the nozzle exit (Fig. 17). As the distance between the nozzle and the irradiated region was increased, along with suppression and clustering, the vibrational predissociation of clusters began. The cluster signal is therefore caused by these two processes. For large distances from the nozzle, a decrease in the cluster signal is mainly caused by the dissociation of clusters [188]. It was found in [212, 288] that the laser-induced signal strongly depends on the excitation wavelength, the distance between the nozzle and the irradiated region, and gas parameters above the nozzle, which is related to the dependence of the IR absorption of molecules and clusters in the beam on these parameters.

The suppression of clustering was observed under excitation of both  ${}^{32}SF_6$  and  ${}^{34}SF_6$  molecules [188, 212, 288]. It was found in [212, 213, 284–288] that selective excitation of the chosen  $SF_6$  isotopomers at the nozzle exit can suppress the clustering of excited molecules both with other  $SF_6$  molecules and with the carrier gas (argon) atoms. Experimental studies [212, 213, 284–288] confirmed the possibility of using approaches considered above for isotope separation [188]. These approaches [188, 291] most likely underlie the development of the recent technology of separation of isotopes by laser excitation (SILEX) [292–295].

Recent studies on controlling the composition and content of  $(CF_3I)_n$  molecular cluster beams (where *n* is the number of molecules in the cluster) are presented in [193]. The

choice of the CF<sub>3</sub>I molecule and its  $(CF_3I)_n$  clusters is motivated by several reasons. The CF<sub>3</sub>I molecules are easily excited by a CO<sub>2</sub> laser and readily produce clusters; their clustering is well studied [172, 175, 177]. These molecules, along with SF<sub>6</sub> molecules, are well studied in terms of spectroscopy [247] and selective IR multiphoton dissociation [240, 266, 268], in particular, in molecular beams and jets [266, 268]. The  $(CF_3I)_n$  clusters can easily be detected due to the presence of molecular I<sub>2</sub><sup>+</sup> ions in their mass spectrum, which are formed under multiphoton excitation of clusters by UV laser radiation [172, 175, 177, 182]. The fragmentation product of the cluster I<sub>2</sub><sup>+</sup> ion is the atomic I<sup>+</sup> ion. Therefore, the I<sub>2</sub><sup>+</sup> and I<sup>+</sup> ions are convenient markers for studying the formation and dissociation of  $(CF_3I)_n$  clusters.

### 6.2 Experimental realization of the method

We consider the IR laser control of molecular clustering with the example of study [193]. The experimental setup (Fig. 18) includes a high-vacuum chamber with a pulsed molecular cluster beam source, a photoionization time-of-flight mass spectrometer, and a tunable CW CO<sub>2</sub> laser [172, 175, 186]. The chambers of the beam source and the time-of-flight mass spectrometer were evacuated by turbomolecular pumps to respective pressures  $\leq 10^{-5}$  and  $\approx 10^{-7}$  Torr. The setup also contained pulsed UV and IR lasers, a pulse synchronization system, and a data acquisition and processing unit.

The 15–18 W CO<sub>2</sub> laser can be tuned from 9.2 to 10.7  $\mu$ m (1087–933 cm<sup>-1</sup>). A laser beam with a Gaussian transverse distribution was focused into the gas expansion region at the nozzle exit. A steering mirror and a lens mounted on a translation stage provided laser beam focusing in any region on the molecular beam axis in front of a skimmer (Fig. 18). The laser beam was focused with a lens with the focal distance f = 200 mm. The laser beam waist diameter at the lens focus was  $D_{IR} = 0.43$  mm and the waist length (according to the Rayleigh criterion) was 8–9 mm. Taking radiation transport losses into account, the radiation power in the beam irradiation region was  $\approx 10-11$  W (the power density was 6.9–7.6 kW cm<sup>-2</sup>).

A CF<sub>3</sub>I molecular cluster beam was generated during the gasdynamic cooling of the gas mixture of molecules under study with a carrier gas (argon or xenon) at the nozzle exit. In



**Figure 18.** Experimental setup for controlling the composition and content of molecular cluster beams by IR lasers: (1) vacuum chamber; (2) mass spectrometer; (3) pulsed nozzle; (4) skimmer; (5) plane mirror; (6) UV radiation source; (7) CW CO<sub>2</sub> laser; (8) lens; (9) beamsplitter; (10) mechanical modulator; (11) optoacoustic detector; (12) laser radiation detector [193].



