Apparatus and techniques for the investigation of methods of generating molecular beams

N. N. Kudryavtsev, O. A. Mazyar, and A. M. Sukhov

Moscow Physicotechnical Institute, Dolgoprudnyi, Moscow District
(Submitted 27 October 1992; resubmitted 16 March 1993)
Usp. Fiz. Nauk **163**, 75–93 (June 1993)

This paper is a review of methods of generating molecular beams. Conventional effusion and gasdynamic sources are examined in detail and a comparative analysis is made of them. Methods of producing high-energy beams (>1 eV), an area of present intense development, are discussed at length. Particular attention is focused on fast molecular beams that contain atomic oxygen and are used for the study of physicochemical processes on solid surfaces (erosion, chemoluminescence).

1. INTRODUCTION

The method of molecular beams—directional beams of atoms and molecules—is widely used in research in various fields of physics and chemistry. The use of molecular beam techniques makes it possible to study the properties of individual particles in the absence of collisions between the particles. The molecular beam method has been used to obtain such classical physical results as the experimental verification of the existence of magnetic moments in atoms and the quantization of these moments (Stern and Gerlach, 1922) and the formula for the de Broglie wavelength (Stern, Frisch and Estermann, 1931). On the other hand, this method can be effectively used in investigations of processes induced by collisions between the particles. Standard areas of research with the use of atomic and molecular beam methods are experimental studies of the scattering of atoms and the mechanisms of elementary chemical reactions in the gas phase. In the molecular beam method as applied to chemical problems it is assumed that there is only a single collision between two reacting particles, so that it is possible to avoid the averaging of the characteristics of the processes that occurs under conditions of multiple collisions. By this method one can obtain detailed information concerning the effect of the velocity of the particles and of the quantum states of the reagents on the probability of the formation of products and the distribution of the products over the internal states and velocities. The possibility of polarization and orientation of the molecules in molecular beams makes it possible to study the role of steric factors in chemical reactions.[1] The molecular beam method occupies a leading place in investigations of elementary chemical reactions in the gas phase. In 1986 D. Herschbach and Y. T. Lee were awarded the Nobel prize in chemistry for the development of the molecular beam method.

In recent years the molecular beam method has become widely used for investigations of the dynamics of the gas-surface interaction. Molecular beams have a number of properties that simplify the study the kinetics of reactions taking place on solid surfaces. Molecular beams provide a high flux of reacting particles to the surface at a low background gas pressure. Since there are no collisions in the gas phase, one observes only those reactions that take place on the surface of the solid, the rates of these reactions not being limited by the diffusion of the gas particles to the surface and away from it.[2]

Molecular beam experiments permit a detailed study of the adsorption of gases on solid surfaces, which is the first step in such technologically important processes as epitaxial growth of semiconductor structures, heterogeneous catalytic reactions, and the effects due to various factors, such as the state, velocity, and angle of incidence of the particles, the surface temperature, and so forth.[3,4] Investigations of the scattering of molecular beams on solid surfaces are a source of information on the mechanism of energy transport in collisions and the gas-surface interaction potential,[5,6] which is important for developing a theory of scattering of molecules by surfaces to be used in the description of chemical reactions occurring with participation of the solid surface.[7]

In the travel of spacecraft in near-earth orbit, the beams of atoms and molecules of the surrounding atmosphere create radiation on the surface of the spacecraft that affects the operation of optical detectors, reducing the accuracy of optical measurements in the infrared, the ultraviolet, and in the visible regions of the spectrum.[8] Moreover, the various materials, interacting with the atmosphere surrounding the spacecraft are damaged and their properties are altered.

It has been established[9,10] that this is due to the interaction between chemically active oxygen atoms and the material covering the spacecraft. The spacecraft, travelling with a velocity of ~ 8 km/s at altitudes of from 230 to 310 km, are subjected to the action of a flux of oxygen atoms of intensity $4 \cdot 10^{14} - 2 \cdot 10^{15}$ $cm^{-2}s^{-1}$ (Ref. 9). It is essential that these effects be studied in the laboratory.

