Studies on high-intensity pulsed molecular beams and flows interacting with a solid surface

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<u>Abstract.</u> A high-intensity, pulsed, gasdynamically cooled supersonic molecular flow (beam) interacting with a solid surface produces a pressure shock with nonequilibrium conditions $T_{2, tr} \ge T_{2, rot} \ge T_{2, vib}$ inverse to those in the incident beam, $T_{1, tr} \le T_{1, rot} \le T_{1, vib}$, $(T_{i, tr}, T_{i, rot}, and T_{i, vib}$ are the translational, rotational, and vibrational molecular temperatures, respectively). This provides the possibility for studying the isotopically selective IR multiphoton molecular dissociation under new nonequilibrium conditions and for considerably increasing the efficiency of the process. Due to pressure shock formation near the surface, duration-controlled molecular

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Received 30 November 2002 Uspekhi Fizicheskikh Nauk **173** (9) 913–940 (2003) Translated by E Yankovsky; edited by S N Gorin beam pulses, intense kinetic-energy-variable secondary molecular beams, and intense beams of accelerated cold radicals can be obtained. In the present paper, research aimed at producing duration-controlled molecular beams, high-intensity secondary pulsed molecular beams, high-energy secondary pulsed molecular beams with IR-laser-controlled kinetic energy, and lowenergy molecular beams is reviewed.

1. Introduction

In recent years, molecular (atomic) beams have been widely used in experiments in which the structure of matter is studied and in research of many physicochemical processes that take place on the atomic and molecular levels. It may be said without exaggeration that the progress in many areas of physics and chemistry is due to the development of methods of molecular beams and their combination with laser methods that has taken place in the last 20-30 years (e.g., see Refs [8–27]). This, in particular, is true of spectroscopy [15, 17, 18, 24, 28-42] and the study of cluster structure [15, 17, 18, 20, 21, 24, 43-46], scattering processes [3, 10, 11, 14, 47-55],

elementary physicochemical processes on a surface [16, 27, 56-63], the dynamics of intramolecular relaxation [19, 22, 23, 64-71], and chemical reactions [10-14, 19, 22, 23, 26, 64-68]. Many areas of research use high-energy (low-energy) molecular beams [72-74] in which the kinetic energy of molecules or atoms E_{kin} is much higher (lower) than their thermal energy. At room temperature, $E_{\rm kin} \leq 0.05 \text{ eV}$. Intense molecular beams (with no fewer than 10^{20} molecules per steradian per second) whose molecules have a kinetic energy ranging from roughly one millielectronvolt to several electronvolts are needed to study chemical reactions with energy barriers, elastic and inelastic collisions, and the interaction of molecules with a surface. Lately, low-energy molecular beams whose molecules have low velocities have been used in experiments in molecule trapping [75-78]. Intense molecular jets and flows are needed to produce molecular beams and to do spectroscopic studies [33, 35, 36] and research in selective photochemistry, including laser isotope separation [79-86].

Section 2 is a brief review of the different methods of producing intense pulsed molecular beams and jets and the widespread methods of their detection. The method of detection of molecular beams by an uncooled pyroelectric detector used in our research is discussed in greater detail. It is shown that when such a detector is combined with an IR laser, it can be successfully used to measure both the kinetic and the internal energies of the molecules in the beam.

Section 3 discusses the nonequilibrium conditions in gasdynamically cooled jets and flows and in the shock wave that forms near the surface upon which an intense gasdynamically cooled pulsed supersonic molecular beam impinges. It is shown that the nonequilibrium conditions in the shock wave are the reverse of those in the incident beam, which opens the possibility of studying selective photochemical processes under new nonequilibrium conditions.

Section 4 is a review of the research in isotopically selective IR multiphoton molecular dissociation (using the examples of SF₆ and CF₃I) under the nonequilibrium conditions of a gasdynamically cooled pulsed molecular flow interacting with a solid surface. The experimental setup and method are described, and the results of studying the selective dissociation of molecules when they are excited in the shock wave and in the flow incident to the surface and the undisturbed flow are given. These results are compared with each other and with similar data on the dissociation of molecules under static conditions in a cell at room temperature and in the molecular beam. Also examined are the results of measurements of the characteristics of the incident flow and the gas parameters in the shock wave. It is shown that, because of the formation of a compression shock in front of the surface, the efficiency of selective IR multiphoton dissociation of molecules in gasdynamically cooled flows can be substantially increased.

Section 5 is devoted to a review of the results of research in the compression-shock control of the duration of pulses of intense molecular beams. An experimental method is described in which the shock that arises in front of the surface is used as a gate for shortening the pulses of the primary molecular beams. It is shown how this method can be used to produce intense pulsed molecular beams with a duration of less than 10 μ s and a length of approximately 1-2 cm.

Section 6 gives a review of experiments on producing intense secondary pulsed molecular beams and of investigations of the characteristics of such beams. In such experiments the compression shock is used as a source of secondary beams. The results of experiments in production of secondary beams of SF_6 and CF_3I molecules without a carrier and with a carrier gas (H₂, He, and CH₄) are also given in this section. It is shown that by forming a compression shock in front of the surface one can produce intense secondary pulsed molecular beams with characteristics comparable to those of primary molecular beams.

Section 7 is devoted to a review of investigations into the production of high-energy molecular beams with their kinetic energy controlled by high-power IR laser radiation. The method is based on the formation of a shock wave in front of the surface and on its use as a source of a secondary beam for producing high-energy molecules. The molecules in the beam are accelerated via resonant vibrational excitation by the radiation from a high-power IR laser in the shock wave (in the very source of the molecular beam) and subsequent vibrational-translational (V-T) relaxation, which occurs when the gas escapes into a vacuum. The results of the research in the production of accelerated molecular beams of SF₆ and CF₃I molecules without a carrier gas and with carrier gases are also given in this section. It is shown that the method can be used to produce intense molecular beams with controllable kinetic energy in a range from approximately 0.1-0.2 eV to 2-3 eV. It is also shown that the same method can be employed to produce accelerated beams of free radicals.

Section 8 reviews the research into the production of intense low-energy molecular beams with the kinetic energy of the molecules varying from several millielectronvolts to several dozen millielectronvolts. The method of producing such beams is based on the formation of a cold (\approx 77 K) compression shock in front of the solid surface and the use of this compression shock as a source of low-energy molecules. The results of studies of the production of low-energy molecular beams of H₂, He, CH₄, and other molecules are given in this section. It is shown that the intensities of the beams produced by this method exceed those of 'standard' effusive beams, which are usually used to produce low-energy molecules, by four to five orders of magnitude. Finally, in the concluding Section 9, the main results and the conclusions that follow from them are given.

2. Producing intense pulsed molecular beams and methods used for detecting them

2.1 Ways of producing intense molecular beams

The most common way of producing intense molecular beams is to extract them with the help of skimmers from gasdynamically cooled jets produced in pulsed nozzles [73, 87]. There are several types of nozzles for producing pulsed molecular beams [73]. The common ones are the following: (1) nozzles with a control mechanism that uses a solenoid (the automobile fuel injector belongs to this type), (2) nozzles with a piezoelectric control mechanism, and (3) nozzles of the 'current-loop' type [73, 87]. A characteristic feature of nozzles of the first type is that their pulse duration varies from several hundred microseconds to several milliseconds, while in the second type this range is approximately from 100 µs to 10 ms. Current-loop nozzles usually produce pulses with durations ranging from 30-40 to 150 µs. The builders of such nozzles were able to produce molecular beams with a record short pulse duration of roughly 7 µs [88].

The use of molecular beams in various experiments requires from researchers the knowledge of beam characteristics [73, 87]. Hence, the development of methods used in detecting molecular beams and in measuring the beam characteristics is a very important aspect of the problem. Among the main characteristics of pulsed molecular beams are intensity, duration, velocity of propagation, and the spread of velocities of the molecules in the beam (the extent to which the gas is cooled). A very important characteristic of molecular beams and jets is the energy distribution over the internal degrees of freedom of the molecules (the distribution of molecules over quantum states).

2.2 Methods of detecting molecular beams

2.2.1 The most common methods of beam detection. Among detectors of molecular beams the most common one is an electronic ionizer [10, 73] operating with a mass spectrometer, often of the quadrupole type. Hence, this device is a mass-selective detector. Such an ionizer has a high time resolution (\approx 10 µs) and can be employed in time-of-flight measurements [89], usually used to determine the distribution of the kinetic energy of molecules in the beam. However, the ionization-type detector cannot be used for quantitative analysis of the energy distribution over the internal degrees of freedom of the molecules since the efficiency of the ionization of molecules by electron impact is practically independent of the internal energy of the molecule [90].

Another common type of detector used in diagnosing molecular beams is represented by cooled (usually by liquid helium) bolometers. A typical response time of semiconductor bolometers is on the order of 10^{-3} s, which is too long for time-of-flight measurements. The response time of a bolometer can be substantially reduced by using thin films of superconducting materials as the sensitive (active) elements [92, 93]. Bolometers can be used to analyze the energy distribution over the internal degrees of freedom of the molecules by employing what is known as the laser-bolometric method [94], which amounts to measuring the energy of IR laser radiation absorbed by molecules in the beam as a function of radiation frequency. This method was already used in the early experiments, including IR sub-Doppler spectroscopy, analysis of molecule distribution over rotational states [96], vibrational predissociation of van der Waals molecules [97], and measurements of the internal energy of molecule excitation [98].

Molecular beams can also be diagnosed by methods based on laser-induced fluorescence (LIF) [28-30, 99], which can be used to study the distribution of the kinetic [100, 101] and internal energies of the molecules [28-30, 99,102], especially simple, mostly diatomic, molecules. Note that the possibility of inducing fluorescence of molecules and their dissociation fragments by IR laser radiation [103-105]broadens the range of the LIF method in studying the distribution of the kinetic and internal energies of particles. Note also the electron-beam fluorescence (EBF) method of excitation of molecules [106, 107], which is widely employed in measuring the internal energy of molecules. This method is also used in time-of-flight measurements [108]. There are many other methods for diagnosing molecular beams and jets, including those based on the excitation of molecules by laser radiation (e.g., see Refs [109, 110] and the literature cited therein).

The above methods are fairly sensitive and can be used to detect both pulsed and continuous molecular beams and jets.

However, their practical implementation is quite complex (they require electron guns, tunable lasers of the visible and UV ranges, and cryogenic techniques). More than that, the use of the LIF and EBF methods in time-of-flight measurements is limited to molecules (atoms) with long excited-state lifetimes. Apatin et al. [110] developed a method for detecting the kinetic and internal energies of molecular beams and jets that uses a noncooled pyroelectric detector (PED) and a pulsed CO_2 laser. We used this method to diagnose the molecular beams and jets in the works discussed in this review. Earlier such a detector was successfully used to measure IR multiphoton absorption under static conditions in a cell [111, 112] and in a molecular beam [113, 114]. Below is a brief description of the pyroelectric detector and the method of detecting molecular beams.

2.2.2 Detection of pulsed beams with a noncooled pyroelectric detector. The principle of operation of a PED is based on recording the changes in the spontaneous dipole moment or spontaneous polarization of a pyroelectric element caused by changes in temperature. The design of the PEDs we used differs substantially from that of ordinary PEDs produced commercially and described in the literature. The pyroelectric element in our detector was a thin ($\leq 1 \mu m$) polycrystalline film that was a conglomerate of small spatially oriented crystals of a polycyclic organic compound.

The design of the detector is described in detail in Ref. [111]. The detector consists of a glass (or ruby) substrate approximately 1×10 mm (2-3 mm thick) onto which a lower electrode, a pyroelectric film, and an upper electrode are deposited by sputtering one after another. The electrodes are made of aluminum in the form of mutually perpendicular strips 2-4 mm wide. Both electrodes and the pyroelectric layer are no thicker than 1 μ m. The size of the active PED element is 4×4 mm. The internal resistance of the PED is roughly 1 G Ω and the capacitance is on the order of 100 pF. A PED of this type has the lowest possible level of acoustic noise. Another important advantage of the PED in question is a rather good time resolution, i.e., rapid cooling of the PED after instantaneous pulse heating ($\tau_T = 3-5 \mu s$). The cooling time τ_T is determined by the heat capacity of the pyroelectric element and the rate at which heat is transferred to the massive substrate. A pyroelectric detector with such a time resolution makes it possible to record time-of-flight spectra of the molecules in a pulsed beam or jet, and thus measure the kinetic and internal energies of the molecules.

The method of detecting molecular beams using a PED has been described in detail in Refs [110, 115]. It amounts to measuring the energy of the molecules that have reached the active element of the detector, where this energy is transformed into heat that generates a signal. The signal induced in the PED by the beam molecules was amplified $(\times 100)$ and applied to the input of an oscillograph. The experiments were carried out with a molecular beam formed by a skimmer, as well as with one not formed by a skimmer. In both cases the detector measured the energy of the molecules propagating within a solid angle determined by the size of the PED active element $(4 \times 4 \text{ mm})$ and the distance from nozzle to detector. This distance could be changed by mechanically moving the PED along the beam axis, which made it possible to measure the time-of-flight spectra of the molecules in the beams at different distances from the nozzle. These time-of-flight spectra were used to determine the kinetic-energy distribution of the beam molecules. When the molecules in the beam were excited by laser light, we also measured their internal energy.

Without preliminary excitation of the molecules by a laser pulse, the signal from the detector is

$$S_0 \sim nv \left(E_a + E + \frac{mv^2}{2} \right) \sim nv E_0 \,, \tag{1}$$

where *n* is the density of molecules at the surface of the detector, *v* and *m* are, respectively, the velocity and mass of a molecule, *E* is the energy of a molecule (sum of vibrational, rotational, and 'local' translational energies), E_a is the heat of adsorption per molecule, and E_0 is the total energy of a molecule (the expression in parentheses). In the case where the beam molecules are vibrationally excited by a laser pulse, the signal is

$$S_{\rm L} \sim nv(E_0 + E_{\rm ab}), \qquad (2)$$

where E_{ab} is the energy of the laser pulse absorbed by a molecule. Thus, the additional signal (i.e., the signal absent in unexcited molecules) induced in the detector is the measure of the energy of the laser pulse absorbed by the beam molecules under vibrational excitation [110, 115].

The translational, rotational, and vibrational temperatures of the beam molecules were found by analyzing the experimentally observed time-of-flight distributions of 'cold' and vibrationally excited molecules [110, 115]. In such analyses we used the standard (two-parametric) expression for the velocity distribution of the density of the molecules in a supersonic molecular beam [4, 116]

$$n(v) \sim \left(\frac{v}{u}\right)^2 \exp\left[-\frac{(v-u)^2}{\alpha^2}\right],$$
 (3)

where *u* is the mean velocity of molecules in the beam and $\alpha = (2kT/m)^{1/2}$ is the most probable velocity of the molecules in the coordinate system linked to the beam. We also allowed for the balance of the energies of molecules before and after they left the nozzle. Thus, the method in question made it possible to measure both the kinetic energy of molecules in a beam and their internal energy [110, 115].

3. Nonequilibrium conditions in a gasdynamically cooled molecular flow and in the shock wave

The following relations hold for an isentropic flow of ideal gases [4]:

$$\frac{T_0}{T_1} = 1 + \frac{\gamma - 1}{2} M^2, \tag{4}$$

$$\frac{\rho_0}{\rho_1} = \left(1 + \frac{\gamma - 1}{2} M^2\right)^{1/(\gamma - 1)},\tag{5}$$

$$\frac{p_0}{p_1} = \left(1 + \frac{\gamma - 1}{2} M^2\right)^{\gamma/(\gamma - 1)}.$$
(6)

Here T_0 , ρ_0 , and p_0 are the temperature, density, and nozzle pressure of the gas; T_1 , ρ_1 , and p_1 are the local temperature, density, and pressure of the gas in the flow; $\gamma = c_p/c_V$ is the heat-capacity ratio; and M is the Mach number (the ratio of the hydrodynamic velocity to the speed of sound).