**Figure 19.** Details of pulsed nozzles in the valve region: (a) commercial nozzle, (b) new design nozzle. (*1*) nozzle body, (*2*) valve core [193].

the experiments in [193], pulsed nozzles of two types were used: a commercial General Valve nozzle with an exit hole 0.8 mm in diameter and an exit cone, and a nozzle developed in [193] with an exit hole 0.22 mm in diameter (Fig. 19). In both cases, the duration of the current nozzle opening pulse was varied from 0.2 to 2.0 ms. The gas pressure  $p_0$  above the nozzle could be varied from 0 to 5 atm. Using a skimmer (with the hole diameter 0.66 mm) located at a distance of 38.5 mm from the nozzle, a molecular/cluster beam was cut off from the central part of a supersonic jet and directed to the time-offlight mass spectrometer chamber. At a distance of 96.5 mm from the entrance hole of the skimmer, this beam intersected with mutually perpendicular axes of the mass spectrometer and the ionizing UV laser beam (the UV laser wavelength was tuned between 215 and 237 nm). Such a combined use of UV multiphoton ionization and mass spectrometric detection provided the diagnostics of cluster beams and investigations of the IR and UV laser fragmentation of clusters [172, 175, 182, 186, 187, 192].

The UV photoionization of clusters was performed with the second harmonic of a dye laser ( $\lambda_{dye} \approx 430-474$  nm, with the laser linewidth  $\Delta v_{dye} \approx 0.5 \text{ cm}^{-1}$ ) pumped by an excimer XeCl laser. The second harmonic was generated in a barium borate crystal (BBO). The produced ions were detected with a secondary electron multiplier (SEM). The UV laser radiation was focused by a lens with the focal length f = 12 cm to the region of intersection of the molecular-cluster beam with the mass-spectrometer axis [186, 187]. The laser spot diameter (at the 1/e level) at the lens focus was  $\approx 0.13$  mm. The laser pulse FWHM was 7–10 ns and the energy density in the waist region did not exceed  $\Phi_{UV} \approx 2$  J cm<sup>-2</sup>. The ion SEM signal and UV radiation pulses were recorded with a digital oscilloscope and were fed to a computer for storage and subsequent processing.

The time-of-flight spectrum S(t, Y = 0) of the beam, i.e., the time dependence of the concentration of particles in the beam propagated to the detection region (Y is the coordinate along the mass spectrometer axis) was recorded by changing the delay between the nozzle opening moment and the UV radiation pulse [172, 175, 182]. The space-time characteristics of the cluster beam and fragmentation products were measured depending on the parameters of the UV laser pulse and beam-formation conditions (the gas temperature  $T_0$ , the composition, and the pressure  $p_0$  above the nozzle),  $S(t, X; T_0, p_0; E_{\text{UV}}, \lambda_{\text{UV}}; m/z)$ , where *m* and *z* are the ion mass and ionization degree and X is the coordinate along the cluster beam axis [172, 175]. By a signal with specified parameters we understand a quantity proportional to the ion current charge in the region of the chosen mass peak:  $S(m/z) = \int_{\Delta t} j(\tau) \,\mathrm{d}\tau.$ 

A molecular cluster beam was irradiated by a  $CO_2$  laser in the region between the nozzle and the skimmer perpendicular



**Figure 20.** Transverse scan of a cluster beam by UV laser radiation in the time-of-flight mass spectrometer detection region. (*I*) The  $S_0(Y_{\rm UV})$  signal distribution without IR laser irradiation of the beam, (*2*) the  $S_{\rm IR}(Y_{\rm UV})$  signal distribution for a beam irradiated by an IR laser at the distance X = 21 mm from the nozzle. The 10.2 W, 1074.65 cm<sup>-1</sup> 9R(14) CO<sub>2</sub> laser line was used (the power density was 7.03 kW cm<sup>-2</sup>), (*3*) the difference  $S_0(Y_{\rm UV}) - S_{\rm IR}(Y_{\rm UV})$  signal. The gas pressure and composition above the nozzle were  $p_0(\rm CF_3I + Ar; 1:15) = 1.1$  atm [193].

to the beam axis (see Fig. 18). To find the optimal signal and to measure the concentration of clusters in the beam (without and with beam irradiation), radiation was scanned along the Y axis (See Fig. 18). Then, by scanning the UV radiation also along the Y axis (the mass spectrometer axis), the clusterbeam region irradiated by the laser was found in the detection zone from the measured signal from the clusters (the  $I_2^+$  ion signal) (Fig. 20).

The cluster signal strength and its behavior depend on both the gas expansion conditions at the nozzle exit (the gas composition and pressure above the nozzle and the nozzle design and operation regime) and IR laser radiation parameters (the laser line and its power, and the laser beam cross section in the interaction region). The intensity of the I<sub>2</sub><sup>+</sup> (m = 254) and I<sup>+</sup> (m = 127) ion peaks characterizing the content of (CF<sub>3</sub>I)<sub>n</sub> clusters in the beams was measured. A decrease in the intensity of the I<sub>2</sub><sup>+</sup> and I<sup>+</sup> ion signals depending on the conditions of irradiation of particles in the beam by the IR laser demonstrates the suppression of clustering of CF<sub>3</sub>I molecules and (or) the dissociation of (CF<sub>3</sub>I)<sub>n</sub> clusters by IR radiation.