Intense beams of oxygen atoms are used for the study of the mechanism of oxidation of the surface of silicon.[11] Despite the fact that atomic oxygen plays a key role in the

 1063-7869/93/060513-16$10.00

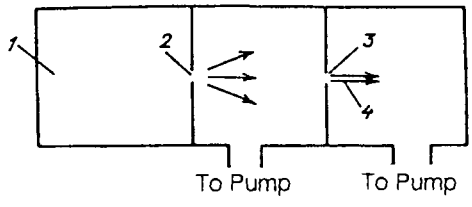

FIG. 1. Effusion source. *1*) Stationary gas; *2*) aperture; *3*) diaphragm; *4*) molecular beam.

plasma oxidation of silicon and the preparation of Si–SiO_2 structures, which occupy an important place in microelectronics, the interaction of atomic oxygen with the silicon surface has been insufficiently studied.[11,12]

Since the end of the 1960s vigorous development has occurred in the technique of molecular beam epitaxy—the method used to prepare semiconducting structures used in microelectronics (transistors, integrated circuits, LEDs), quantum electronics (multilayer semiconducting heterostructures, injection lasers) computer technology (magnetic-bubble memory elements)—which is based on the interaction of atomic and molecular beams with the substrate surface under conditions of ultrahigh vacuum. Molecular beam epitaxy has important advantages over other methods of epitaxial growth of structures: The process occurring under vacuum conditions can be monitored by ellipsometry and Auger spectroscopy, which makes it possible to grow structures of exceptionally high quality and with prescribed properties.[13]

The successful development of the above-mentioned fields of science and technology, in which the method of molecular beam epitaxy is used (the standarized name for atomic, molecular, and cluster beams), is largely dependent on the advances in the method itself, and in particular it depends on the status of beam sources. In this paper we present a review of the methods of generating molecular beams and describe their characteristics and the directions of their development. Particular emphasis is placed on intense beams of atoms and molecules with kinetic energies of 1–5 eV.

We focus especially on methods of producing intense fast beams of atomic oxygen. In this review we summarize the experience of many groups of investigators and present the results obtained in recent years.

2. CONVENTION METHODS OF PRODUCING MOLECULAR BEAMS

2.1. Effusion sources

Molecular beams were produced for the first time in 1911 by the effusion method.[14,15] The method of forming an effusion molecular beam is shown in Fig. 1. The molecules of a gas at rest *1*, whose mean free path λ is greater than the dimensions of the aperture *2*, pass through this aperture into a vacuum chamber, in which essentially no collisions occur between the molecules and then travel along straight trajectories (Troitskii[16] has shown that the mean free path at any point of effusion molecular beam,

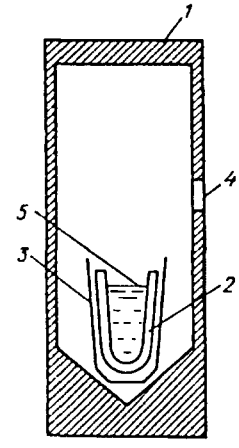

FIG. 2. Source of aluminum atoms.[17] *1*) Graphite cylinder; *2*) aluminum oxide crucible; *3*) tantalum foil; *4*) effusion slit; *5*) aluminum sample.

assuming a Maxwellian velocity distribution, is almost three times that in a gas of the same density). A diaphragm *3* separates out a beam of molecules *4* in essentially parallel motion.

If n is the number of molecules in 1 cm^3 in the source, $c=(8RT/\pi M)^{1/2}$ is the average velocity of the molecules, T is the temperature of the source, R is the universal gas constant, and M is the molecular mass, then the intensity of the beam at a distance r from the source is[23]

$$I=\tfrac{1}{4}nca\frac{\cos\theta}{\pi r^2}\ [\mathrm{cm^{-2}s^{-1}}], \tag{2.1}$$

where a is the area of the aperture in a wall of negligible thickness, and θ is the angle between r and the normal to the aperture. If n is expressed in terms of the gas pressure P in the source in torr, then the expression assumes the form

$$J=1.11\cdot 10^{22}\frac{aP}{r^2(MT)^{1/2}}\times\cos\theta[\mathrm{cm^{-2}s^{-1}}]. \tag{2.2}$$

Let us consider an example of the intensity of a beam. We take the width of the slit to be 0.01 mm. To avoid collisions of the particles in the aperture the pressure in the source must be lower than 1 torr. Let the height of the aperture be 1 mm, and $r=50$ cm, $T=1000$ K, $M=29$ g/mole; then $I=2.6\cdot 10^{12}$ $\mathrm{cm^{-2}s^{-1}}$ for $\theta=0$.

The use of a channel instead of the aperture 2 (Fig. 1) improves the angular distribution of the molecular velocities, while at the same time the number of molecules issuing from the source per unit time is reduced below that for the effusion of gas through an aperture in a thin wall.[24] To increase the intensity of the effusion beams, sources are used with several apertures, or channels, spaced at a distance that should be greater than their diameters.[25]

There are a large number of different designs of effusion sources. We shall examine some of them. The diagram of a typical source for atomic beams of aluminum is shown in Fig. 2 (Ref. 17).