The above relations are valid only for a gas of monatomic molecules. In the case of polyatomic molecules, the heat capacities and, correspondingly, γ are rather strongly depen-

dent on temperature. Therefore, for a gas of polyatomic molecules equations (4)-(6) do not hold even approximately.

In the event of the flow of a molecular gas through a nozzle, all degrees of freedom of the molecules initially contribute to the heat capacity. As the gas expands, it rapidly cools, and the thermodynamic equilibrium between the different degrees of freedom is violated because of the difference in relaxation times: $\tau_{tr} \leq \tau_{rot} \leq \tau_{vib}$. The extent to which the system deviates from local equilibrium depends on the number of collisions, z_{col} , needed for the relaxation of a given degree of freedom. For polyatomic molecules, usually $z_{tr} \leq z_{rot} \leq z_{vib}$. Hence, the following condition imposed on the effective temperatures in the flow [4] is realized:

$$T_{1,\,\mathrm{tr}} \leqslant T_{1,\,\mathrm{rot}} \leqslant T_{1,\,\mathrm{vib}} \,. \tag{7}$$

According to Refs [117–119], in the pressure shock, which is formed in interaction of a pulsed gasdynamically cooled molecular flow and a surface, the nonequilibrium conditions may be the reverse of (7) because of the difference in the rates of the translational, rotational, and vibrational relaxations [120]:

$$T_{2, \text{tr}} \ge T_{2, \text{rot}} \ge T_{2, \text{vib}}$$
 (8)

Here, due to the large time of vibrational-translational relaxation (e.g., for SF₆ the rate constant $p\tau_{V-T} \approx 150 \ \mu s$ Torr [121], and for CF₃I $p\tau_{V-T} \approx 350 \pm 100 \ \mu s$ Torr [122]), the vibrational temperature of the molecules in the shock can be almost the same (provided that a pulsed flow of a rarefied gas is used) as the vibrational temperature of the molecules in the incident flow $(T_{2, vib} \approx T_{1, vib})$, while the translational and rotational temperatures of the molecules in the shock are much higher than in the incident flow: $T_{2,tr} > T_{1,tr}$ and $T_{2,rot} > T_{1,rot}$. Thus, new nonequilibrium conditions are created in the shock, with the vibrational temperature of the molecules much lower than the translational and rotational temperatures. Such conditions are of great interest to researchers who study selective photochemical processes, since these results and their comparison with the results of similar studies in gasdynamically cooled beams and jets make it possible to establish the role that the vibrational and rotational temperatures of molecules play in the formation of selectivity and to estimate the effect of concentration and collisional effects on the product yield and the selectivity of the process. It is under these conditions that the selective dissociation of SF₆ and CF₃I molecules has been studied in Refs [123-130]. The next section is devoted to a review of this work.

4. Selective IR dissociation of SF_6 and CF_3I under the nonequilibrium conditions of a pulsed flow interacting with a solid surface

4.1 Brief review of earlier work

It must be noted that over the years the isotopically selective IR multiphoton molecular dissociation has been thoroughly studied (e.g., see Refs [82, 131-133]). The main factors that determine the selectivity and the dissociation yield are known. On the basis of this method, separation of carbon isotopes via selective dissociation of CF₂HCl molecules (Freon-22) has been developed in Russia. IR multiphoton excitation and dissociation of SF₆ molecules are the most studied processes.

The majority of experiments on isotopically selective dissociation of SF₆ have been carried out under static conditions in a cell at room temperature [134-136] and at low temperatures of the gas ($T \approx 190$ K [137], $T \approx 175$ K [138], and $T \approx 140$ K [136]). There have also been investigations into the selective dissociation of SF₆ under the nonequilibrium conditions of a molecular beam [139-141] and gasdynamically cooled jet [79] and flow [80]. The CF₃I molecule has also been thoroughly studied as an object of research in IR multiphoton excitation and dissociation. Selective dissociation of CF₃I has been studied in a cell at room and low temperatures (e.g., see Ref. [82]) and in dynamically cooled molecular flows [83-86]. In view of this, it was also interesting to study the selective dissociation of CF₃I under the nonequilibrium conditions of pulsed flow interacting with a solid surface. Such research has been done in Refs [123, 128].

Note that, because of the rapid cooling of the gas in jets and flows, the IR absorption bands of the molecules narrow very fast, with the result that the selectivity of excitation and dissociation increases [79-81]. However, the efficiency of photochemical processes in jets and flows is very low. The rates of chemical reactions, including those that lead to the production of the target products, are very low because of the low concentration of the molecules and the low temperature of the gas. In some cases where the concentration of molecules in the flow is low, a substantial number of radicals is lost on the walls without forming products (as is the case with the dissociation of $CF_{3}I[83-86]$). In Ref. [123] we reported that in the case of excitation of molecules (SF₆ and CF₃I) in a pulsed flow impinging on a solid surface, there is a considerable increase (severalfold) in product yield with an almost unchanged selectivity of the process, while Refs [124, 125] present the first results in selective dissociation of SF₆ under the nonequilibrium conditions of a compression shock. The results of detailed studies of isotopically selective dissociation of the SF₆ and CF₃I molecules are presented in Refs [126, 127] and Ref. [128], respectively. In this research the selective dissociation of the molecules was studied (1) under the nonequilibrium conditions of a compression shock, (2) in a flow impinging on a surface, and (3) in an undisturbed flow. In Sections 4.2 - 4.7, the experimental setup and a brief review of the results are given.

4.2 Experiment and method

4.2.1 Experimental setup. The experimental setup used for studies of the selective dissociation of molecules under nonequilibrium conditions of a compression shock is given schematically in Fig. 1. The molecular flow was produced using a pulsed current-loop nozzle [87]. The diameter of the opening of the nozzle was 0.75 mm. The opening time of the nozzle amounted to about 100 μ s (at half maximum). The nozzle pressure could be varied from 0.1 to 3.5 atm. The nozzle was cut in the shape of a cone with an opening angle of 60°. The length of the cone was 15 mm. The number of molecules flowing out of the nozzle in each pulse, $N_{\rm fl}$, depended on the nozzle pressure and could be varied in the experiments from approximately 5×10^{15} to 1.5×10^{17} [126, 127]. The nozzle could operate in a single-pulse mode and in a mode with a pulse repetition rate of 1 Hz.

The vacuum chamber (with a volume $V_{ch} = 20$ l) in which the molecular flow was formed was pumped down to a residual pressure of $(1-2) \times 10^{-6}$ Torr by a diffusion pump (the pumping rate was 500 l s⁻¹). The molecular flow was



Figure 1. Experimental setup, which schematically shows the section in the xz plane. The laser beam propagates along the y axis.

formed by two thin metallic strips attached to the opening cone of the nozzle in such a way that they formed a dihedral angle with the edge parallel to the *y* axis. In the *xz* plane these two strips had a varying curvature radius.

At a distance x = 50-150 mm from the nozzle a solid surface (plates of the KBr, CaF₂, and LiF crystals were used) was placed at right angles to the beam's direction. As a result of the interaction of the supersonic molecular flow with the surface, in front of it there forms a compression shock [117– 119] within which the conditions are essentially inhomogeneous, time-dependent, and nonequilibrium. Under the experimental conditions in question, the characteristic size of the shock front, which is equal by an order of magnitude to the mean free path of the molecules [117, 118], amounted to 0.2-5 mm [126–128].

The excitation of the molecules was done by the radiation from a frequency-tunable high-power transversely excited atmospheric-pressure (TEA) CO₂ laser, which generated pulses with an energy of up to 3 J. The molecules were excited near the surface at a distance $\Delta x = 1.5-8$ mm from it. The laser radiation was focused on this area by a cylindrical lens with a focal distance of 12 cm, with the lens axis parallel to the surface. The cross-sectional area of the laser beam at the lens focus was 0.18 × 12.5 mm.

The nozzle, the CO₂ laser, and the registering system, which included a detector of luminescence of vibrationally excited HF^{*} molecules (or a PED with an amplifier) and a S9-8 digital oscillograph, were powered by a GI-1 pulse delay generator. The synchronization of the laser pulse and the molecular beam was monitored with the help of a PED by the signal induced in the receiver by the vibrationally excited molecules of the beam [110, 115] or by the HF^{*} luminescence signal.

4.2.2 Method. The dissociation of SF₆ molecules was studied by detecting HF^{*} luminescence ($\lambda \approx 2.5 \,\mu$ m). The vibrationally excited HF^{*} molecules were produced in the reaction between fluorine atoms (the primary products of SF₆ dissociation) and hydrogen or methane [142]. The HF^{*} luminescence intensity correlates well with the SF₆ dissociation yield [79, 143]. Luminescence was detected by a PbS-based IR detector with a detecting area of 1 × 1 cm. The pass band of the detector with the amplifier (×100) was 16 kHz. The spectral composition of the IR-luminescence radiation was determined with the help of color filters. Note that the weak IR-luminescence signal at roughly 2.5 µm was also observed in the case of excitation of SF6 molecules in the absence of H₂ or CH₄ [126, 127], probably because of the presence in the initial SF₆ gas of minute quantities of hydrocarbon compounds, although before the initial SF₆ gas was fed into the nozzle it was purified by condensation and pumping. When H₂ or CH₄ was added, the luminescence intensity increased by a factor greater than 10. Most results reported in Refs [126, 127] were obtained when the excitation of SF_6 was achieved with SF_6 in a mixture with H_2 or CH_4 . Experiments in the dissociation of SF_6 in a flow without hydrogen or methane or with minute quantities of these gases were also carried out. Such experiments were needed to compare the results with the data on SF₆ dissociation in a molecular beam without a carrier (see Section 4.3).

In our experiments we also measured the yield of SF₄ and its enrichment with the isotope ³⁴S. The procedure of gathering and IR analysis of the products and the gas that remained after the dissociation of molecules in the gasdynamic flow has been described in detail in Refs [83, 85]. The ³⁴S enrichment factor for SF₄ was determined by the formula

$$K_{34}^{\text{prod}} = \frac{[{}^{34}\text{SF}_4]}{[{}^{32}\text{SF}_4]} \frac{1}{\zeta} , \qquad (9)$$

where $[{}^{34}SF_4]/[{}^{32}SF_4]$ is the ratio of concentrations of the corresponding molecules (in square brackets) in the SF₄ product, and $\zeta = {}^{34}S/{}^{32}S \approx 0.044$ is the ratio of the percentages of the sulfur isotopes in the initial SF₆ gas. The ${}^{34}SF_4$ -to- ${}^{32}SF_4$ concentration ratio in the product was measured by the IR-absorption spectra of the v_6 vibration of the molecule ($\approx 728 \text{ cm}^{-1}$ for ${}^{32}SF_4$ [144]), in which the isotope shift for ${}^{32}SF_4$ and ${}^{34}SF_4$ amounts to about 12.3 cm⁻¹ [145].

In experiments with the CF₃I molecule we measured the C_2F_6 product yield and the ¹³C enrichment factor. These measurements were done by analyzing the IR spectra and mass spectra of the products and the gas that remained after irradiation. The isotope composition of C_2F_6 was determined by the ion fragment $C_2F_5^+$. The enrichment factor for C_2F_6 was determined by the formula

$$K_{13}^{\text{prod}} = \frac{2I_{121} + I_{120}}{(I_{120} + 2I_{119})\zeta}, \qquad (10)$$

where I_{119} , I_{120} , and I_{121} are the intensities of the mass peaks of the C₂F₅⁺ ion, and $\zeta = {}^{13}\text{C}/{}^{12}\text{C} \approx 0.011$ is the ratio of the percentages of carbon isotopes in the initial CF₃I gas.

4.3 Measuring the parameters of a molecular flow

The main parameters of a pulsed molecular flow that influence the formation and characteristics of the compression shock are the velocity and length (duration) of the flow, the concentration of molecules in it, and the translational, rotational, and vibrational temperatures of the molecules in the flow. The duration and mean velocity of the molecular flows of SF₆ and CF₃I were determined with the help of a PED by the time-of-flight method described in Refs [110, 115] (see Section 2.2). The mean flow velocities for SF₆ and CF₃I in the excitation zone (at a distance $x \ge 50$ mm from the nozzle) amounted to $v_x = 420 \pm 20$ m s⁻¹ and 400 ± 20 m s⁻¹, respectively. The time-of-flight SF₆ spectra were also studied by detecting HF* luminescence. These spectra are discussed in Section 4.5. The temperature of the molecules in the flow was not measured in these experiments. However, earlier it was thoroughly studied in Ref. [115], where we used a pulsed nozzle similar in design to that described in the papers being discussed. Hence, one may assume that the translational, rotational, and vibrational temperatures of SF_6 molecules in the flow are comparable to those obtained in Ref. [115].

The concentration of molecules in the flow, N_1 , was estimated on the basis of the measured value of the total number of particles $N_{\rm fl}$ ejected by the nozzle in one pulse, and the calculated value of the flow volume $V_{\rm fl}$ ($N_1 \approx N_{\rm fl}/V_{\rm fl}$). The number of molecules $N_{\rm fl}$ was estimated by the pressure increment Δp in the vacuum chamber in the course of *n* nozzle pulses without evacuation:

$$N_{\rm fl} = \frac{\Delta p V_{\rm ch}}{nkT} , \qquad T \approx 300 \text{ K} . \tag{11}$$

The same number was also determined from the IR absorption spectrum of the molecules (SF₆, CF₃I) collected from the chamber into an optical cell after n nozzle pulses. This value of $N_{\rm fl}$ was found to correlate well with the measured value. Figure 2 plots $N_{\rm fl}$ as a function of the nozzle pressure of SF₆. The flow volume $V_{\rm fl}$ was estimated on the basis of measurements of the flow length $\Delta x_{\rm fl}$ and the flow's cross section $s_{\rm fl} \ (V_{\rm fl} = \Delta x_{\rm fl} \, s_{\rm fl})$. The flow length in the zone of molecule irradiation was determined by the time-of-flight method with the help of a PED [110, 115]. In the case of SF_6 , it was also determined from the dependence of the HF*-luminescence intensity on the delay time τ_d between the nozzle-opening pulse and the exciting-radiation pulse from the CO₂ laser (from the time-of-flight spectra of SF_6 ; see Section 4.5). The duration of the molecular flow (at half maximum), $\Delta \tau_{\rm fl}$, was approximately 100 µs (e.g., see curve 1 in Fig. 5 in Section 4.5). The flow length in the zone of irradiation of the molecules, $\Delta x_{\rm fl}$, was $\Delta x_{\rm fl} = v_x \Delta \tau_{\rm fl} \approx 4.2$ cm. The crosssectional area at a distance $x \approx 50$ mm from the nozzle was $s_{\rm fl} \approx 7.2 \text{ cm}^2$, which was determined by the opening angle of the nozzle cone, the strips limiting the flow, and the distance from nozzle to solid surface. Hence, the flow volume was $V_{\rm fl} \approx 30 \text{ cm}^3$. The parameters of molecular flows of SF₆ and CF₃I are listed in Table 1.



Figure 2. Number of SF₆ molecules in the flow as a function of the nozzle pressure; N_{fl} is the number of molecules per pulse.