#### 6.3 Results of studies and their analysis

Gas clustering at the nozzle exit involves several stages [193] (Fig. 21) proceeding predominantly in different regions of the jet.

Region I near the nozzle slit and at distances of several calibers (nozzle diameters) from the nozzle slit is characterized by the most rapid cooling of the translational and internal degrees of freedom of the molecules, accompanied by the transfer of their internal energy to the kinetic energy of the directional motion of the jet and the transition of the medium into an oversaturated state, resulting in the formation of cluster nuclei.

Collisional region 2 of the expanding jet is characterized by continuing gasdynamic cooling and by the growth of clusters in the jet, accompanied by some heating of the system caused by the condensation energy.

Region 3 behind the 'freezing' boundary is where the transition to the collisionless motion of particles and stabilization of the cluster system occurs.



Figure 21. Formation of a cluster beam in a pulsed jet [193].

Region 4 between the skimmer and the time-of-flight mass spectrometer detection region is the free-flight region of the cluster beam. The beam properties in the detection region are determined by the geometrical divergence, composition, and velocity distribution of particles during their propagation in the skimmer.

To study the influence of the resonance IR excitation of molecules in the jet on the cluster beam formation at different clustering stages, it is necessary to irradiate particles in the corresponding jet regions on the flow trajectory forming the cluster beam and to detect changes in the beam parameters in the detection region. The decrease in the cluster component signal can occur due to several reasons.

*Region 1.* By exciting molecules in this region by IR radiation to produce a local temperature increase preventing the formation of nuclei, it is possible in the ideal case to suppress the further clustering of molecules. In the case of a strong dilution of molecules by an inert gas, when the probability of collisions between molecules is low, it is possible to suppress the clustering of excited molecules.

*Region 2.* Excitation of particles by an IR laser in this region leads to the vibrational heating of molecules and clusters that had already formed in the jet. In this case, a partial fragmentation of clusters is possible. We note that the heating of particles occurs along with their competing gasdynamic cooling (especially in the presence of a carrier gas) and some further changes in the cluster composition of the jet (growth of clusters and evolution of their size distribution).

*Region 3.* When particles are irradiated in this region, where collisions are absent, IR radiation mainly heats clusters, producing their fragmentation, which is manifested in the corresponding decrease in the signal from the cluster component of the beam.

The authors of [193] paid great attention to the choice of the optimal laser-beam cross section in the interaction region. When the beam aperture is large, the laser energy density is insufficient for efficient excitation of molecules. If the laser beam is tightly focused, the excitation region is small and can be 'smeared' by the time the beam arrives at the detection region. A lens with the focal distance f = 200 mm used in experiments gave a waist with the diameter  $D_{IR} = 0.43$  mm, which was comparable to the nozzle and skimmer diameters  $D_{NZ} = 0.8$  mm and  $D_{SK} = 0.66$  mm in the setup.

An important parameter in experiments of this type is the energy density  $\Phi_{IR}$  incident on the particles intersecting the laser beam. It depends on the laser radiation power W, the laser beam cross section  $\pi R^2$ , and the time of flight of particles through the laser beam  $\Delta t = 2R/U$ , where U is the directional motion velocity. For the central part of the irradiated volume,

$$\Phi_{\rm IR} = \frac{2RW}{\pi R^2 U} = \frac{2W}{\pi R U} \, [\rm J \, cm^{-2}] \,. \tag{6.1}$$

For the typical IR radiation power W = 8 W, the laser radiation power density in the beam excitation region was  $5.52 \text{ kW cm}^{-2}$  and the energy density was  $\Phi_{IR} = 5.5 \text{ mJ cm}^{-2}$ . Assuming for an estimate that the linear absorption cross section for CF<sub>3</sub>I molecules in the region of the 1074.65 cm<sup>-1</sup> 9R(14) CO<sub>2</sub> laser line is  $\sigma_{CF_3I} = 5.7 \times 10^{-18} \text{ cm}^2$  [247], we obtain the energy absorbed per molecule  $\sigma \Phi_{IR} = 0.192 \text{ eV}$ . This is a small value, taking into account that detaching one CF<sub>3</sub>I molecule from a (CF<sub>3</sub>I)<sub>n</sub> cluster (with the number of molecules  $n \approx 50$ ) requires an energy of about 0.35 eV [181].