A heated oven is used to obtain a beam of aluminum atoms. A crucible of aluminum oxide *2* with the outer side covered with a tantalum foil *3* is placed in a thin-walled graphite cylinder *1* (inner diameter 0.63 cm, outer diameter 0.83 cm). The oven is heated by passing an ac current directly through the graphite cylinder. To obtain a working temperature of 1670 K in the vicinity of the slit *4* (aluminum oxide begins to decompose at 1700 K) requires a power of 800 W. The aluminum to be evaporated is placed into the crucible in the form of a wire *5*. The amount of aluminum evaporated in 6 h of operation is 0.17 g.

A furnace with local heating, different in construction by having an electron beam produced by field emission from carbon fibers,[18] has been described in Ref. 19. The oven consists of a cylindrical tube (22 mm long and 3 mm in diameter) made of tantalum foil 20 μm thick, rolled into two layers, or made of spectroscopically pure graphite (inner diameter of the oven 2 mm). It is heated by a beam of electrons emitted by two ring-shaped cathodes placed near the evaporated material and near the exit aperture of the oven in an electric field produced by a high-voltage source (to 8 kV). The oven is placed in a quartz chamber in which the gas pressure is maintained at 0.01 Pa. The maximum temperature of the oven (2400–2600 °C) is limited by the destruction of the material of the tube.

To obtain hydrogen atoms, Kellogg *et al.*[20] used a Wood discharge tube. Since the presence of the metal in the tube severely reduces the yield of atomic hydrogen, the electrodes must be located far from the region of effusion of the atomic hydrogen. Kellogg *et al.*[20] made tubes ~ 5 m long with an effusion slit 0.025 mm wide in the middle of the tube. With 10 kV on the electrodes and a hydrogen pressure of 1 torr in the tube the concentration of atomic hydrogen in the tube was 80%.

Atoms of oxygen, hydrogen, and halogens are usually produced with the aid of rf or microwave dissociators. The sources described in Refs. 21 and 22 are electrodeless glass discharge tubes 7 mm in diameter with a slit of length 0.45 cm and width 0.076 mm on one of the ends. The tube was placed in a microwave cavity, to excite the gas discharge at a distance of ~ 1 cm from the slit. The source generated beams with 60% concentration of atoms with a microwave discharge at a frequency of 3 GHz and a power of 50 W. The gas pressure was 0.25 torr.

Beams of atoms from a solid material are best produced by the direct heating of the evaporated material by an electron beam or by laser radiation, since in this way the interaction of the evaporated material with the walls of the oven is reduced to a minimum. When the electron beam or the laser beam is focused directly onto the evaporated substance only a limited volume of the substance is heated, so that the walls of the source can be maintained at a low temperature. This method of producing beams of particles has yet another important advantage: modulation of the intensity of the electron beam (or laser radiation) modulates the intensity of the beam of particles, an important feature for experimental investigations and for controlling epitaxial growth of semiconducting structures.

In sources with heating by an electron beam the electron flux, which is accelerated by a potential difference of 5–10 kV, enters a magnetic field that bends the trajectories and focuses the electron flux onto the evaporated material. When an electron hits the solid, most of its kinetic energy is converted into heat. With the use of electron bombardment it is thus possible to produce high temperatures (above 3000 °C) in the evaporating material. By way of example, let us consider the source of a silicon beam (Fig. 3), described by Ota.[26,27] In this device, an electron beam was used, in which the electron source was a tungsten filament *1* placed outside the wall of a water-cooled copper crucible *2* containing the material to be evaporated *3*, so that contamination of the tungsten filament by the evaporating material was eliminated. The electron beam *4* was bent through 270° and focused onto the silicon surface by a magnetic field. The sample of evaporated material (Si) was in the form of a truncated cone. The zone of melting of the silicon was located in the center of the base of the cone. A silicon ring *5* shielded the surface of the copper crucible *2* from scattered electrons, and thereby prevented contamination of the melted zone by copper. A silicon bow *6* placed near the evaporating material on the side opposite the electron beam prevented another possible source of contamination—sputtering of particles of the stainless steel apparatus by electrons reflected from the silicon sample *3*.

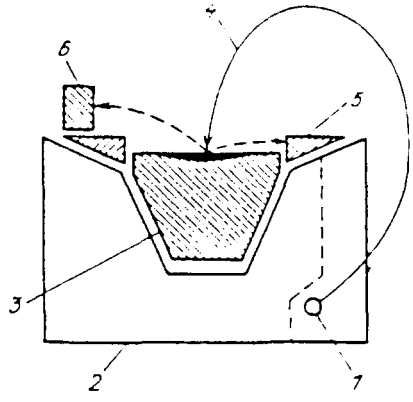

FIG. 3. Source with heating of the evaporating material by an electron beam.[26,27] *1*) Tungsten filament; *2*) copper crucible; *3*) silicon sample; *4*) electron beam; *5*) silicon ring; *6*) silicon bow.