4.4 Exciting molecules in a flow incident to the surface

In Ref. [123] it was shown that when a flow of SF₆ molecules impinging on a surface is excited under conditions where the distance Δx from the excitation area to the surface is

Flow parameters	SF_6	CF ₃ I
Duration, $\Delta \tau_{\rm fl}$	$\approx 100 \ \mu s$	$\approx 100 \ \mu s$
Length, $\Delta x_{\rm fl}$	$\approx 4.2 \text{ cm}$	$\approx 4.0 \text{ cm}$
Velocity, v_x	$420 \pm 20 \text{ m s}^{-1}$	$400 \pm 20 \text{ m s}^{-1}$
Number of		
molecules, N _{fl}	$5 imes 10^{15} - 1.5 imes 10^{17}$	$5 imes 10^{15} - 8 imes 10^{16}$
Volume, $V_{\rm fl}$	$\approx 30 \text{ cm}^3$	
Concentration of		
molecules, N_1	$1.7 \times 10^{14} - 5 \times 10^{15} \text{ cm}^{-3}$	$1.7 \times 10^{14} - 2.7 \times 10^{15} cm^{-3}$
Translational		
temperature, $T_{1,tr}$	≤ 40 K*	
Rotational		
temperature, $T_{1, rot}$	≤ 40 K*	
Vibrational		
temperature, $T_{1,vib}$	≤ 150 K*	

Table 1. Parameters of molecular flows of SF₆ and CF₃I at $x \approx 50$ mm from the nozzle.

* Data taken from Ref. [115].



Figure 3. Typical oscillogram of an HF*-luminescence pulse when SF₆ exists in a mixture with CH₄ ($p(SF_6)/p(CH_4) = 1/1$) and is excited in the molecular flow interacting with a solid surface; p_{noz} is the total nozzle pressure.

approximately equal to, or greater than, 30 mm, the HF*luminescence pulse consists of two peaks (Fig. 3) separated in time and that the larger the distance Δx , the greater the separation. It was also found that the first peak is caused by the dissociation of molecules in the excitation zone and the second by the dissociation of molecules in the region where the flow hits the surface, i.e., in the shock wave. When $\Delta x \leq 20$ mm, these peaks could not be resolved because of the small pass band of the IR detector (16 kHz), but there was strong dependence of the HF*-luminescence intensity on whether or not there is a surface in the way of the flow. This is especially clear from the plots in Fig. 4, which give the dependence of the HF*-luminescence intensity on the nozzle pressure when SF_6 is excited in the undisturbed flow (curve 1) and when it is excited in the flow incident to the surface (curve 2). The distance from nozzle to surface was 51 mm, and $\Delta x = 2.5$ mm. The delay time between the nozzle-opening pulse and the exciting laser pulse $\tau_d = 260 \ \mu s$. Such delay time ensured the irradiation of the most intense part of the flows (see Fig. 5 in Section 4.5.1). The molecules were excited at a frequency of 947.74 cm^{-1} (the 10P(16) laser line), which is just in resonance with the v_3 vibration of the molecule $(\approx 948 \text{ cm}^{-1} \text{ [146]})$. The energy density of the exciting pulse



Figure 4. HF*-luminescence intensity plotted as a function of the nozzle pressure with SF₆ excited in the undisturbed flow (curve 1) and in the flow incident to the surface (curve 2); ϕ is the exciting-pulse energy density. For more details see the main text.



Figure 5. HF*-luminescence intensity plotted as a function of the delay time τ_d between the nozzle-opening pulse and the laser-light pulse when SF₆ exists in a mixture with CH₄ and is excited in the undisturbed flow (curve *I*) and in the flow interacting with the surface (curve *2*). The total nozzle pressure $p_{noz} = 1.25$ atm. The molecules were excited on the 10P(16) laser line with an energy density $\Phi = 12$ J cm⁻². \

was 7.3 J cm⁻². Clearly, within the entire range of nozzle pressures used in the experiments the luminescence intensity in the flow incident to the surface is five-to-eight times higher than that in the undisturbed flow.

The increase in HF*-luminescence intensity in the case where molecules are excited in the flow incident to the surface is caused by the increase in the molecule dissociation yield due to the formation of a shock wave in front of the surface [123-125]. When there is IR multiphoton excitation, an ensemble of highly excited molecules with a rather broad distribution over vibrational states is formed [82, 131]. As a result, some of the molecules dissociate radiatively (not experiencing collisions), while others dissociate by collisions between the highly excited molecules. In the undisturbed flow there is only radiative dissociation, while collisional dissociation of the highly excited molecules, whose contribution to the total yield is usually very large (e.g., see Ref. [82]), is absent because of a deficit of collisions. In the shock wave that arises in front of the surface, where the excited molecules land, the gas density and temperature are much higher than in the incident flow (see Section 4.7). Hence, the conditions within this wave are conducive to collisions of highly excited molecules between each other, as a result of which the dissociation yield increases.

4.5 Exciting molecules in the shock wave

4.5.1 Time-of-flight spectra of molecules in a flow interacting with a surface. When the distance Δx from the irradiation zone and the surface is comparatively small, the molecules can be excited directly in the shock wave. Figure 5 shows the characteristic curves representing the dependence of the HF*-luminescence intensity on the delay time τ_d between the nozzle-opening pulse and the laser-light pulse when SF₆ exists in a mixture with CH₄ (with a SF₆-to-CH₄ pressure ratio $p(SF_6)/p(CH_4) = 10/1$ and is excited in the undisturbed flow (curve 1) and in the flow interacting with the surface (curve 2) [124, 125]. The molecules were excited on the 10P(16) laser line (947.74 cm⁻¹). The distance from nozzle to surface is x = 51 mm, and $\Delta x = 2.5$ mm. Clearly, when SF₆ is excited in the flow interacting with the surface, the maximum value of the HF*-luminescence intensity is at least 10 times higher than when the excitation of molecules takes place in the undisturbed flow. The sharp shock front is formed in the zone where the molecules are excited (at a distance $\Delta x = 2.5$ mm from the surface), with $\tau_d = 260 \ \mu s$. The mean flow velocity was $v_x = 420 \pm 20 \text{ m s}^{-1}$.

With decreasing (increasing) distance Δx from the excitation zone to the surface, the intensity of HF^{*} luminescence in the shock wave was found to increase (decrease), while the delay time τ_d , at which the maximum intensity of HF^{*} luminescence in the excitation zone exists, was found to decrease (increase). Figure 6 shows the dependence of the HF^{*}-luminescence intensity on Δx when SF₆ is excited in the shock wave [126, 127]. This dependence characterizes the width and slope of the shock front. Clearly, the width is approximately 3 mm when the nozzle pressure is 1.25 atm and the nozzle – surface distance x = 51 mm.

The same experiments (see Refs [126, 127]) established that as the intensity of the primary beam (nozzle pressure) increases, the intensity of luminescence in the shock wave increases dramatically, while the delay time τ_d , at which the luminescence intensity is at its maximum, decreases. The



Figure 6. HF*-luminescence intensity plotted as a function of the distance Δx for the case where the molecules are excited in the shock wave. The nozzle pressure of SF₆ $p_{noz} = 1.25$ atm, and nozzle-surface distance x = 51 mm. The frequency and energy density of the exciting laser radiation are the same as in Fig. 5.



Figure 7. C₂F₆ yield plotted as a function of the delay time τ_d between the nozzle-opening pulse and the laser pulse when CF₃I is excited in the undisturbed flow (curve *I*) and in the flow interacting with the surface (curve 2). The molecules were excited on the 9R(12) laser line with an energy density $\Phi = 1.4$ J cm⁻².

luminescence intensity increases because the gas density in the shock wave does, while the decrease in τ_d is due to the increase in flow velocity and in the rate of the shock-front buildup because of the increase in gas density in the shock wave. Under low nozzle pressures (≤ 0.2 atm), with the molecular concentration in the flow N_1 no higher than $N_1 \leq 3 \times 10^{14}$ cm⁻³, the compression shock manifests itself only weakly in the luminescence signal. Under comparatively high nozzle pressures (≥ 1 atm), the intensity of luminescence in the shock wave is much higher (by a factor of 20 to 30) than in the undisturbed flow.

Results similar to those for SF₆ molecules were obtained for excited CF₃I molecules [128]. Figure 7 shows the curves representing the dependence of the C₂F₆ yield on the delay time τ_d between the nozzle-opening pulse and the laser pulse when $CF_{3}I$ is excited in the undisturbed flow (curve 1) and in the flow interacting with the surface (curve 2). The molecules were excited at a frequency of 1073.3 cm⁻¹ (the 9R(12) laser line) in resonance with the vibration v_1 of the molecule [147]. The nozzle pressure amounted to 1.5 atm. Clearly, when CF₃I is excited in the flow interacting with the surface, the C_2F_6 yield is higher than when CF_3I is excited in the undisturbed flow, and this is true for all delay times τ_d . When the delay times are short ($\tau_d \leq 300 \ \mu s$), the compression shock has no time to form in the excitation area, the C_2F_6 yield increases because of the increase in the CF_3I dissociation yield due to the collisions of excited molecules between each other in the shock wave [123, 128]. But if the molecules are excited directly in the shock wave (with $\tau_{d} \approx 325 - 400$ s), the C₂F₆ yield is much higher than in the case where the molecules are excited in the undisturbed flow. For instance, at the peak of curve 2 (with $\tau_d = 360 \ \mu s$) the C₂F₆ yield is approximately 15 times higher than in the undisturbed flow. The dependence of the C2F6 product yield on Δx has been studied in Ref. [128]. It was found that the width of the shock front is approximately 3.5-4 mm when the nozzle pressure is 1.5 atm and the distance x from nozzle to surface is 51 mm.

4.5.2 Spectral and energy characteristics of the dissociation of molecules. The spectral and energy characteristics of the



Figure 8. Dependence of the HF*-luminescence intensity on the energy density in the case of excitation of SF₆ molecules (mixed with CH₄ molecules) in the undisturbed flow (curve *1*), in the flow incident to the surface (curve 2), and in the shock wave (curve 3). The total nozzle pressure $p_{noz} = 2.4$ atm. The distance from nozzle to surface (for curves 2 and 3) x = 51 mm, and $\Delta x = 2.5$ mm. The molecules are excited at a frequency equal to 945.98 cm⁻¹ (the 10P(18) laser line).

dissociation of SF₆ and CF₃I molecules when these molecules are excited under the nonequilibrium conditions of a pulsed flow interacting with a solid surface have been studied in Refs [125-127] and Ref. [128], respectively. As a result of these studies, it was found that within a broad range of energy densities the HF*-luminescence intensity is much higher when the SF_6 molecules are excited in the shock wave and in the flow incident to the surface than when they are excited in the undisturbed flow. This is quite evident if we look at Fig. 8, which shows the curves representing the dependence of the HF*-luminescence intensity on the energy density when SF₆ mixed with CH₄ $(p(SF_6)/p(CH_4) = 1/1)$ is excited in the undisturbed flow (curve 1), in the flow incident to the surface (curve 2), and in the shock wave (curve 3) [125, 126]. The delay times correspond to the maxima in the time-of-flight spectra of the molecules, as shown in Fig. 5 ($\tau_d = 240 \ \mu s$ for curves 1 and 2 and $\tau_d = 310 \ \mu s$ for curve 3). The intensity of HF* luminescence in the flow incident to the surface is approximately 4 times higher, and in the shock is more than 30 times higher than the intensity in the undisturbed flow. This difference is even greater for excitation energy densities lower than 3 J cm^{-2} , which is an indication that at low energy densities the contribution of collisional dissociation of molecules in the shock wave to the total dissociation yield is very large.

The above results show that when the molecules are excited in the shock wave and in the flow incident to the surface, there is a substantial increase in the product yield as compared to the case where the molecules are excited in the undisturbed flow. Hence the interest in studies of the selectivity in the dissociation of molecules in the flow interacting with the surface. Such research was done in Refs [125–129]. The dependence of the HF*-luminescence intensity on the frequency of the exciting laser radiation (the spectral dependence of the dissociation yield) was studied in Refs [125–127, 129], while the spectral dependence of the C_2F_6 product yield when CF_3I is excited was studied in Ref. [128]. Figure 9 shows the curves representing the spectral dependence of the HF*-luminescence intensity



Figure 9. HF*-luminescence intensity plotted against the laser radiation frequency for the case where SF₆ is excited in the flow incident to the surface (curve 2) and in the shock wave (curve 3). The nozzle pressure is 1.25 atm, the distance from nozzle to surface x = 51 mm, and $\Delta x = 2.5$ mm. The energy density is 10 J cm⁻². For comparison, the plot shows the frequency dependence of the SF₄ product yield (curve *1*) taken from Ref. [80].

obtained for the case of SF₆ excitation in the flow incident to the surface (curve 2) and in the shock wave (curve 3). For comparison, the same figure shows the frequency dependence of the SF_4 product yield (curve 1), which was obtained (see Ref. [80]) for the case of excitation of SF_6 in a molecular flow under experimental conditions similar to those described in Refs [126, 127]. Possibly, this curve can be interpreted as the spectral dependence of the SF₆-dissociation yield in an undisturbed flow. The spectra are normalized at the maxima. The ratio of the intensities of spectra 2 and 3 at the maxima is $I_2/I_3 = 1/3.9$. The spectral widths at half maximum are $\sim 11 \text{ cm}^{-1}$ (1), $\sim 12.5 \text{ cm}^{-1}$ (2), and $\sim 16.5 \text{ cm}^{-1}$ (3). Note that the wings of spectrum 3 (in the vicinity of 937 and 953 cm⁻¹), especially the high-frequency wing, are more pronounced than the wings of spectrum 1. There are two reasons for this: the relatively high rotational temperature of SF_6 in the compression shock as compared to that in the undisturbed wave, and the collisional dissociation of molecules in the shock wave. We see that although the widths of spectra 2 and 3 are larger than the width of spectrum 1, the ratios of the intensities at the maxima and in the wings (near the absorption band of the vibration v_3 of ${}^{34}SF_6$, roughly 930.5 cm^{-1} [148]) for all three spectra do not differ too much. This indicates that the selectivities of the dissociation of molecules in all these cases should not differ too much either. At the same time, comparing these spectra, we see that the selectivity in the shock wave must be weaker than in the undisturbed or incident flow. This assumption is corroborated by the results discussed in Section 4.6.

Figure 10 shows the spectral curves of the C_2F_6 yield when CF₃I is excited in the undisturbed flow and in the shock wave [128]. Clearly, when CF₃I is excited in the shock wave, the C_2F_6 yield at all investigated frequencies is much higher than in the case where the molecules are excited in the undisturbed flow. At the maxima [on the lines 9R(10) and 9R(12)] the yield in the second case is 12–15 times higher, and in the low-frequency wing (e.g., on line 9P(20), which coincides with the absorption band of ¹³CF₃I) the C_2F_6 yield in the second case is more than 200 times higher. Such a large difference in the distant wing of the spectrum occurs mainly because of the strong dependence of the product yield on the concentration



Figure 10. C_2F_6 yield plotted against the laser radiation frequency for the case where CF_3I is excited in the undisturbed flow (curve *1*) and in the shock wave (curve *2*). The distance from nozzle to surface x = 51 mm, and $\Delta x = 2.5$ mm. The exciting-radiation energy density and the nozzle pressure are the same as in Fig. 7. Curve 3 is the CF_3I linear absorption spectrum. The lasing lines of the CO_2 laser are shown at the top of the figure.

of irradiated molecules [83, 86, 149] due to C_2F_6 formation caused by pair collisions of CF_3 radicals. Another reason for such a strong difference is a fairly high rotational temperature of CF_3I in the shock wave as compared to that in the undisturbed flow (see the estimates made in Section 4.7).