The irradiation energy density must be known, for example, in order to compare results obtained upon dissociation of clusters by CW and pulsed IR lasers. Such a comparison allows gaining deeper insights into the nature of cluster fragmentation (see Section 6.3.1). It was shown in [187] that the results on the dissociation of  $(CF_3I)_n$  clusters by resonance radiation from CW and pulsed (100 ns) CO<sub>2</sub> lasers are in good agreement. This suggests that the fragmentation of clusters by IR radiation on a time scale  $\ge 10^{-7}$  s can be treated as a quasistationary process of the successive evaporation of molecules from a cluster [187, 192].

6.3.1 Results of studies with a standard nozzle. Experiments with a standard commercial nozzle have shown [193] that the location of the molecular clustering onset region depends on the mixture composition and the degree of dilution of molecules in the carrier gas, as well on the total gas pressure above the nozzle. It was shown that for a relatively strong dilution of molecules in the carrier gas and (or) a high total gas pressure above the nozzle, the molecular clustering region is located not at the nozzle exit but inside the nozzle channel, in the narrowest place of the gas expansion region, between the nozzle body and a movable core (Fig. 19a). Therefore, in this case, it is impossible to control clustering by laser radiation. This is confirmed by the study of the IR excitation of particles in front of the skimmer. In particular, the transverse scanning of a molecular-cluster jet by radiation for a  $CO_2$  laser has shown in [193] that when the laser beam intersected the trajectory of particles passing through the skimmer to the beam detection region, the  $S(I^+)$  and  $S(I_2^+)$ cluster signals exhibited a distinct trough (up to 20-25%) with the characteristic width close to the laser beam diameter (Fig. 22). The results obtained in these experiments have shown that the laser-induced signal is the same for excitation of the molecular beam near the nozzle exit (at the distance X = 0.25 mm) and at a large distance from the nozzle (X = 21 mm), where the molecular clustering has completed. These data show that molecular clustering occurs inside the nozzle channel. The laser-induced decrease in the signal from  $(CF_3I)_n$  clusters is caused not by clustering suppression but by the laser-induced dissociation of clusters.

Only in the case of low total gas pressures above the nozzle  $(\leq 0.3-0.5 \text{ atm})$  and (or) a weak dilution of the CF<sub>3</sub>I molecular gas by an atomic carrier gas (Ar, Xe) (with ratios of about 1:2 and 1:3) does the molecular clustering region 'pass' from the nozzle outside to the gas expansion region. This is explained by the fact that for these gas parameters above the nozzle, the conditions for clustering are considerably deteriorated, resulting in the 'stretching' of the clustering



**Figure 22.** Changes in the  $S(I^+)$  and  $S(I_2^+)$  ion signals during the transverse scan of a supersonic jet by CW CO<sub>2</sub> laser radiation: (a) probing in the region close to the nozzle (X = 0.25 mm), (b) probing in the region far from the nozzle (X = 21 mm). The 10 W, 1074.65 cm<sup>-1</sup> 9R(14) CO<sub>2</sub> line (with the power density 6.9 kW cm<sup>-2</sup>). The gas pressure and composition above the nozzle were  $p_0(CF_3I + Ar; 1:15) = 1.1$  atm [193].

process in time and space. In particular, the fraction of nonclustered molecules near the nozzle slit increases, which is reflected in the intensity of the cluster component of the signal depending on the location of IR irradiation of particles between the nozzle cut and the skimmer. In this case, the influence of IR excitation at different clustering stages can be observed. The results of such experiments with mixtures of different compositions and different dilution degrees of molecules in the carrier gas are presented in Fig. 23.

Curve *1* in Fig. 23 shows the dependence of the  $I_2^+$  cluster ion signal on the distance from the nozzle slit to the particle excitation region for a CF<sub>3</sub>I/Xe mixture with  $p_0(CF_3I + Xe; 1:2) = 0.5$  atm. The behavior of the I<sup>+</sup> ion signal in this case is similar to that of the  $I_2^+$  signal. In curve *1*, the suppression of clustering of CF<sub>3</sub>I molecules and dissociation of the produced (CF<sub>3</sub>I)<sub>n</sub> clusters are distinctly reflected in the dependence of the  $I_2^+$  and I<sup>+</sup> cluster ion signals on the distance between the particle excitation region and the nozzle. A drastic decrease in the  $I_2^+$  cluster signal at small distances from the nozzle ( $X \le 1$  mm) is caused by the suppression of clustering of the particle excitation region increases (for  $X \approx 1-7$  mm), both molecular clustering and dissociation of clusters are suppressed. At even longer distances between the nozzle and



**Figure 23.** Dependences of the relative intensities of  $I_2^+$  and  $I^+$  ion cluster signals on the distance between the nozzle slit and the IR irradiation region in a mixture with  $p_0(CF_3I + Xe; 1:2) = 0.5$  atm (curve *I*) and a mixture with  $p_0(CF_3I + Ar; 1:15) = 0.52$  atm (curves 2). The normalization was performed to the signal in the absence of IR radiation. The 1074.65 cm<sup>-1</sup> 9R(14) CO<sub>2</sub> line was used, the radiation power was 4 W (with the power density 2.76 kW cm<sup>-2</sup>) (curve *I*) and 7.8 W (with the power density 5.38 kW cm<sup>-2</sup>) (curves 2) [193].

the excitation region  $(X \ge 7 \text{ mm})$ , the dissociation of clusters occurs. We note that in this case the clustering region was completely outside the nozzle channel and, as a result, the almost complete (100%) suppression of clustering was observed. The clustering region was displaced from the nozzle channel to the outside due to the slower cooling of the gas escaping from the nozzle, because a weakly diluted mixture of CF<sub>3</sub>I molecules with the heavier Xe carrier gas at a low pressure, stretching the molecular clustering processes in time and space, was used.

Curves 2 in Fig. 23 show the dependences of the  $I_2^+$ and I<sup>+</sup> ion signals on the distance between the nozzle slit and the particle excitation region for a CF<sub>3</sub>I/Ar mixture with  $p_0(CF_3I + Ar; 1:15) = 0.52$  atm. In this case, the behavior of the  $I_2^+$  and  $I^+$  cluster signals considerably differs from that shown by curve 1 and from the behavior of signals in Fig. 22 when a similar mixture was used, albeit at a higher total pressure, and CF<sub>3</sub>I molecules formed clusters inside the nozzle channel. At a relatively low pressure  $p_0(CF_3I + Ar; 1:15) = 0.52$  atm, when the clustering region starts moving from the nozzle outside, the suppression of molecular clustering and dissociation of clusters also start affecting the dependence of the  $I_2^+$  and  $I^+$ cluster ion signals on the distance between the nozzle and the particle excitation region. It can be seen that as the IR excitation region moves away, the initial decrease in the cluster signal is superseded by the leveling of the signal.

The decrease in the cluster signal under excitation of particles at small distances from the nozzle ( $X \le 5$  mm) is caused by the suppression of clustering of free molecules in the jet and by the dissociation of clusters produced inside the nozzle channel. In the case of excitation of particles at long distances from the nozzle ( $X \ge 5$  mm), the dissociation of clusters predominantly occurs. The intensity of the cluster signal observed in this region is mainly determined by the laser power and by the size and temperature of the clusters [175, 181, 187].

The dependence of the cluster dissociation probability on the laser energy density under excitation of particles near the nozzle exit (at the point  $X_1 = 0.5$  mm (Fig. 22)) and far from the nozzle (at the point  $X_2 = 16$  mm) was studied in [193]. In



**Figure 24.** Dependences  $S(I_2^+; \Phi_{IR})$  of normalized  $I_2^+$  cluster signals on the laser energy density for the excitation of particles near the nozzle exit (at the point  $X_1 = 0.5$  mm (see Fig. 23) (curve *I*) and far from the nozzle (at the point  $X_2 = 16$  mm) (curves 2 and 3). The normalization was performed to the signal in the absence of IR radiation. The 1074.65 cm<sup>-1</sup> 9R(14) CO<sub>2</sub> line was used in all cases. The pressure and composition of mixtures were  $p_0(CF_3I + Xe; 1:2) = 0.5$  atm (curves *I* and *2*) and  $p_0(CF_3I + Ar; 1:15) = 0.52$  atm (curve 3) [193].

the region of  $X_1$ , clusters are formed and both molecules and clusters are present. Under excitation of particles in this region, molecular clustering is efficiently suppressed due to excitation of free molecules followed by mixture heating and due to the excitation and dissociation of small clusters, which are the nuclei of large clusters. Around  $X_2$ , the clustering process completely terminates and, during the excitation of particles, their heating leads to the dissociation (fragmentation) of clusters. The laser energy density was calculated from (6.1).

The results obtained for two mixtures with different compositions are presented in Fig. 24. Curves 1 and 2 show the dependences of the  $I_2^+$  cluster signal intensity on the exciting radiation energy density obtained for a CF<sub>3</sub>I/Xe mixture with  $p_0(CF_3I + Xe; 1:2) = 0.5$  atm at points  $X_1 = 0.5$  mm and  $X_2 = 16$  mm. Curve 3 shows a similar dependence obtained at the point  $X_2 = 16$  for the CF<sub>3</sub>I/Ar,  $p_0(CF_3I + Ar; 1:15) = 0.52$  atm. We can see that dependence 1 greatly differs from dependences 2 and 3. Experimental results averaged over six measurement cycles are shown with different symbols. The scatter of the results obtained in each cycle is shown by error bars. The solid curves correspond to the approximation of experimental data by exponential functions with some additions (see below), while the dashed curves show approximations of experimental data by monoexponential functions without any additions.