Let us now compare our results [126, 127] concerning SF₆ dissociation with the existing data on SF₆ dissociation in a molecular beam. Such comparison is useful if we want to understand the role that the rotational and vibrational temperatures of molecules play in the formation of selectivity. In a continuous molecular beam the rotational temperature of SF₆ is usually relatively low (≤ 50 K) while the vibrational temperature is high (≥ 250 K). The situation is just the opposite in the shock wave: the vibrational temperature of SF_6 is lower than the rotational. The dissociation of SF_6 has been most thoroughly studied by Schulz et al. [140]. The researchers found the frequency dependence of the SF_6 dissociation yield for different nozzle temperatures (which means for different vibrational temperatures of the beam molecules). A comparison of our spectral dependence of the HF*-luminescence intensity in the case where SF₆ molecules are excited in the shock wave and the frequency dependence of the SF₆ dissociation yield in the molecular beam $(T \approx 300 \text{ K} \text{ at the nozzle and an energy density of 7 J cm}^2)$ of Schulz et al. [140] shows (spectrum 1 in Fig. 11) that the low-frequency wing of our spectrum (near the absorption band of ${}^{34}SF_6$) is less intense than the low-frequency wing of the spectrum registered in the molecular beam. Hence, it may be assumed that the selectivity of molecule dissociation in the shock wave is higher than in the molecular beam.

The research described in Refs [126, 129] also shows that the spectral dependences of the SF₆-dissociation yield for molecules excited in the shock wave are much narrower than for molecules excited in a cell at room temperature. For comparison, Fig. 11 also shows our spectral dependence [129]



Figure 11. Frequency dependences of the HF*-luminescence intensity when SF₆ is excited in the shock wave (curve *I*) and of the SF₆ dissociation yield in the molecular beam (curve 2) obtained by Schulz et al. [140]. For comparison, the plot also shows the frequency dependence of the HF*-luminescence intensity when SF₆ is excited at $T \approx 300$ K under a pressure of 25 mTorr (curve 3).

of the HF*-luminescence intensity when SF₆ molecules are directly excited at room temperature and a pressure of 25 mTorr in the chamber in which the molecular beam is formed (curve 3). At such a pressure, the concentration of molecules in the chamber is comparable to that of molecules in the undisturbed flow [126, 127]. The conditions under which the molecules were excited and luminescence was detected were the same as in the case of curve 1. The spectra are normalized at the maxima. The width of spectrum 3 at half maximum amounted to ~ 22 cm⁻¹. Clearly, spectrum 1 is much narrower than spectrum 3. The reason is that the vibrational temperature of the molecules in the shock wave is much lower than room temperature.

4.5.3 Effect of parameter Δx on the spectral characteristics of the dissociation yield. As shown in Section 4.5.1, the moleculedissociation yield rapidly increases as the parameter Δx (the distance from the excitation zone to the surface) decreases. Hence the interest in the frequency dependence of the molecule dissociation yield at different values of Δx . Note that the interest in studies of the spectral characteristics of the molecule-dissociation yield stems mainly from the fact that these spectral characteristics determine the selectivity of the process. In addition, these characteristics can be used to estimate the effect of the vibrational and rotational temperatures of the molecules on the selectivity formation. Apatin et al. [129] studied the spectral characteristics of the SF₆-dissociation yield in the flow interacting with the surface at a fixed value $\Delta x = 2.5$ mm. A detailed investigation of the spectral characteristics of IR multiphoton dissociation of SF₆ when the molecules were excited in the shock wave at different values of Δx was done in Ref. [130]. The results were obtained in conditions where the nozzle-surface distance was varied in the 55–59-mm range, while Δx was varied from 4 mm to 1.5 mm. The experimenters used an SF_6/CH_4 mixture with a 3-to-1 pressure ratio.

In the course of that research it was found (see Ref. [130]) that for $\Delta x \ge 2.5$ mm the spectral dependences of the HF*-luminescence intensity practically coincided in width with a similar dependence obtained for an undisturbed flow. This suggests that the selectivities of dissociation of ${}^{34}SF_6$ molecules in all these cases do not differ very significantly, which was also corroborated by the findings reported in

Refs [125–127]. However, for $\Delta x \leq 1.5$ mm, when the molecules are excited fairly close to the surface, the low-frequency wing of the spectral dependence is more intense than in the undisturbed flow. Hence, the selectivity of dissociation in this case is weaker. Nevertheless, the resulting spectral dependences are still much narrower than a similar dependence of the gas obtained at room temperature [130].

4.6 Product yield and process selectivity

The direct measurements of the yield of the final products $(SF_4 \text{ and } C_2F_6)$ and the process selectivity when SF_6 and CF_3I molecules are excited in the flow interacting with the surface and in the unperturbed flow were done in experiments described in Refs [125-127] and Ref. [128], respectively. The method used in these measurements was described in Refs [80, 85, 86]. In the case of SF_6 excitation, the SF_4 yield in the undisturbed flow was measured at $\tau_d = 260 \ \mu s$, while in the flow interacting with the surface the yield was measured at $\tau_d = 260 \ \mu s \ and \ \tau_d = 370 \ \mu s$. These delay times correspond to the maxima in the time-of-flight spectra of the molecules [125-127]. The nozzle-surface distance was x = 51 mm, and $\Delta x = 2.5$ mm. The nozzle pressure of SF₆ amounted to 1.25 atm. It was found that in the case of excitation of molecules in the flow incident to the surface, the SF4 yield at $\tau_d=260\;\mu s$ is 2.5 times, and in the shock wave (at $\tau_{\rm d} = 370 \ \mu s$) approximately 12 times, higher than the yield in the undisturbed flow.

The process selectivity was studied by measuring the ³⁴Sand ¹³C-enrichment factors for the products SF_4 and C_2F_6 when the SF₆ and CF₃I molecules were excited in the flow incident to the surface, in the shock wave, and in the undisturbed flow. The SF₆ molecules were excited at 929 cm⁻¹ (the 10P(36) CO₂ laser line) in resonance with the v_3 vibration of ³⁴SF₆ [148], and the CF₃I molecules were excited at 1046.85 cm⁻¹ (the 9P(20) CO₂ laser line) in resonance with the v_1 vibration of ¹³CF₃I [147]. Note that it was within this frequency range [on the 9P(20) - 9P(24) lines] that we earlier observed (see Ref. [83]) the largest enrichment factor in C₂F₆. The results are listed in Table 2, together with data on the product yield. When SF₆ was excited in the undisturbed flow, the enrichment factor at an energy density of 10 J cm⁻² was $K_{34}^{\text{prod}} = 17 \pm 5$, and when excitation took place in the shock wave, $K_{34}^{\text{prod}} = 14 \pm 3$. When CF₃I was excited in the undisturbed flow, the enrichment factor at an energy density of 1.5 J cm⁻² was $K_{13}^{\text{prod}} = 21 \pm 3$, and when excitation took place in the shock wave, $K_{13}^{\text{prod}} = 15 \pm 3$. Thus, the selectivity of dissociation of molecules in the shock wave is only slightly (approximately by 25-30%) lower than that in the undisturbed flow, while the product yield in the shock wave is more than 10 times higher.

The increase in the product yield when the excitation of molecules takes place in the shock wave is caused by the increase in the gas density and on the molecule-dissociation yield. In turn, the increase in the molecule-dissociation yield is caused, first, by the more effective excitation in the shock wave and, second, by the collisional dissociation of molecules that are excited by the IR pulse below the dissociation limit and in the undisturbed flow do not dissociate due to a deficit of collisions [126, 127]. The comparatively high selectivity in the shock wave is the consequence of the vibrational temperature of the molecules in it being fairly low.

4.7 Estimates of gas density and temperature in a compression shock

Note that the essentially inhomogeneous, time-dependent, and nonequilibrium conditions realized in a compression shock and the large number of processes that take place in it complicate making quantitative estimates of the gas parameters in it. Hence, the gas density and temperature can be estimated only very roughly.

The maximum increase in density in a normal shock wave for a gas with a constant heat capacity is given by the relation [117-119]

$$\frac{\rho_2}{\rho_1} = \frac{\gamma+1}{\gamma-1} , \qquad (12)$$

where ρ_1 and ρ_2 are the gas densities in the incident flow and at the shock front, respectively, and $\gamma = c_p/c_V$ is the heatcapacity ratio. For instance, for SF₆ at $T \approx 300$ K, $\gamma \approx 1.1$ [150, 151], which implies that $\rho_2/\rho_1 \approx 21$. This, however, cannot be considered a satisfactory estimate, since in our experiments not all degrees of freedom contribute to the heat capacity. Let us estimate the maximum increase in gas density and the mean molecular concentration in a compression shock using the parameters of a molecular flow discussed in Section 4.3 [126, 127]. For a crude estimate of ρ_2/ρ_1 , we assume that it is equal to the ratio of the flow length $\Delta x_{\rm fl}$ to the shock-front width $\Delta x_{\rm sh}$:

$$\frac{\rho_2}{\rho_1} = \frac{\Delta x_{\rm fl}}{\Delta x_{\rm sh}} \,. \tag{13}$$

Inserting into (13) the appropriate value of an SF₆ molecular flow ($\Delta x_{\rm fl} \approx 4.2$ cm in the excitation zone at a distance of 51 mm from the nozzle, with $\Delta x_{\rm sh} \approx 3$ mm; see Fig. 6), we find that $\rho_2/\rho_1 \approx 14$. With a nozzle pressure of 1.25 atm for SF₆, the total number and concentration of molecules in the flow are $N_{\rm fl} \approx 4.2 \times 10^{16}$ cm⁻³ (see Fig. 2) and $N_1 \approx 1.4 \times$ 10^{15} cm⁻³, respectively. Hence, the mean concentration of SF₆ molecules in the shock wave is $N_2 \approx 2 \times 10^{16}$ cm⁻³.

Table 2. Results of measurements of SF_4 and C_2F_6 product yields and ³⁴S and ¹³C enrichment factors with SF_6 and CF_3I molecules excited in an undisturbed flow and in a flow interacting with the surface.

Gas composition and nozzle pressure, atm		CO ₂ laser line	Energy	Product yield (SF ₄ , C ₂ F ₆), rel. units			Enrichment factors $(K_{34}^{\text{prod}}, K_{13}^{\text{prod}})$		
			J cm ⁻²	Undisturbed flow	Incident flow	Compression shock	Undisturbed flow	Incident flow	Compression shock
SF_6	1.25	10P(16)	12	1 ± 0.2	2.5 ± 0.5	12 ± 3			
	1.25	10P(36)	10				17 ± 5	15 ± 3	14 ± 3
CF ₃ I	1.5	9R(12)	1.3	1 ± 0.2	2.5 ± 0.5	14 ± 3			
	1.5	9P(20)	1.5				21 ± 3	19 ± 3	15 ± 3

Similarly, for a CF₃I molecular flow ($\gamma \approx 1.13$ at $T \approx 300$ K [150, 151]), Eqn (12) yields $\rho_2/\rho_1 \approx 17$. Using the experimentally measured parameters of the flow from Ref. [128] ($\Delta x_{\rm fl} = 4$ cm and $\Delta x_{\rm sh} = 3.5$ mm) and Eqn (13), we find that $\rho_2/\rho_1 \approx 11$. With a nozzle pressure of 1.5 atm for CF₃I, the total number and concentration of molecules in the flow are $N_{\rm fl} \approx 5.2 \times 10^{16}$ cm⁻³ and $N_1 \approx 1.7 \times 10^{15}$ cm⁻³, respectively. Hence, the mean concentration of molecules in the shock wave is $N_2 \approx 1.9 \times 10^{16}$ cm⁻³.

In our first works [124, 125], the heating of the gas caused by the slowing-down of the molecules was estimated by the relation [118, 119]

$$\Delta T = \frac{v_1^2}{2c_p} , \qquad (14)$$

where v_1 is the flow velocity and c_p is the heat capacity of the gas at constant pressure. When we used the appropriate values for SF₆ ($v_1 \approx 420$ m s⁻¹, $c_p \approx 665$ J kg K⁻¹ [150, 151]), we found that $\Delta T \approx 130$ K. However, in our experiments the heat capacity of SF₆ was lower than the above value at 300 K, so that the heating of the gas is, probably, much more intense. This was corroborated by further investigations [126, 127]. For instance, if one assumes that the vibrational degrees of freedom of a molecule do not have enough time to heat up, then energy conservation for SF₆ molecules in the incident flow and the shock area,

$$\frac{mv_1^2}{2} = 3k\Delta T, \qquad (15)$$

suggests that the temperature of the translational and rotational degrees of freedom increased by $\Delta T \approx 530$ K. Hence, $T_{2,tr} \approx T_{2,rot} \approx (T_{1,tr} + \Delta T) \approx 570$ K. On the other hand, the vibrational temperature of the molecules in the shock wave was $T_{2,vib} \approx T_{1,vib} \leqslant 150$ K (see Table 1).

For the CF₃I molecular flow ($v_1 \approx 400 \text{ m s}^{-1}$ and $c_p \approx 335 \text{ J kg}^{-1} \text{ K}^{-1}$ [150, 151]), Eqn (14) yields $\Delta T \approx 240 \text{ K}$ and Eqn (15) $\Delta T \approx 580 \text{ K}$. Hence, while in the incident flow the translational and rotational temperatures were $T_{1, \text{tr}} \approx T_{1, \text{rot}} \approx 40 \text{ K}$, in the shock wave $T_{2, \text{tr}} \approx T_{2, \text{rot}} \approx 620 \text{ K}$. On the other hand, the vibrational temperature in the shock wave was, probably, $T_{1, \text{vib}} \leq 150 \text{ K}$.

Why, in the case of excitation of molecules in the shock wave, where their rotational temperature is fairly high, does selectivity of dissociation remain comparatively high? This question has been thoroughly studied by Apatin et al. [129], who analyzed the linear absorption spectra of the v_3 vibration of SF₆ at various temperatures and estimated the contribution of the vibrational and rotational temperatures of the molecules to the width of the absorption spectra. They found that the main contribution to the spectrum width with increasing temperature is provided by the vibrational distribution of molecules ('hot bands') rather than by the rotational distribution. They also found that if the molecules are deep-cooled vibrationally ($T_{\rm vib} \leqslant 150$ K), even at a fairly high rotational temperature ($T_{\rm rot} \approx 570$ K) they have a much narrower spectrum of linear (and also multiphoton) absorption than at room temperature. Hence, it is the low vibrational temperature of the molecules that is responsible for the comparatively high selectivity of dissociation in the shock wave. Moreover, since the vibrational temperatures of molecules in the incident flow and in the shock wave do not differ too much [126, 127], the selectivity of dissociation of molecules excited in the shock wave should not differ too

much from that for molecules excited in the undisturbed flow, which we actually observed in our experiments. It must also be noted that when the molecules are excited in the shock wave, the decrease in selectivity caused by the increase in the gas temperature may in some cases be balanced by an increase caused by the rise in the concentration of the irradiated molecules [149]. Thus, the research discussed in the above papers shows that the formation of a compression shock in front of a solid surface can lead to a significant increase in the efficiency of the isotopically selective IR multiphoton dissociation of molecules in gasdynamically cooled molecular flows. It has also been established that the dominating factor in the formation of the process selectivity is the vibrational temperature of the molecules rather than the rotational.

5. Compression-shock controlled pulsed molecular beams

In Section 2.1 we stated the main types of sources for producing pulsed molecular beams and the characteristic durations of the pulses generated by these sources. The current section, based on the results of research discussed in Refs [152-154], is devoted to the problem of how a compression shock can be used to control the duration of the pulses of intense molecular beams and how to generate short pulses.