We analyze these results in the model of IR laser-induced fragmentation of homogeneous molecular clusters [181]. The IR laser-induced fragmentation of clusters can be regarded as

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a quasistationary evaporation of molecules from a cluster at the evaporation temperature  $T_{ev}$  determined by the balance between the energy absorbed by the cluster and the energy spent for successive detachments of molecules from the cluster [181]. The fragmentation efficiency can be characterized by the steepness of the decaying dependence of the ion signal on the IR radiation energy density  $S(I_2^+; \Phi_{IR})$ . In some cases, this dependence can be approximated [175, 181] by an exponential,

$$S(\mathbf{I}_2^+; \boldsymbol{\Phi}_{\mathrm{IR}}) \propto \exp\left[-k(\boldsymbol{\Phi}_{\mathrm{IR}} - \boldsymbol{\Phi}_0)\right], \qquad (6.2)$$

where  $\Phi_0$  is the IR radiation energy density required for cluster heating to the temperature  $T_{\rm ev}$  at which a quasistationary cluster evaporation process sets in and k is a parameter depending on particular conditions of cluster excitation and fragmentation. The cluster fragmentation efficiency depends on the relation between its absorption cross section  $\alpha(n)$ , its size n, and the energy  $\Delta E(n)$  required for the detachment of one molecule [175]. In the simplified case, assuming that  $\alpha(n) = \sigma n$  and  $\Delta E(n) = \Delta E$ , we obtain  $k = \sigma/\Delta E$ , where  $\sigma$  is the absorption cross section of one molecule.

The evaporation rate constant  $k_{ev}$  is defined by a relation [31, 296] similar to the Arrhenius equation,

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

where  $\Delta E$  is the evaporation energy (heat) per particle,  $T_{cl}$  is the cluster temperature, and A is a preexponential factor. At fixed temperature, the constant  $k_{ev}$  increases with deceasing  $\Delta E$ . The energy of evaporation of molecules from a cluster decreases with decreasing the cluster size [31, 36]. Therefore, the smaller the cluster size, the larger is the fragmentation rate constant [31, 36, 187].

The data presented in Fig. 24 (dependence 1) are well approximated by the biexponential function

$$S(\Phi_{\rm IR}) = A_0 + A_1 \exp(-k_1 \Phi_{\rm IR}) + A_2 \exp(-k_2 \Phi_{\rm IR}), \quad (6.4)$$

where  $A_0 = 0$ ,  $A_1 = 0.9235$ , and  $A_2 = 0.3355$  are preexponential factors, and  $k_1 = 3627.3$  and  $k_2 = 469.5$  cm<sup>2</sup> J<sup>-1</sup> are the evaporation rate constants of clusters. Experimental data 2 and 3 are approximated quite well by the monoexponential function

$$S(\Phi_{\rm IR}) = A_0 + A_1 \exp(-k_1 \Phi_{\rm IR})$$
(6.5)

with the parameters  $A_0 = 0.3484$ ,  $A_1 = 0.656$ , and  $k_1 = 125 \text{ cm}^2 \text{ J}^{-1}$  for dependence 2 and  $A_0 = -0.404$ ,  $A_1 = 1.376$ , and  $k_1 = 95.6 \text{ cm}^2 \text{ J}^{-1}$  for dependence 3. The results in Fig. 24 on the dissociation of clusters for the excitation of a particle far from the nozzle are in good agreement with results on the fragmentation of (CF<sub>3</sub>I)<sub>n</sub> clusters by a pulsed CO<sub>2</sub> laser [187].

A rather strong decrease in the ion cluster signal with increasing the energy density (for minimal values) in the case of dependence I is explained by the fact that molecular clustering is mainly suppressed in this region because laser radiation is tuned in resonance with molecules whose resonant absorption cross section is high. The higher cluster fragmentation rate constant for dependence 2 compared to dependence 3 indicates that in the latter case, because of the use of argon as the carrier gas and a stronger diluted

molecular mixture, colder  $(CF_3I)_n$  clusters were formed, which are more stable with respect to fragmentation [181, 187, 192].

We note that although in the case of a standard commercial nozzle, the molecular clustering process could be 'taken out' beyond the nozzle slit under some conditions, these conditions were restricted by a narrow  $CF_3I$  gas pressure range and a narrow range of relations between molecular and carrier gases. Because of this, in [193], a new design nozzle was developed that provided the location of the molecular clustering onset region in the gas expansion region at the nozzle exit.