Note that it is extremely difficult to produce molecular beams of short duration ($\leq 20 \ \mu$ s): it is difficult to design the nozzle proper and it is difficult to solve the problems associated with the injection of large amounts of energy $(\ge 20 \text{ J})$ so that the nozzle opens very rapidly [73]. With large amounts of energy being injected, the nozzle cannot operate with a high repetition frequency without cooling. Moreover, the lifetime of such nozzles is very short compared to that of nozzles operating in the ordinary regime. And yet small-duration (length) molecular beams are needed in many experiments, especially those that deal with the excitation and dissociation of molecules in beams by high-power laser pulses [84, 85]. In Ref. [152] we proposed a fairly simple method for controlling the length of pulses of intense molecular beams that makes it possible to produce short-duration molecular beams. In Sections 5.1-5.3 we discuss this method and the main results obtained in Refs [153, 154] with its help.

5.1 Experimental method

Our method of shortening molecular beams uses a compression shock [117–119] that forms as a result of the interaction of the primary molecular beam and a solid surface. The compression shock acts as a high-speed gasdynamic gate (shutter). Here is the essence of the method [152]. An intense ($\geq 10^{20}$ mol. sr⁻¹ s⁻¹) wide-aperture (divergence $\omega \approx 0.05$ sr) pulsed molecular beam hits a solid surface, which is a thin ($\approx 100 \ \mu$ m) metal plate at the center of which is an opening 2–3 mm in diameter.

When the intensity of the beam was low (the molecular concentration $N_{in} \leq 3 \times 10^{14} \text{ cm}^{-3}$), no compression shock formed in front of the surface [126, 127]. In this case the molecular beam incident to the surface, which propagated within a solid angle determined by the area of the opening and the distance from nozzle to surface, passed through the opening in full. The molecules reflected by the surface reduced the beam intensity only slightly. But when the intensity of the incident beam was fairly high ($I_{in} \ge 10^{20} \text{ mol. sr}^{-1} \text{ s}^{-1}$ and $N_{in} \ge 10^{15} \text{ cm}^{-3}$), only the leading (the least intense) part of

the beam passed through the opening in the plate, while the next, more intense, part of the beam was scattered completely (was 'absorbed') by the compression shock that formed in front of the surface. This led to a significant shortening of the pulse of the primary molecular beam. Note that the situation is similar to the one encountered in the shortening of a light, e.g., laser, pulse due to the formation of optical breakdown in the focus of a lens or telescope, when there is complete absorption of the tail part of the pulse in the plasma that forms as a result of such a breakdown.

The setup used in these experiments (and also in the experiments discussed in the sections below) differs somewhat from the experimental setup described in Section 4.2. We will therefore briefly discuss its elements. In the experiments we also used a pulse nozzle of the current-loop type [87]. The diameter of the opening of the nozzle was 0.75 mm. The opening time varied depending on the gas composition and nozzle pressure from 50 to 100 μ s (at half maximum). The nozzle pressure varied from ≈ 0.1 to 7 atm. The nozzle was cut in the form of a cone with an opening angle of 15°, and the length of the cone was 35 mm. Such a design made it possible to produce molecular beams with a higher intensity. The vacuum chamber in which the molecular beam was formed was pumped down to a pressure of 1×10^{-6} Torr by a turbomolecular pump. The number of molecules ejected by the nozzle in a single pulse varied, in the case of SF₆, from approximately 3×10^{15} to 1.1×10^{17} .

In our experiments we studied the dependence of the duration and intensity of shortened molecular beams on the intensity of the incident beam and the diameter of the opening in the plate [153, 154], and we also measured the mean velocity of the molecules in the shortened beam and the spread of velocities in it. The measurements were carried out by the time-of-flight method that used a pyroelectric element as a detector of the molecular beam. We measured the time-of-flight spectra of the molecules at different distances from the nozzle. These spectra were then used to determine the beam velocities and the spread of the velocities of molecules in the beams.

5.2 Time evolution of pulses of shortened beams

In our investigations we used molecular beams of SF_6 , H_2 , and He and the mixtures SF_6/H_2 (1/10), SF_6/He (1/10), and SF_6/CH_4 (1/10), where in parentheses we give the ratios of gas pressures in the corresponding mixture. In all the cases we observed a considerable (by a factor of 2 to 7) shortening of the pulse of the primary molecular beam. Figure 12 shows the time evolution of a pulse of a molecular beam (the time-offlight spectrum of the molecules) passing through the opening the plate, with increasing nozzle pressure in $(p(SF_6)/p(He) = 1/10)$. The distance from nozzle to surface is 68 mm and from nozzle to detector 143 mm. When the nozzle pressure is low (≤ 0.15 atm), the intensity of the incident beam is low and no compression shock forms in front of the plate [126, 127]. In this case the molecular beam passes through the opening in the plate without shortening (Fig. 12a). As the nozzle pressure grows, a compression shock begins to form in front of the surface, and the incident-beam pulse is shortened (Fig. 12b). As the intensity of the primary beam (nozzle pressure) increases still further, the pulse becomes even shorter (Fig. 12c), but this process is accompanied by the formation of a fairly intense secondary pulsed beam, whose source is the compression shock [155-157].



Figure 12. Time evolution of a molecular-beam pulse passing through the opening (with a diameter $h_0 = 2$ mm) in the plate, with increasing nozzle pressure p_{noz} .

In our experiments [153, 154] we found that as the distance between nozzle and detector increased, the signal induced by the secondary beam fell off much more rapidly than the signal induced by the primary beam (Fig. 13). There are two reasons for this. First, the quadratic dependence of the signal strength (in the case of deep-cooled beams) on the distance between detector and beam source: the source of the secondary beam is closer to the detector, with the result that the signal from it falls off more rapidly with increasing distance. Second, the extent to which the gas in the second beam is cooled is much smaller than in the shortened primary beam. Hence, the signal from the secondary beam falls off (with increasing distance) more rapidly also because of the larger spread of the



Figure 13. Dependence of the ratio of the amplitudes of the signals induced in the detector by the primary and secondary molecular beams of H_2 on the nozzle – detector distance; p_{noz} is the nozzle pressure of H_2 . The conditions are the same as in Fig. 12.

molecular velocities in this beam. At distances $x \ge 173$ mm from the nozzle (≥ 105 mm from plate), the signal from the secondary beam was weaker than the signal from the primary beam by a factor of 10.

To suppress the formation of the secondary beam, the plate was rotated through an angle $\alpha \approx 60-70^{\circ}$ in relation to the incident beam. In this case, in front of the plate there formed an oblique shock, in which the gas pressure and density were much lower (for pressure, by a factor of $1/\cos^2 \alpha$) than in a normal compression shock [118, 119]. As a result, the intensity of the secondary beams was negligible compared with that of the shortened primary beam [154]. Note that at large angles of incidence ($\alpha \ge 75^{\circ}$), when the condition $1/\cos \alpha \approx M_{\rm in}$ (with $M_{\rm in}$ the Mach number in the primary beam) is met, no compression shock in front of the surface was formed [117–119] and the incident beam was not shortened.

5.3 Dependence of shortened-beam duration on nozzle

pressure and the diameter of the opening in the substrate In our experiments [153, 154] we found that the higher the intensity of the incident molecular beam and the smaller the diameter of the opening, the greater the shortening of the beam. When the intensity of the incident beam was $I_{in} \ge 10^{21} - 10^{22}$ mol. sr⁻¹ s⁻¹ ($N_{in} \ge 10^{16}$ cm⁻³), the duration of the pulse of the molecular beam passing through an opening that was 2 mm in diameter amounted to 10 to 15 µs. Figure 14 plots the dependence of the length of the pulse of the H₂ molecular beam on the nozzle pressure. The angle of incidence of the beam on the plate was $\alpha \approx 65^{\circ}$, and the duration of the incident beam was approximately 78 µs. Clearly, for nozzle pressures ≤ 0.15 atm the pulse was not shortened, while for nozzle pressures of 4-5 atm the duration of the pulse passing through the opening was 10 to 12 µs.

Results of our measurements [152, 153] of the intensity, duration, and mean velocity of molecular beams and the molecular-velocity spread in the beams obtained for a molecular beam with $p(SF_6)/p(He) = 1/10$ passing through openings of various diameters are displayed in Table 3. The nozzle-surface distance was 68 mm. It was found that as the diameter of the opening through which the beam passes becomes smaller, the beam duration decreases dramatically. This decrease is accompanied by an increase in the mean



Figure 14. Dependence of the duration of a molecular beam pulse passing through the opening (with a diameter of 2 mm) in the plate on the nozzle pressure. The conditions are the same as in Fig. 12.

Table 3. Results of measurements of pulse shortening in a molecular beam $SF_6/He = p(SF_6)/p(He) = 1/10$.

D	Parameter	s of molecula	ar beams		
of open- ing, mm	Pulse duration, μs	Intensity, rel. units	Beam velocity, v , m s ⁻¹	Molecule velocity spread in beam, m s ⁻¹	$v/\Delta v$
Undis- turbed beam	78	100	980	105	9.3
4	68	60	1005	120	8.4
3	59	40	1040	150	6.8
2,5	51	22	1070	180	5.9
2	23	9	1095	240	4.6

beam velocity and the spread of molecular velocities in the beam. The reason why a decrease in the diameter of the opening brings about a decrease in pulse duration is that as the area of the opening becomes smaller, the time for which the compression shock is formed in front of the surface diminishes. The increase in the mean velocity can be explained by the fact that as the pulse becomes shorter, more and more molecules with higher velocities belonging to the primary molecular beam pass through the opening. As for the increase in the spread of velocities, this can be explained by the buildup of the effect of the beam being scattered by molecules reflected from the surface and the walls of the opening. In a shortened beam the velocity spread was 1.5 to 2 times larger than in the incident beam. At the same time, it was found that in the shortened pulse the gas is fairly cold (the Mach numbers $M \approx v/\Delta v \approx 5-8$) [153, 154].

Note that, according to Eqn (12), when the molecules have a small heat-capacity ratio γ , a fairly dense compression shock forms in front of the surface [126, 127] (e.g., for SF₆ $\gamma \approx 1.1$ at $T \approx 300$ K [150] and $\rho_{\rm sh}/\rho_{\rm in} \approx 21$), and this compression shock dramatically shortens the initial pulse, but at the same time it is a source of an intense secondary beam. When the molecules have a high γ , as, e.g., in the case of He ($\gamma \approx 1.66$ [150]) or, H₂ ($\gamma \approx 1.4$ [150]), the maximum increase in gas density in the shock wave is much smaller ($\rho_{\rm sh}/\rho_{\rm in} \approx 4$ and 6, respectively). In this case, a compression shock of moderate density is formed in front of the surface, with the result that the intensity of the secondary beam is much lower than in the case of SF₆ molecules.

We assume, as we did before, that the ratio of molecular concentrations in the shock wave, $N_{\rm sh}$, and in the primary beam, $N_{\rm in}$, is equal to the ratio of the length of the incident beam, $\Delta x_{\rm b}$, to the width of the shock front, $\Delta x_{\rm sh}$, i.e., $N_{\rm sh}/N_{\rm in} \approx \Delta x_{\rm b}/\Delta x_{\rm sh}$. For SF₆, $\Delta x_{\rm b} \approx 4.6$ cm and $\Delta x_{\rm sh} \approx 3$ mm [156, 157]. Hence, $N_{\rm sh} \approx 15 N_{\rm in}$. For instance, at a nozzle pressure of 1 atm, the number of SF₆ molecules emitted by the nozzle in one pulse was $N_{\rm b} \approx 3.5 \times 10^{16}$ [157]. According to the estimates made in Refs [156, 157], the volume of the primary beam is $V_{\rm b} \approx 14$ cm³. Hence, $N_{\rm in} \approx 2.5 \times 10^{15}$ cm⁻³ and $N_{\rm sh} \approx 3.8 \times 10^{16}$ cm⁻³.

5.4 Estimates of beam scattering in the shock wave

Following Refs [153, 154], let us make estimates related to the weakening of the beam due to scattering in the shock wave. We use the example of an SF_6 molecular beam, since the

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parameters of this beam have been thoroughly studied [156, 157]. In our estimates we use an expression for the intensity of a molecular beam passing though the shock wave:

$$I_{\rm sh}(t) = I_{\rm in}(t) \exp\left[-\sigma N_{\rm sh}(t)\Delta x_{\rm sh}(t)\right].$$
 (16)

Here, $I_{in}(t)$ is the intensity of the incident beam, σ is the cross section for the interaction of SF₆ molecules, $N_{\rm sh}(t)$ is the molecular concentration in the pressure shock, and $\Delta x_{sh}(t)$ is the length (thickness) of the compression shock in front of the surface. We immediately note that Eqn (16) is valid only for low nozzle pressures and single collisions, which in our case occurs only in the initial stage of compression-shock formation. At the same time, this equation can be used for a rough estimate of the beam's intensity at which the beam is scattered almost completely in the shock wave. Under a nozzle pressure of 1 atm, the concentration of SF₆ molecules in the shock wave (see Section 5.3) is $N_{\rm sh} \approx 3.8 \times 10^{16} {\rm ~cm^{-3}}$, and $\Delta x_{\rm sh} \approx 3$ mm [156, 157]. If we assume that the SF₆ interaction cross section is equal to the gaskinetic cross section of the molecule ($\sigma \approx 2.4 \times 10^{-15} \text{ cm}^2$ [158]), under the specified conditions the exponent in (16) is $\sigma N_{\rm sh} \Delta x_{\rm sh} \approx 28$. Hence, an SF₆ molecular beam of such intensity is almost completely scattered in the shock wave. Only the leading part of the pulse may pass through the shock wave, and in this part the intensity is more than 10 times lower than the above intensity, while the value of the exponent does not yet exceed one to two units. It was the passage of the leading part of the pulse that we observed in our experiments. Note that here the intensity of the incident SF₆ molecular beam is $I_{in} \ge 7 \times$ 10^{21} mol. sr⁻¹ s⁻¹. The intensities of the H₂ and He molecular beams for nozzle pressures equal to those in the case of SF₆ are approximately 10 times higher. Hence, although the intensities of the shortened pulses produced in our experiments [153, 154] were 10 or more times lower than those of the primary beams, they were still rather high. Thus, we found, through our experimental work [152-154], that by forming a compression shock in front of the surface one can control the duration of pulses of intense molecular beams and produce short pulses.

6. Formation of intense secondary pulsed molecular beams

In Section 5 we noted that when an intense beam (or flow) interacts with a solid surface, in front of this surface there forms a fairly dense compression shock that can serve as a source of a secondary molecular beam. The production of intense secondary pulsed molecular beams with a compression shock acting as a source of such a beam was observed for the first time in our experiments [155], and this was followed by detailed study of the parameters of secondary beams in Refs [156, 157]. The various ways in which such production of secondary molecular beams can be used in applications are discussed in Sections 7 and 8, while in the current section we discuss the essence of the method and the main findings of studies of the characteristics of secondary beams.

6.1 Method of formation of secondary molecular beams

The experimental setup and method are in many respects similar to those described in Section 5.1. Hence, here we mention only those aspects that are needed for an understanding of the problem. The method consists of the following (Fig. 15). A highly intense ($\ge 10^{21}$ mol. sr⁻¹ s⁻¹) wide-



Figure 15. Experimental setup. Formation of a secondary molecular beam by a substrate with an opening shaped like a divergent cone.

aperture (divergence $\omega \approx 0.05$ sr) molecular beam hits a solid surface, a substrate with an opening in the center. The polished substrate was made of aluminum and had a thickness of 7.5 mm. It was placed at a distance x = 60 mm from the nozzle. The opening was made in the form of a divergent cone with an entrance diameter $d_{\rm in} = 2$ mm and an exit diameter $d_{\rm out} = 5$ mm. The walls of the opening were polished.

When the primary beam hit the substrate, a compression shock formed in front of the substrate, and the gas pressure and temperature in the shock wave were much higher than in the incident beam [126, 127]. According to estimates made in Ref. [157], the concentration of SF_6 molecules in the shock wave varied approximately from 10^{16} cm⁻³ to 5×10^{17} cm⁻³, depending on the intensity of the primary beam. As long as there is a compression shock in front of the surface, the gas from this region flows through the opening in the substrate into the high-vacuum part of the chamber, with the result that a new, secondary, pulsed molecular beam is formed with characteristics that differ from those of the primary beam. To produce secondary molecular beams we also used hollow convergent truncated cones and convergent-divergent cones of the Laval nozzle type (instead of substrates with conical openings). The intensities of secondary molecular beams produced by cones were substantially higher (by a factor of five to seven) than those of beams produced with the help of a substrate [156, 157]. When the primary beam interacted with the cone, a compression shock formed inside the convergent part of the cone.

The primary beam was produced by a pulsed nozzle of the type described in Section 5.1. Nozzle pressure in our experiments varied from approximately 0.1 to 7 atm. The number of molecules ejected by the nozzle in one pulse varied from approximately 3×10^{15} to 1.1×10^{17} . The molecular beams were detected by PEDs, with the time-of-flight spectra of the molecules measured at different distances from the sources of the primary and secondary molecular beams. These spectra were used to determine the beam velocities and the spread of molecular velocities in the beams. Attention was focused on studying the characteristics of secondary molecular beams.

6.2 Characteristics of secondary molecular beams

Figure 16 shows the time evolution of a molecular beam pulse (the time-of-flight spectrum of the molecules) passing



Figure 16. Time evolution of a molecular beam pulse passing through a hollow convergent truncated cone. The input diameter of the cone $d_{in} = 11$ mm, the output diameter $d_{out} = 2.8$ mm, and the cone length L = 32 mm. The distance from the nozzle to the cone's 'waist' is x = 83 mm and from nozzle to detector, 143 mm. p_{noz} is the total nozzle pressure.

through a hollow cone under increasing nozzle pressure $(p(SF_6)/p(H_2) = 1/6)$. The distance from the nozzle to the cone's 'waist' is 83 mm and from nozzle to detector 143 mm. At low nozzle pressures (≤ 0.2 atm), when the intensity of the primary beam is low and the compression shock has yet not been formed in front of the surface [155, 156], only the primary molecular beam passes through the cone (Fig. 16a). As the nozzle pressure grows, a compression shock begins to form in the cone (or in front of the surface), and the pulse duration of the primary beam decreases. Parallel to this process, there emerges with rapidly growing strength a pulse of a secondary molecular beam (Figs 16b and c).

When the intensity of the primary molecular beam is comparatively high ($\ge 10^{20}$ mol. sr⁻¹ s⁻¹), the intensity of the secondary beam becomes comparable to that of an undisturbed primary beam (i.e., no substrate in the beam's path). Figure 17 plots the dependence of the intensities of an undisturbed primary SF_6 molecular beam (curve 1) and secondary molecular beams (curves 2 and 3) on the nozzle pressure. In the case of curve 2, the secondary beam was formed by a convergent cone ($d_{in} = 11 \text{ mm}, d_{out} = 2.8 \text{ mm},$ and total length 32 mm), while in the case of curve 3 the secondary beam was formed by a convergent-divergent Laval nozzle ($d_{in} = 14 \text{ mm}, d_0 = 2 \text{ mm}, d_{out} = 7 \text{ mm}, \text{ total}$ length 40 mm, and length of convergent portion 30 mm). The distance from nozzle to detector was 143 mm and from the cone's 'waist' to the detector 79 cm. Clearly, under nozzle pressures ≥ 1.0 atm the pyroelectric signal induced in the detector by the secondary molecular beam (curve 3) is stronger than the signal from the primary beam (curve 1).



Figure 17. Dependence of the intensities of an undisturbed primary SF_6 molecular beam (curve *I*) and secondary molecular beams (curves 2 and 3) on the nozzle pressure. The secondary beams were formed by cones. The parameters of the cones and the experimental conditions are specified in the main text.

Hence, even if we allow for the approximately quadratic dependence of the pyroelectric signal strength on the distance between the source of the beam and the detector, the intensity of the secondary band produced by a convergent – divergent Laval nozzle is comparable to that of the primary beam.

Table 4 lists the results of measurements of the parameters of the primary and secondary molecular beams [156, 157]. In our experiments we found that the duration and velocity of the primary and secondary beams differ insignificantly. The spreads of molecular velocities differ much more significantly, as expected. In the secondary beam the velocity spread was by 20-40% greater than in the primary beam. The results displayed in Table 4 suggest that the gas in the secondary beam is cooled significantly (the Mach number $M_2 \approx v_2/\Delta v_2$ amounted to approximately 5). Thus, in the papers we are discussing here (Refs [155-157]) it was shown that a pressure shock can be used to produce intense secondary pulsed molecular beams with parameters close to those of undisturbed (primary) beams.

Table 4. Results of measurements of parameters of primary and secondary molecular beams.

Gas	Nozzle pressure, atm	Primary beam			Secondary beam		
compo- sition		$v_1,$ m s ⁻¹	$\Delta v_1, \ { m m \ s^{-1}}$	$v_1/\Delta v_1$	$v_2, m s^{-1}$	$\Delta v_2, \ { m m \ s^{-1}}$	$v_2/\Delta v_2$
SF_6	5.0	560	62	9.1	476	82	5.8
SF_6	3.0	545	88	6.2	517	133	3.9
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 ₃ I	4.6	417	53	7.9	406	57	7.1
CF ₃ I	2.7	410	57	7.2	380	62	6.1

7. Producing intense pulsed molecular beams with kinetic energy controlled by high-power IR laser radiation

In Section 1 it was noted that many experiments require the use of intense molecular beams with kinetic energies that substantially exceed the thermal energy of molecules at room temperature. The present section is devoted to studies in the production of intense pulsed molecular beams in which the kinetic energy of the molecules can be controlled by the radiation from a high-power IR laser with energies ranging from approximately 0.1-0.2 eV to 1-3 eV. Such studies have been carried out in Refs [155–157]. But first we will briefly examine some other common ways of producing high-energy beams of neutral molecules.

7.1 Methods of producing high-energy molecular beams

Note that it is very difficult to master the above energy range and that today there is no universal method for producing molecular (atomic) beams in this range. There are a number of ways of producing such beams [72] (see also Ref. [159, 160] and the literature cited therein). However, most of these ways are fairly complicated (say, the implementation of optical breakdown, radiofrequency, or arc discharge inside the nozzle) and can be used only with atomic beams and not molecular beams. Most of these methods have been realized with continuous beams. The method of aerodynamic acceleration proposed by Becker et al. [161] and Kolodney and Amirav [162] is most often used for this purpose. In this method the molecules under study are diluted with a lighter carrier gas (He, H₂, etc.). Another way is heating the gas in the nozzle to high temperatures ($T_0 \cong 3000$ K). A combination of these two approaches is also used. The method of aerodynamic acceleration is not very effective when the mass ratio of the gas under investigation to the carrier gas is low.

When the nozzle is heated, the energy of the molecules in the beam is determined by the gas temperature prior to expansion through the nozzle:

$$\frac{1}{2}mv^{2} = \frac{\gamma}{\gamma - 1}k(T_{0} - T), \qquad (17)$$

where v is the steady-state velocity of the flow, m is the molecular mass, $\gamma = c_p/c_V$ is the heat-capacity ratio, k is the Boltzmann constant, and T is the steady-state temperature.

In 1980, Comparque et al. [163] described an experiment in which argon atoms diluted with helium were accelerated in a continuous beam up to several electronvolts by a combination of nozzle heating and aerodynamic acceleration. In the same year Buck et al. [164] described an experiment in which continuous beams of xenon atoms diluted with hydrogen $(p(Xe)/p(H_2) = 0.23/100)$ were produced, and the kinetic energy was about 30 eV.

The heating of pulsed nozzles up to high temperatures is highly problematic since the materials used in the experiments (e.g., elastomers and plastic materials) are destroyed at high $(T \ge 200 \text{ °C})$ temperatures [73]. In our experiments [165, 166], in order to produce accelerated molecular beams, we suggested using vibrational excitation of molecules by an IR laser pulse within the gasdynamic expansion zone at the exit from the nozzle. Accelerated beams of SF₆ and CF₃I molecules with kinetic energies of approximately 0.5 eV and 0.74 eV, respectively, were produced (see Refs [160, 167]). However, in this approach it is impossible to achieve high excitation energy densities because of optical breakdown at the exit from the nozzle. Besides, only a small fraction of the molecules in the beam can be effectively accelerated in this way.

The above reasoning suggests that high-energy molecular beams could be produced through excitation of the molecules by high-power IR laser radiation within the very source of the pulsed beam, i.e., before the gas is ejected by the nozzle. This possibility was first realized by the method we proposed in Refs [155, 156] for producing a secondary pulsed molecular beam. This led to the formation of intense beams of accelerated SF₆ molecules with kinetic energies up to approximately 1.5 eV [157]. Below we discuss this method and the main results reported in the above-cited papers.

7.2 Method of producing accelerated molecular beams via vibrational excitation of molecules in the source

Our method (see Refs [155, 156]) consists in forming a compression shock in front of a solid surface and using it as a source of a secondary beam for producing high-energy molecules. High-energy molecular beams were produced via resonant vibrational excitation of the molecules by high-power IR laser radiation in the shock wave, i.e., in the very source of the secondary molecular beam. The essence of the method is clarified in Fig. 15.

As Fig. 15 shows, it is very simple to excite the molecules in a compression shock by laser radiation. When the cone design was chosen for production of secondary beams, the convergent part of the cone was replaced by a tetrahedral hollow truncated pyramid made of thin NaCl plates, which are transparent to the radiation of a CO₂ laser. This made it possible to excite the molecules inside the pyramid just before they were to leave the second nozzle. Multiphoton absorption of molecules in a strong IR field [82] led to an increase in the internal energy (mostly vibrational) of the molecules. The subsequent process of vibrational-translational relaxation, which took place when the gas expanded into vacuum, transferred energy from the vibrational degrees of freedom to the translational, with the result that the molecules were accelerated. Hence, schematically the process of acceleration of molecules induced by IR laser radiation can be represented as follows:

$$\mathbf{M}(v_0) + nhv \to \mathbf{M}^*(v_0) \stackrel{\mathrm{VT}}{\to} \mathbf{M}(v_{\mathrm{L}}), \qquad (18)$$

where M and M^{*} are the molecules in the ground and vibrationally excited states, respectively, v_0 and v_L are the velocities of unexcited molecules and molecules excited by a laser pulse, respectively, and *nhv* is the energy of the laser pulse absorbed by a molecule. Since under the conditions of the experiments examined here the concentration of molecules in the pressure shock was fairly high (corresponding to pressures of one to several Torrs), both multiphoton excitation and V–T relaxation proceeded rather effectively and resulted in a substantial increase in the molecular velocity in the secondary beam. The heating of the gas in the shock wave caused by deceleration (see Section 7.4) also led to an increase in the molecular velocity in the secondary beam. The primary beam was produced with the help of a pulsed nozzle, whose design is described in Section 5.1.

The molecules were vibrated by means of the radiation from a frequency-tunable high-power TEA CO_2 laser, which generated pulses with energies up to 3 J. The molecules were excited in the shock wave just before they left the second nozzle. The laser radiation was slightly focused on the excitation zone by a lens made of NaCl with a focal distance of 2 m. The laser beam was directed parallel to the surface, i.e., at right angles to the primary beam. The laser spot in the excitation zone was approximately 10×10 mm.

The molecular beams were detected by a PED [110, 115] that could be moved along the beam axis. In our experiments we measured the time-of-flight spectra of the molecules at various distances from the sources of the primary and secondary molecular beams [110]. These spectra were used to determine the beam velocities and the spreads of molecular velocities in the beams. Attention in this research was focused primarily on the possibility of producing high-energy molecular beams and on studying the beam characteristics.

7.3 Producing accelerated molecules in the secondary beam

Research in the production of high-energy beams has been done with SF₆ and CF₃I molecular beams without carrier gases and with H₂, He, and CH₄ as carrier gases. We found (see Refs [156, 157]) that the kinetic energy of the molecules in the secondary beam increases dramatically with the energy density of the exciting laser radiation. This becomes especially evident if we turn to Fig. 18, which plots the dependence of the velocities of the secondary beams of SF₆ and CF₃I on the energy density of the radiation from a CO₂ laser. The molecules were excited in the source of the secondary beam just before ejection from the nozzle (inside a tetrahedral hollow truncated pyramid made of thin NaCl plates, which was attached to the front wall of the substrate with a conical opening). For SF₆ molecules the laser was tuned to 938.7 cm^{-1} (the 10P(26) laser line) in resonance with the v_3 vibration of SF₆ (\approx 948 cm⁻¹ [146]). For CF₃I the laser was tuned to 1071.9 cm⁻¹ (the 9R(10) laser line) in resonance with the v_1 vibration of $CF_3I \approx 1075 \text{ cm}^{-1}$ [147]). The mean velocities of the SF₆ and CF₃I molecules were $v_0 = 460 \text{ m s}^{-1}$ and 415 m s⁻¹, while under laser excitation the value increased to $v_{\rm L} \approx 1400 \text{ m s}^{-1}$ and 1065 m s⁻¹, respectively.

We also studied the dependence of the kinetic energy of SF_6 molecules in the secondary molecular beam on the frequency of the exciting CO_2 laser radiation. Such research



Figure 18. Dependence of the velocities of the secondary molecular beams of SF₆ and CF₃I on the energy density of the exciting laser radiation. The SF₆ molecules were excited at 938.7 cm⁻¹ (the 10P(26) laser line). The nozzle pressure in this case is $p_{noz} = 5.8$ atm. The CF₃I molecules were excited at 1071.9 cm⁻¹ (the 9R(10) laser line). The nozzle pressure in this case is $p_{noz} = 4.6$ atm. \



Figure 19. Dependence of the kinetic energy of the SF₆ molecules in the secondary molecular beam on the frequency of the exciting laser radiation: (a) molecular beam of SF₆ without a carrier gas, E_{kin}^0 is the mean kinetic energy of the molecules without laser excitation; and (b) molecular beam of SF₆ mixed with H₂. For comparison, we have plotted in both figures the linear absorption spectrum (curve 2) of the v_3 vibration of SF₆ at $T \approx 300$ K (the spectrum was taken from Ref. [131]).

is needed in order to find the optimal conditions for the production of highly energetic molecules. The dependence is shown in Fig. 19a (curve 1). The secondary molecular beam was formed by a cone described earlier in this section. The nozzle pressure of SF_6 was 5.8 atm. The energy density of the laser radiation was 3.9 J cm⁻². The mean kinetic energy of molecules without laser excitation was $E_{\rm kin}^0 \approx 0.163$ eV. Curve 2 in Figs 19a and 19b gives, for comparison, the linear absorption spectrum, obtained in Ref. [131], of the v_3 vibration of SF₆ at $T \approx 300$ K. Our spectral dependence is fairly wide. This is probably due to the comparatively high pressure and the fairly high vibrational and translational temperatures of SF_6 in the shock wave (see Section 7.4) below). Maximum acceleration was observed when the molecules were excited at roughly 940 cm⁻¹ (on the 10P(22) - 10P(26) laser lines). It is within this range that the energy of the IR laser field absorbed by SF₆ molecules in collisional excitations is at its maximum [82, 168]. Note that the small peak at roughly 931 cm⁻¹ is, probably, caused by the excitation of the v_3 vibration of ${}^{34}SF_6$ molecules $(\approx 930.5 \text{ cm}^{-1} \text{ [148]})$. The ³⁴SF₆ content in the natural mixture of SF₆ used in the experiments was $\sim 4.2\%$. A similar dependence (curve 1) obtained for an SF_6/He beam $(p(SE_6)/p(He) = 1/10)$ is shown in Fig. 19b. Clearly, this

spectral dependence is much narrower than the one in Fig. 19a — a phenomenon that can be explained by the fairly rapid V-T relaxation of SF₆ in the H₂ carrier gas (see Section 7.5 below). Here, the vibrational temperature of SF_6 in the shock wave is much lower than in the case of SF_6 excitation without a carrier gas. The IR multiphoton absorption spectrum of the molecules is narrower and is shifted to the range of the linear-absorption spectrum [82, 168]. As a result, the spectral dependence of the acceleration of the molecules is also narrower.