6.3.2 New nozzle design. Comparison of results obtained with different nozzles. A new nozzle design had a flange (the nozzle body) with the exit hole with two different diameters, but without an exit cone (Fig. 19b) [193]. The diameter of the larger hole, which was coupled with a core, as in the commercial nozzle, was 0.8 mm. The exit diameter of the hole was 0.22 mm. The channel length of the narrow part of the hole was about 0.3 mm and of the broad part, about 1.4 mm. Therefore, the new nozzle design resembled a twostage nozzle in which the narrowest region for gas expansion was the exit hole 220 µm in diameter. Studies performed with such a nozzle showed that the gas clustering itself and the clustering onset process occur not inside the nozzle but in the gas expansion region behind the nozzle cut. We note that this condition is satisfied in experiments with different gases, gas compositions, and pressures above the nozzle in a broad range, as well as for different nozzle opening pulses (in the range from 200  $\mu$ s to 2 ms).

For comparison, curve 1 in Fig. 25a shows results obtained with a standard nozzle for a CF<sub>3</sub>I/Xe mixture with  $p_0(CF_3I + Xe; 1:2) = 0.5$  atm. Such a choice of parameters (a low total gas pressure above the nozzle and a weaker role of the cooling carrier gas) delays the onset of molecular clustering. As a result, the clustering process can be controlled by exciting molecules by IR radiation at the nozzle exit. It can be seen from Fig. 25a that in this case, a strong (almost 100%) suppression of molecular clustering is observed upon excitation of the gas jet at a distance  $X \leq 1$  mm from the nozzle exit. Curve 2 presents the results of measurements with a CF<sub>3</sub>I/Xe mixture with  $p_0(CF_3I + Xe; 1:2.3) = 0.95$  atm using the new nozzle design (with a small aperture). We can also observe an almost 100% signal suppression in this case, but at distances closer to the nozzle slit. This is explained by the difference between the exit apertures of the nozzles.

Figure 25b shows the results presented in Fig. 25a depending on the distance expressed in calibers, i.e., in quantities X/D, where D is the nozzle hole diameter. The presentation of results in calibers allows comparing data obtained with nozzles with different exit diameters. We can see from Fig. 25b that the results obtained with nozzles of the two types are in good agreement. We note that it is the distance in calibers that is most often used in the literature for describing various phenomena and processes in molecular beams, because the caliber is a more fundamental quantity for the scale of relevant processes than the distance from the nozzle in millimeters.

It was found in [193] that the suppression of molecular clustering with the new design nozzle was observed at different pressures and different relations between the CF<sub>3</sub>I molecular gas with Ar and Xe carrier gases in a broad range.



**Figure 25.** Dependences of the  $I_2^+$  ion signals on the distance *X* obtained with a commercial nozzle with a cone (curves *I*) and with a new design nozzle (curve 2) for a CF<sub>3</sub>I + Xe gas mixture with pressure ratios 1:2 and 1:2.3 and the respective total gas pressure above the nozzle of 0.5 atm and 0.95 atm. The molecular beam was irradiated by the 1074.65 cm<sup>-1</sup> 9R(14) CO<sub>2</sub> laser line with powers of 4 and 6.4 W (power densities 2.76 and 4.42 kW cm<sup>-2</sup>). The distance from the nozzle to the excitation region is presented in (a) millimeters and (b) calibers, i.e., in quantities *X/D*, where *D* is the nozzle hole diameter [193].

For example, an almost 100% suppression of CF<sub>3</sub>I clustering was observed in the 1:2 CF<sub>3</sub>I + Ar mixture at a total pressure of 3 atm and in the 1:2.3 CF<sub>3</sub>I + Xe mixture at the same total pressure above the nozzle. In both cases, the molecular beam was irradiated by the  $\approx$  7 W, 1074.65 cm<sup>-1</sup> 9R(14) laser line with a power density of about 4.8 kW cm<sup>-2</sup> [193].

Thus, the control of molecular clustering by IR lasers has been demonstrated in [193, 212, 213, 284–288]. It was shown in [193] that in order to successfully control clustering in molecular beams, it is necessary to 'take out' the clustering region to the nozzle exit region. Under these conditions, the molecular clustering can be controlled by the gasdynamic cooling of a mixture of studied molecules with the carrier gas under vibrational excitation of molecules and clusters by resonance IR radiation at the nozzle exit. The control of molecular clustering has been studied with the example of SF<sub>6</sub> and CF<sub>3</sub>I molecules, and the optimal conditions for this process have been found.

### 7. Conclusions

Based on investigations performed in the papers discussed above, a number of original methods have been proposed and developed for controlling the parameters of atomic and molecular beams and the composition and content of molecular cluster beams, in particular, by using IR lasers for resonance vibrational excitation of molecules and clusters. We considered and analyzed methods and results of studies on the acceleration (deceleration) of atomic and molecular beams, the production of high-energy molecules in intense molecular beams, and studies aimed at determining the composition and content of pulsed molecular cluster beams and the control of these parameters. These investigations have led to the following conclusions.