We also studied the dependence of the kinetic energy of CF₃I molecules in the secondary molecular beam on the frequency of the exciting CO₂ laser radiation. The beam was formed in the same way as described above in this section. At a nozzle pressure of 5.8 atm and an excitation-radiation energy density of 1.3 J cm⁻², maximum acceleration was observed when the molecules were excited on the 9R(8)-9R(14) laser lines (in the 1070-1075-cm⁻¹ range). It was on these lines that we earlier observed the maximum absorption of IR laser radiation by CF₃I molecules [169].

Table 5 displays the results of our experiments on laserinduced acceleration of SF₆ and CF₃I in the secondary molecular beam [157]. We produced molecular beams of SF₆ with a kinetic energy $E_{kin}^{L} \approx 1.5$ eV without a carrier gas and approximately 2.5-2.7 eV with carrier gases (He, CH₄, and H_2), as well as molecular beams of CF_3I with a kinetic energy $E_{\rm kin}^{\rm L} \approx 1.2$ eV. These values are significantly larger than those obtained in Refs [160, 167].

Table 5. Results of experiments on accelerating SF6 and CF3I in secondary molecular beam.

Gas compo- sition	Nozzle pressure, atm	CO ₂ laser line	Energy density, J cm ⁻²	Mean flow velocity, m s ⁻¹		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	3.0	10P(20)	3.7	474	1265	0.173	1.23
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 ₆ /CH ₄ (1/10)	5.0	10P(24)	3.7	1020	1835	0.8	2.6
CF_3I	4.6	9R(10)	1.8	417	1065	0.18	1.2
$CF_{3}I$	5.3	9R(12)	1.7	420	1050	0.182	1.17

7.4 Estimates of the concentration and temperature of SF_6 in the shock wave

Now let us briefly examine the parameters of SF_6 in a normal shock under the conditions of our experiments. In the compression shock that forms inside the cone, the SF_6 concentration was probably higher than in the shock wave in front of the surface. We begin by making estimates with the help of Eqn (13). According to Eqn (13), the concentration ratio for SF_6 molecules in the shock wave, N_2 , and in the incident (primary) beam, N_1 , is $N_2/N_1 \approx \Delta x_b/\Delta x_{sh}$. In our case, $\Delta x_b \approx 4.8$ cm and $\Delta x_{sh} \approx 3$ mm [156, 157], with the result that $N_2 \approx 16N_1$. For instance, when the nozzle pressure

was 3 atm, the number of SF_6 molecules ejected by the nozzle in one pulse was $N_{\rm b} \approx 9 \times 10^{16}$ [157]. According to the estimates made in Ref. [157], the volume of the primary beam was $V_b \approx 15 \text{ cm}^3$. Hence, $N_1 \approx 6 \times 10^{15} \text{ cm}^{-3}$ and $N_2 \approx 9.6 \times 10^{16} \text{ cm}^{-3}$.

Since in our experiments we used a pulsed beam with a small divergence (≈ 0.05 sr; see Section 7.2), to estimate the maximum value of N_2 we can use the relationship for the pressure p_2 in the shock wave $(N_2 = p_2/kT_2)$. This pressure can be estimated by the following formula:

$$mv_1N_1 = p_2 S_b \Delta \tau_b \,, \tag{19}$$

where mv_1N_1 is the molecular momentum in the beam incident to the surface, S_b is the cross-sectional area of the beam at the surface, and $\Delta \tau_b$ is the beam duration. Taking the appropriate values for the SF₆ molecular beam $(m = 146 \times 1.67 \times 10^{-24} \text{ g}, v_1 \approx 4.8 \times 10^4 \text{ cm s}^{-1}, N_b \approx 9 \times$ 10^{16} , $S_b \approx 3 \text{ cm}^2$, $\Delta \tau_b \approx 10^{-4}$ s, and $T_2 \approx 600$ K; see below), we find that $p_2 \approx 38$ mbar (≈ 28.6 Torr) and $N_{2 \max} \approx 5 \times$ 10^{17} cm⁻³.

An increase in the gas temperature in the shock wave, ΔT , caused by deceleration can be estimated by using the law of energy conservation for the SF₆ molecules in the incident beam and in the shock wave [157]. If we assume that the vibrational degrees of freedom of SF₆ in the shock wave do not have enough time to heat up, ΔT can be estimated by Eqn (15). Inserting the appropriate values for SF_6 into (15), we obtain $\Delta T \approx 635$ K. However, despite the fact that V-T relaxation in SF₆ is comparatively slow ($p\tau_{V-T} \approx 150 \ \mu s$ Torr [121]), with the nozzle pressure being several Torrs, the vibrational degrees of freedom of the molecules (at least some of them) had enough time to heat up. So ΔT is probably somewhat lower than the above value. Since the translational and rotational temperatures of SF₆ in the incident beam are $T_{1, tr} \approx T_{1, rot} \leqslant 40$ K [115], in the shock wave we have $T_{2, tr} \approx T_{2, rot} \leqslant 675$ K. The vibrational temperature of SF₆ in the incident beam was $T_{1,vib} \leq 150$ K [115], but in the shock wave it was probably higher.

7.5 Estimate of the amount of absorbed energy used for acceleration

Using the data on the amount of energy that the SF_6 molecules take away from the IR field of the laser pulse and our results in the acceleration of SF₆, one can estimate the amount of absorbed energy that goes into the acceleration of molecules. As noted earlier, the SF_6 pressure inside the forming compression shock ranges approximately from one to several Torrs. Under such pressure, all the molecules in the volume of the gas irradiated by laser light participate in absorption [82, 168], i.e., the fraction of the excited molecules equals unity. The number of photons absorbed (per molecule) in the case of SF_6 excitation, e.g., on the 10P(16) laser line, with the energy density in the exciting pulse being approximately 3.5-4 J cm⁻², is approximately 25 [115, 168]. Hence, the mean absorbed energy per SF₆ molecule is $E_{ab} = \langle n \rangle hv \approx 2.94 \text{ eV}$ (hv = 0.1176 eV is the energy of a laser photon on the 10P(16) line). On the other hand, the kinetic energy of the accelerated SF₆ molecules in the case of excitation on the 10P(16) laser line is $E_{kin}^{L} \approx 1.3 \text{ eV}$ (Fig. 19a). Hence, approximately 45% of the absorbed energy goes into acceleration of the molecules.

Note that some absorbed energy is lost in collisions of molecules with the nozzle walls, another part goes into the heating of the gas within the shock wave, and still another part probably remains with the internal degrees of freedom, mostly in the form of vibrational excitation. The translational and rotational degrees of freedom of SF₆ have enough time to cool to $T \leq 50$ K during expansion, which follows from the results displayed in Table 5. On the other hand, a substantial fraction of the absorbed energy probably remains with the vibrational degrees of freedom. The reason is that V-T relaxation in SF₆ molecules (and also in CF₃I molecules) is rather slow $(p\tau_{V-T} \approx 150 \,\mu s \text{ Torr for } SF_6 \text{ [121] and}$ $p\tau_{V-T} \approx 350 \pm 100 \ \mu s$ Torr for CF₃I [122]). It must be noted, however, that in a strong IR field at high levels of vibrational excitation the process is much more rapid [170]. The V-Trelaxation of SF_6 is also rapid in such gases as, say, H_2 , He, and CH₄ ($p\tau_{V-T} \approx 9.3 \ \mu s$ Torr in H₂, $p\tau_{V-T} \approx 41 \ \mu s$ Torr in He, and $p\tau_{V-T} \approx 30 \ \mu s$ Torr in CH₄ [121]). When these gases are used as carriers, the V-T relaxation of SF₆ proceeds more effectively than in SF₆ without a carrier, so that the acceleration of the molecules in the secondary beam is more effective, too (see Table 5).

7.6 Producing accelerated radicals in the secondary beam

We studied the possibility of producing accelerated radicals in the secondary beam in the dissociation of CF₃I molecules [157]. Figure 20 shows the time-of-flight spectra of CF₃ radicals and also of accelerated and unaccelerated CF₃I molecules. The secondary molecular beam was formed by a substrate with a conical opening, to which a hollow tetrahedral pyramid made of NaCl plates was attached. The nozzle pressure of CF₃I was 3 atm. As the pyramid was hit by the primary beam, a compression shock formed inside it. The CF₃I molecules in the shock wave were excited at a frequency of 1073.3 cm⁻¹ (the 9R(12) laser line) in resonance with the v_1 vibration of CF₃I [147]. This frequency coincides with the peak in the spectral dependence of the yield of IR multiphoton dissociation of CF₃I in a gasdynamically cooled flow [83]. The energy density of the exciting radiation was 3 J cm^{-2} . With such energy density, the CF₃I dissociation yield amounts to more than 80% [169, 171].

To record the time-of-flight spectrum of the CF_3 radical, the molecules were excited at the very beginning of shock formation. When the delay times between the pulse of the



Figure 20. Oscillogram representing the time-of-flight spectra of the CF_3 radicals (second peak) and the accelerated and unaccelerated CF_3I molecules (the third and fourth peaks, respectively) in the secondary molecular beam. The first peak is induced at the detector by the scattered radiation of the exciting laser pulse.

primary molecular beam and the laser pulse are long, the time-of-flight spectra of the CF3 radicals and the accelerated CF₃I molecules were found to overlap, with the result that it proved impossible to detect CF₃ radicals by the method of recording time-of-flight spectra that we used. Note that only CF₃ radicals and iodine atoms are the products of IR multiphoton dissociation of CF₃I. Hence, in this specific case, because of the fairly large difference in the masses of the CF₃ radical, the CF₃I molecule, and the iodine atom, we were still able to record the time-of-flight spectrum of CF₃ radicals. Another factor that could have contributed to this is that the iodine atoms that formed as a result of dissociation were sorbed on the nozzle walls in collisions with these walls. We measure the velocity of the CF₃ radicals and the spread of their velocities in the secondary beam. The values amounted to $v_2 \approx 800 \text{ m s}^{-1}$ and $\Delta v_2 \approx 120 \text{ m s}^{-1}$, respectively (the value of the Mach number $M_2 \approx v_2/\Delta v_2$ was approximately six). Thus, in these experiments we produced an intense beam of cooled CF₃ radicals with a kinetic energy $E_{kin} \approx 0.25$ eV. The acceleration of CF₃ radicals in the secondary beam was caused by the increase in gas temperature because of deceleration and V-T relaxation of excited molecules, which could not dissociate in view of the lack of energy. CF₃ radicals with high kinetic energies can be produced through IR or UV dissociation of CF₃I molecules accelerated in the secondary beam. For instance, with IR dissociation of CF₃I molecules accelerated to $E_{\rm kin}^{\rm L} \approx 1.2$ eV, we can produce CF₃ radicals with $E_{kin} \ge 0.42$ eV. With dissociation of SF₆ molecules accelerated in the secondary beam to $E_{\rm kin}^{\rm L} \approx 1.5$ eV, we can produce accelerated SF₅ radicals with $E_{\rm kin} \ge 1.23$ eV. Thus, we have established (see Refs [155– 157]) that through IR multiphoton excitation of molecules in the shock wave that forms in front of the surface one can produce intense pulsed molecular beams with controllable kinetic energy and beams of accelerated cold radicals.

8. Producing intense pulsed molecular beams with low kinetic energy

In this section we discuss the results of our research [172-174]in the production of intense low-energy molecular beams. Equation (17) implies that when the gas in the source is at room temperature, the kinetic energy of the molecules in the beam varies from 50-60 meV (for a monatomic gas) to 150-200 meV (for gas of polyatomic molecules), depending on the value of γ . The production of low-energy molecular beams requires cooling the gas in the source. However, the cooling of pulsed sources of molecular beams to low temperatures (as well as heating) is highly problematic, since the material from which the sources are made (e.g., elastomers and plastic materials) lose their elastic and plastic properties and become brittle. Moreover, as the temperature becomes lower, the gas pressure decreases, with the result that it becomes more difficult to form gasdynamically cooled jets.

The common way to produce molecular beams with low kinetic energy ($\leq 50 \text{ meV}$) is the use of effusion sources, which operate at room temperatures and at liquid-nitrogen temperatures, and even at liquid-helium temperatures when helium beams must be produced [74, 175]. The kinetic energy of the molecules in an effusive beam is determined by the temperature of the gas in the source ($E_{\text{kin}} \approx kT_0$). However, the intensities of the beams produced by this method are relatively low ($\leq 10^{16}-10^{17}$ mol. sr⁻¹ s⁻¹) [74]. Also, the spread of molecular velocities in such beams is substantial.

Hence the need to isolate monoenergetic molecules, which leads to additional reduction in beam intensity.

At the same time, in many experiments with molecular beams, it is the intensity of the beam that is the crucial factor [8, 72-74]. Hence the importance of developing new methods for the production of intense beams of low-energy molecules. In 2002 we proposed (see Ref. [172]) a fairly simple method for the production of such beams, and the results were promising. In the work that followed (see Refs [173, 174]) we studied in detail the process of producing intense low-energy molecular beams with controllable kinetic energy in the range of approximately one to several dozen millielectronvolts. Below we discuss this method of producing low-energy molecular beams and the results obtained by it.

8.1 Experimental setup and method

In the method that we proposed for producing low-energy pulsed molecular beams we used the compression shock [117-119] that forms when an intense, pulsed, gasdynamically cooled molecular beam (or flow) interacts with a solid surface. Here is the essence of the method [172]. In our experiments, an intense ($\ge 10^{21}$ mol. sr⁻¹ s⁻¹) wide-aperture (divergence $\omega \approx 0.05$ sr) pulsed molecular beam hit a cold copper conductor and a multichannel plate attached to the conductor (both conductor and plate were cooled by liquid nitrogen). The plate was made of duralumin, its thickness was L = 4 mm, and the diameter of the channels in it was $d_0 = 0.5$ mm. The channels were arranged in a closepacked manner. The distance between the centers of the openings was 0.75 mm. The cold conductor had an opening in the form of a convergent cone. The opening was aligned with the beam axis and placed directly in front of the multichannel plate. The diameters of the entrance and exit openings were 11 and 9 mm, respectively. The cold conductor was 8 mm thick. The distance from the nozzle edge to the surface of the multichannel plate amounted to 70 mm. To exclude the possibility of the plate operating in the 'transparent' mode, the plate was rotated through a small angle $\alpha \ge d_0/L \approx 7^\circ$ in relation to the axis of the incident beam.

When an intense supersonic molecular beam interacted with the cooled multichannel plate, a cold compression shock formed in front of the plate and in the channels [118, 119], and the characteristic dimensions of the shock wave were on the order of the mean free path of the molecules, Λ [117, 118]. As shown in Section 6, such a compression shock is a convenient source for producing intense secondary pulsed molecular beams [155–157]. When $\Lambda_{\rm eff} \ge d_0$ (here $\Lambda_{\rm eff}$ is the effective mean free path of the molecules in the channels, $\Lambda_{\rm eff} > \Lambda$ [176]), the gas had time, as it passed through the channels, to cool down to the temperature of the walls (approximately to liquid nitrogen temperatures), with the result that a beam of low-energy molecules was produced from the shock wave. In our experiments this condition was almost always maintained. As a result, it became possible to produce gasdynamically cooled intense molecular beams, with the kinetic energy of the molecules determined, according to Eqn (17), by the gas temperature in the shock wave (≈ 77 K). When the gas pressure in the shock wave was low and no gasdynamic outflow could be maintained, a transition to effusive outflow occurred, with the result that the mean molecular velocity in the beams was close to the mean molecular velocity at liquidnitrogen temperatures. Naturally, the spread of molecular velocities in the beams increased in this case.

In our experiments we used a setup with a pulsed source of molecular beams that was described in Section 5.1. The number of molecules ejected by the nozzle in one pulse varied in these experiments from 8×10^{15} to 2×10^{18} , approximately. We studied the dependence of the intensity and velocity of low-energy molecular beams on the intensity and velocity of the primary beam and the gas temperature in the shock wave; we also measured the spread of molecular velocities in both beams (the extent to which the gas was cooled). As in the research discussed earlier in this review, the measurements were carried out by the time-of-flight method, which is based on using a PED, capable of moving along the beam axis, as a molecular beam detector. We measured the time-of-flight spectra of molecules at various distances from the nozzle. The results were used to determine the beam velocities and the spreads of molecular velocities in the beams. We focused in these experiments on measuring the parameters of low-energy molecular beams.

8.2 Results in producing low-energy beams

In our research we studied molecular beams of H₂, He, CH₄, N₂, and Kr. In all the cases we observed the production of molecular beams with low velocities. Figure 21 shows the dependence (curve *I*) of the kinetic energy of a low-energy He molecular beam on the nozzle pressure. For comparison we give similar plots for the secondary beam in the case where the gas was not cooled in the shock wave ($T_0 \approx 300$ K; curve 2) and for the primary beam (curve 3). Clearly, as the intensity of the primary beam (nozzle pressure) decreases, the kinetic energy of the molecules in the low-energy beam decreases dramatically, tending to the mean value of the energy of He atoms, equal to ≈ 6.6 meV at $T \approx 77$ K.

Figure 22 plots the dependence of the kinetic energy of He and CH_4 beams on the gas temperature in the shock wave (the nozzle pressure was 2 atm). Note that, within the investigated temperature range, the kinetic energy of the molecules was found to decrease with temperature somewhat more rapidly than it would if the dependence were linear. The reason is that in our experiments a decrease in temperature also caused a pressure decrease in the shock wave (the source of the low-energy beam), which led to an additional decrease in beam velocity.



Figure 21. Dependence of the kinetic energy E_{kin} of the low-energy He molecular beam on the nozzle pressure (curve *1*). Curves 2 and 3 represent similar dependences for the secondary beam when the gas in the shock wave is not cooled and for the primary molecular beam.



Figure 22. Dependence of the kinetic energy E_{kin} of He and CH₄ molecular beams on the gas temperature in the shock wave.

Table 6. Results of measurements of molecular beam velocities and energies.

Gas composition and nozzle pres- sure, atm		Primary beam			Low-energy beam		
		v, m s ⁻¹	$E_{\rm kin},$ meV	$v/\Delta v$	v, m s ⁻¹	E _{kin} , meV	$v/\Delta v$
H_2							
	1.9	2950	91.7	8.5	1050	11.6	4.3
	0.6	2620	72.4	4.2	810	6.9	1.3
CH ₄							
	2.0	1330	149.2	10.3	450	17.1	4.7
	0.6	1250	131.8	4.5	370	11.5	2.1
N_2							
-	2.2	910	122.2	9.3	355	18.6	5.1
	1.0	860	109.2	8.7	260	9.9	2.7
Kr							
	2.0	385	62.5	6.5	168	11.9	1.8
	1.0	360	54.7	5.4	130	7.1	

Table 6 lists the results of measurements of the mean velocity and the energy of low-energy beams of H₂, CH₄, N₂, and Kr. Also plotted are the results of measurements of the spread of molecular velocities in the beams and similar data for the primary beams. Our experiments produced H₂ molecular beams with kinetic energies $E_{kin} \leq 6.9$ meV and molecular beams of CH₄ ($E_{kin} \leq 11.5$ meV), N₂ ($E_{kin} \leq 9.9$ meV), and Kr ($E_{kin} \leq 7.1$ meV). Note that the mean velocity of Kr atoms in the beam amounted to approximately 130 m s⁻¹.

We also experimented with molecular beams of H_2/Kr and He/Kr (with a pressure ratio of 1/5 in both cases) [174]. With a nozzle pressure of 0.8 atm and a gas temperature in the shock wave of approximately 77 K, the beam velocities amounted to 165 m s⁻¹, which corresponded to a kinetic energy of the molecules in the beams no higher than 0.3 meV for H_2 and no higher than 0.6 meV for He.

The possibility of producing low-energy molecular beams with the help of a convergent-divergent cone of the Lavaltype nozzle cooled to approximately 77 K was also investigated (see Ref. [174]). The cone was made of duralumin. The entrance diameter was $d_{in} = 13$ mm, the 'waist' diameter $d_0 = 2.5$ mm, and the exit diameter $d_{out} = 6$ mm. The total length of the cone was 30 mm, and the length of the convergent part was 24 mm. Note that it was the use of a convergent-divergent Laval nozzle that enabled us to obtain (see Refs [155-157]) intense secondary molecular beams produced in the forming shock wave. To exclude the 'transparent' mode of operation of the cone, we slightly shifted (by 1.5-2 mm) the cone with respect to the primary beam. These experiments produced He and H₂ molecular beams with mean molecular velocities of roughly 640 and 1300 m s⁻¹, which corresponds to kinetic energies of the molecules of roughly 8.6 meV for He and 17.8 meV for H₂. The beam intensities were found to be comparable to those of beams produced by a multichannel plate. However, with a cone the low-energy beams were produced at a much lower intensity of the primary molecular beam (at lower nozzle pressures). For instance, the low-energy beams of He, H₂, and CH₄ were produced at nozzle pressures no higher than 0.6, 0.4, and 0.3 atm, respectively. The reason is that the above condition for gas cooling $(\Lambda_{\rm eff} \ge d_0)$ in the case with a cone was satisfied at a lower concentration in the shock wave, since the 'waist' diameter of the cone was much larger than the diameter of the channels in the plate. At high nozzle pressures this condition was not met, with the result that the gas inside the cone did not have enough time to cool down to the temperature of the walls, and so the produced molecular beams had a higher kinetic energy.

8.3 Estimate of intensities of low-energy beams

To compare the intensities of the low-energy beams with those of the primary beams, we studied the dependence of the signals induced in the detector by the primary and secondary beams on the nozzle pressure. Figure 23 shows the curves



Figure 23. Dependence of pyroelectric signals induced in the detector by the primary He molecular beam (curve *I*) and the secondary molecular beam, in the case where the gas in the shock wave is not cooled (curve 2), on the nozzle pressure. The distance from nozzle to detector is x = 143 mm, and the distance from the multichannel plate to the detector is 73 mm.

representing this dependence for the He molecular beam. The nozzle-detector distance was 143 mm and the multichannel plate-detector distance was about 73 mm. Clearly, at nozzle pressures no less than 1 atm the signal induced by the secondary beam is 20-30 times weaker than the signal induced by the primary beam. If we allow for the difference in the distances between the sources of the primary and secondary beams and the detector, we find that the intensity of the secondary He molecular beam is lower than that of the primary beam by a factor of 100. In our experiments the intensity of the low-energy He beam was even smaller because the decrease in the temperature (and, therefore, in the pressure) in the shock wave also led to a decrease in the beam intensity.

The beam intensities were determined on the basis of measurements of the gas flow rate in n nozzle pulses and of the geometrical dimensions (length and cross section) of the beams (e.g., see Refs [156, 157]). This approach made it possible to determine the beam intensities with a high degree of accuracy. For instance, let us find the intensity of the He molecular beam by using the results of measurements obtained in Ref. [174]. As measurements of the flow rate showed, the total number of He atoms ejected by the nozzle in a single pulse under a nozzle pressure of 2 atm amounted to roughly $\sim 7 \times 10^{17}$. Since the duration of a pulse of the primary molecular beam was about 100 µs and the beam divergence was $\omega \approx 0.05$ sr, the beam intensity is $I_1 \approx 1.4 \times 10^{23}$ mol. sr⁻¹ s⁻¹. The intensity of the low-energy molecular beam in these conditions was approximately 100-150 times lower, i.e., $I_2 \approx 10^{21}$ mol. sr⁻¹ s⁻¹. Hence, the intensities of the low-energy molecular beams produced in our experiments were higher than those of 'standard' effusive beams by four to five orders of magnitude.

The concentration of helium atoms in the primary beam and in the shock wave was estimated on the basis of the results of measurements of the total number of molecules in the beam and the beam volume. This method has been described in detail in Ref. [157]. For instance, with a pulse duration of roughly 100 µs and a mean beam velocity of roughly 1750 m s⁻¹, the length of the He molecular beam in space was roughly 17.5 cm. The cross-sectional area of the beam at the surface of the multichannel plate was approximately 2.4 cm^2 (the value was determined from the values of the cone angle and the distance from nozzle to multichannel plate). Hence, the beam volume near the plate's surface is $V_{\rm b} \approx 42 \text{ cm}^3$. Therefore, at a nozzle pressure of 2 atm, the concentration of helium atoms in the primary beam is $N_1 \approx 1.7 \times 10^{16} \text{ cm}^{-3}$. The concentration of atoms in the shock wave, N_2 , was estimated by Eqn (12) for the maximum concentration value in a normal shock [117-119]: $N_2/N_1 \approx (\gamma + 1)/(\gamma - 1)$, with $\gamma = 1.66$ [150]. The result was $N_2 \approx 7 \times 10^{16} \text{ cm}^{-3}$.

Note that liquid helium can be used in the production of low-energy He and H₂ molecular beams to cool the gas more deeply in the shock wave and produce still slower beams. Also note that when Kr or Xe are used as the carrier gas, the above method can be employed to produce molecular beams of CO, N₂, NO, and O₂ with kinetic energies lower than 1-2 meV. Thus, in the reviewed papers [172-174] we showed that highintensity low-energy molecular beams can be produced by forming a cold compression shock in front of a solid surface. Note that slow pulse beams, as well as pulses of small duration, have a small length in space. In some experiments on the excitation of molecules by laser beams this is an advantage. When the beam length is small, high-power laser pulses are able to excite or dissociate almost all the molecules in the beam, thus substantially increasing the efficiency with which laser radiation acts on the molecular beam [84, 85].

9. Conclusion

Our investigations have shown that when an intense, pulsed, gasdynamically cooled supersonic molecular flow interacts with a solid surface, a compression shock forms in front of that surface, with the nonequilibrium conditions in the shock wave being the reverse of those in the incident (undisturbed) flow. This makes it possible to study selective photochemical processes induced by high-power IR laser radiation under new nonequilibrium conditions, that is, under conditions where the vibrational temperature of the molecules is lower than the translational and rotational temperatures.

We have studied selective IR multiphoton dissociation of SF₆ and CF₃I molecules that occurs under the nonequilibrium conditions of a pulsed flow interacting with a solid surface. What we have found is that when the molecules are excited in the flow incident to the surface, there is a substantial (severalfold) increase in the product yield as compared to the case of excitation of molecules in the undisturbed flow, without a substantial reduction in the selectivity of the process. When the molecules are excited in the shock wave, there is an even larger increase (by a factor greater than 10) in the product yield (as compared to the case of excitation of molecules in the undisturbed flow), with only a slight reduction (by 25-30%) in the selectivity of the process. Thus, it has been established that the formation of a compression shock in front of a solid surface may considerably increase the efficiency of selective IR multiphoton dissociation of molecules in gasdynamically cooled pulsed molecular flows.

We believe that the proposed method is especially useful in the selective dissociation of large polyatomic molecules, which have rather long lifetimes ($\geq 100-200 \ \mu s$) as compared to monomolecular decay, even when the levels of vibrational excitation are much higher than the dissociation energy (e.g., (CF₃)₃CX, where X is a halogen atom or H [177, 178]). For long lifetimes with respect to decay, the overexcited atoms have time to reach the walls of the chamber and relax on them, without forming products. Formation of a compression shock may initiate collisional dissociation of the molecules, with the result that the product yield increases.

In our investigations we have developed a number of new methods of controlling the parameters of intense pulsed molecular beams (the pulse duration and the kinetic energy of the molecules in the beams), and also a method of producing intense secondary pulsed molecular beams. All these methods are based on the use of a compression shock that forms in front of a solid surface when an intense gasdynamically cooled molecular beam or flow interacts with the surface.

We have used the proposed method of controlling the duration of pulses of intense molecular beams to show that it is possible to produce beams of small duration ($\leq 10 \ \mu$ s) whose spatial length is approximately $1-2 \ cm$. We have found that the pulse duration of molecular beams can be controlled by varying the intensity of the primary beam or the aperture of the opening in the surface through which the beam passes. By implementing the method of formation of secondary pulsed molecular beams we have produced

molecular beams in which the intensity and the extent to which the gas is cooled are comparable to those in the undisturbed primary beam. We have shown that convergent-divergent cones of the Laval nozzle are optimal for producing secondary molecular beams.

The method we have developed for the production of intense high-energy secondary pulsed molecular beams with a kinetic energy controlled by high-power IR laser radiation has made it possible to produce molecular beams with kinetic energies ranging approximately from 0.1-0.2 eV to 2-3 eV. We have found that the energy of the molecules in the beam can be controlled by varying the energy density and/or the frequency of the exciting laser pulse. We have also shown that accelerated radicals can be produced through the dissociation of molecules by high-power IR laser radiation in the secondary source or in the beam proper.

The proposed method of producing low-energy molecular beams was used to produce intense pulsed molecular beams with the kinetic energies of the molecules ranging from one millielectronvolt to several dozen millielectronvolts. The energy of molecules in the beams can be controlled by varying the intensity of the primary beam or the gas temperature in the shock wave. We have found that the intensities of the low-energy molecular beams that we produced exceeds by four to five orders of magnitude the intensities characteristic of 'standard' effusive beams usually used in the production of low-energy molecules.

In conclusion, we note that intense molecular beams with controllable kinetic energy in a broad range of energies from approximately 1 meV to 2-3 eV are of great interest to researchers investigating the interaction of molecular beams 17. with surfaces, in particular, in research dealing with physical $_{18}$. and chemical adsorption of molecules on a surface. It is 19. known, for example, that the adsorption probability of some 20 molecules on the surface of certain metals strongly depends on ^{dol 21}. the vibrational energy and on the kinetic energy [27, 62, 179]. We believe that an interesting area of application of intense 23. beams of vibrationally excited molecules with controllable 24. kinetic energy is the study of the interaction of such beams $\frac{1}{100}$ 25. with molecular (cluster) layers that have condensed on a cold 26 surface in order to implement, e.g., component- and/or max 27. 28. isotope-selective processes of molecule reflection from a surface (or adhering to the surface) covered by molecules that have condensed on it. The use in such studies of lowenergy beams of vibrationally highly excited molecules could, and 30. possibly, trigger such a process. It may be assumed that the 31 real possibility of producing intense beams of vibrationally 32. highly excited molecules with controllable kinetic energy will 33. broaden the area of application of such beams.

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