The use in earlier studies of the combination of gas heating in the nozzle (in particular, with the help of microwave, radiofrequency, and optical discharges) to high temperatures  $(T \ge 3000 \text{ K})$  with aerodynamic acceleration provides the generation of accelerated atomic beams with kinetic energies ranging from a few electronvolts to a few tens of electronvolts [56–58, 210]. This method was used to obtain argon atoms with a kinetic energy up to 2.55 eV [56–58] and 30 eV xenon atoms in the xenon/hydrogen mixture. The method of nozzle heating to high temperatures cannot be used to obtain accelerated molecules because of chemical reactions proceeding at high temperatures, the dissociation of molecules, and the destruction of the nozzle material.

The rotating beam source method [70, 71] allows generating both accelerated and decelerated beams of cold atoms and molecules (with a low local temperature) with a controllable kinetic energy. This method was used for obtaining decelerated and accelerated atomic and molecular beams with kinetic energies ranging from  $10^{-4} - 10^{-3}$  eV (for respective argon atoms and oxygen molecules) to  $\approx 0.5$  and  $\approx 0.25$  eV (for respective SF<sub>6</sub> and CH<sub>3</sub>F molecules). The main disadvantage of this method is that only a small part of the gas escaping from the nozzle is used to form the beam, whereas the main part of the gas is scattered, producing an undesirable background in the vacuum chamber.

Precision methods for controlling the motion of atoms and molecules based on the use of periodic potentials (optical gratings) and ponderomotive or dipole forces produced by intense laser pulses are quite interesting for controlling the motion of atoms and molecules and manipulating atomic and molecular beams [73–79], 216–221] and can generate highly accelerated particles. Ponderomotive forces induced by intense laser pulses were used in [217] to generate giant, superstrong accelerations of neutral helium atoms exceeding the gravitational acceleration g by a factor of  $10^{14}$  for a time of only about  $10^{-13}$  s. This is probably the highest acceleration of particles in an external field ever observed.

The method for accelerating intense pulsed molecular beams (with  $\ge 10^{20} - 10^{21}$  molecules per sr s) based on the resonance vibrational excitation of molecules by high-power IR laser radiation at the nozzle exit [62–64] produces accelerated molecular beams with the controlled kinetic energy from 0.02–0.03 eV to 0.5–0.7 eV. A combination with aerodynamic acceleration produced SF<sub>6</sub> and CF<sub>3</sub>I molecular beams with a kinetic energy up to 1.0–1.2 eV. The main disadvantage of the method is that it cannot be used at higher excitation energy densities because of the optical breakdown at the nozzle exit. In addition, only some part of the molecules in the beam can be accelerated.

The method for generating intense secondary pulsed molecular beams proposed and developed in [65–68, 260] produces high-energy molecular beams in which the kinetic energy of molecules can be controlled by high-power IR laser pulses exciting molecules directly in the beam source. This method generated intense SF<sub>6</sub> and CF<sub>3</sub>I molecular beams (with  $\ge 10^{20}$  molecules per sr s) without a carrier gas with the respective kinetic energies  $\approx 1.5$  eV and  $\approx 1.2$  eV, and molecular SF<sub>6</sub> beams with He and H<sub>2</sub> carrier gases with the respective kinetic energies  $\approx 2.5$  eV and  $\approx 2.7$  eV, and also beams with accelerated CF<sub>3</sub> molecular radicals. The optimal conditions for generating high-energy molecules were found. This method is easily realized and can be used with intense pulsed molecular beams and flows.

The method developed in [189] for determining the composition and content of neutral pulsed cluster beams by the ion signals of cluster fragments can be used for determining the composition and content of neutral van der Waals molecular and atomic-molecular clusters in beams, both homogeneous and mixed. The potential of the method was demonstrated with the example of  $(SF_6)_mAr_n$  mixed cluster beams (where  $1 \le m \le 4$  and  $0 \le n \le 9$  are the numbers of molecules and atoms in the clusters). The method can also be applied to detect cluster beams with mass spectrometers with a relatively low mass resolution ( $R \le 300$ ). This method opens up new possibilities for studying clusters themselves and their interactions with particles and radiation.

The method for controlling the composition and content of molecular cluster beams proposed and developed in [193, 212, 213, 284–288] allows controlling clustering and dissociation of small clusters in a beam by IR lasers. The parameters have been found that provide the most efficient control of the suppression of molecular clustering and cluster dissociation. The results obtained have shown the fundamental possibility of using the effects of suppression of molecular clustering and cluster dissociation (or their combination) to control the parameters of molecular and cluster beams, which is necessary in many experiments, and to realize component and (or) istopically selective processes [188, 291, 297–302].

We note in conclusion that the scope of investigations of molecular and cluster beams and the results obtained suggest that new methods, in particular, laser methods for controlling the parameters of molecular and cluster beams, will be proposed and developed in the nearest future. This, in turn, will favor even wider applications of molecular and cluster beams in scientific studies and in practice.

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