For growing epitaxial layers of $Hg_{1-x}Cd_xTe$, CdTe, and HgTe-CdTe superlattices Cheung *et al.*,[28,29] used a source with a polycrystalline CdTe target heated by a pulsed YAG-Nd laser ($\lambda = 1.06$ μm). In the interaction with the laser radiation the temperature of the surface rises sharply and causes the material to evaporate. A time-of-flight analysis showed that the velocity distribution of the evaporated particles conformed to the Maxwell-Boltzmann distribution. This implies that the evaporation process was an equilibrium process. The surface temperature was 1400–3200 °C (with an average laser power of 0.6–4.8 W). Because of the low thermal conductivity of CdTe, the time of cooling of the target was ~ 1 ms, longer than the time between consecutive laser pulses. Therefore sequential pulses could cause additional heating of the evaporated

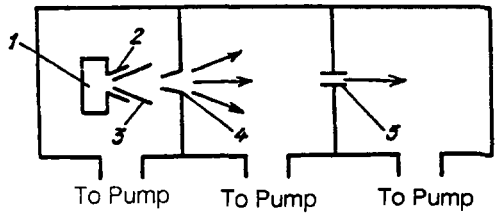

FIG. 4. Gasdynamic source. *1*) Stationary gas; *2*) nozzle; *3*) jet; *4*) skimmer; *5*) collimator.

target and hence an increase in the intensity of the molecular beam.

Effusion sources make it possible to generate beams of known intensity with a known angular distribution. In addition, the state of the particles in the beam is identical to that in the bulk of the source, which greatly facilitates beam diagnostics. These properties of sources of effusion beams allows them to be used effectively for many experiments. The technology of making semiconducting structures by molecular beam epitaxy employs mainly effusion sources of beams.

2.2. Gasdynamic sources

In 1951 it was proposed[30] that the effusion outflow of the usual source be replaced by a supersonic jet with subsequent separation of a molecular beam from the jet. Kistiakowsky and Slichter[31] produced a gasdynamic molecular beam of NH_3 by the method of Ref. 30 and were able to increase its intensity by a factor of 20 over that of an effusion source. However, a significant difficulty in the experiment was to pump out the gas admitted into the system even with the use of small nozzles. The effectiveness of a supersonic jet as a source of a molecular beam was demonstrated in 1954.[32]

In the gasdynamic method of forming a molecular beam (Fig. 4) the gas *1* flowing out from a nozzle *2* forms a supersonic, adiabatically expanding flux, the free jet. The molecules accelerated in the free jet encounter a skimmer *4*. The molecules that are essentially in parallel motion—the gasdynamic molecular beam—are separated out by means of the collimator *5* from the molecules that have passed through the skimmer.

There are two main types of sources of gasdynamic molecular beams. In the source of Fenn the beam is formed from an underexpanded jet, and in the source of Campargue the beam is formed from the overexpanded jet in the "zone of silence", not subjected to the effect of the background gas, located directly ahead of the Mach disk.[119]

In Ref. 34 an estimate was made of the ratio of the intensities of the gasdynamic and effusion molecular beams for the same Knudsen number of the aperture of the effusion source and of the skimmer of the gasdynamic source:

$$\frac{I_{gd}}{I_{ef}} \approx \gamma M^2 \left(\frac{2\pi}{\gamma-1}\right)^{1/2}, \tag{2.3}$$

where $\gamma = c_p/c_v$ and M is the Mach number of the free jet at the entrance to the skimmer. For $\gamma = 1.4$ and $M = 10$ the gain in intensity is 554.

In Ref. 35 an estimate was made of the intensity of a gasdynamic beam on the basis of a model in which the gas flow is isentropic out to a certain spherical transition surface, and beyond this surface the gas is in free molecular flow. The perturbing effect of the skimmer was not taken into account. If l_s is the distance between the nozzle and the skimmer, l_1 is the distance from the nozzle to the spherical surface of transition from isentropic gas flow to free molecular flow, with $l_s > l_1$, and n_s is the density of molecules in the skimmer, r_s is the radius of the aperture of the skimmer, M_1 is the Mach number of the gas at the transition surface, then with $M_1 > 4$ the intensity of the gasdynamic beam on the axis of the nozzle is

$$I \approx n_s \pi r_s^2 u_1 \frac{1}{\pi x^2} \left(\frac{l_s}{l_1}\right)^2 \left(\frac{1}{2}\gamma M_1^2 + \frac{3}{2}\right), \tag{2.4}$$

where u_1 is the velocity of the gas at the transition surface. If $l_1 > l_s$, then u_1, l_1, and M_1 are equal, respectively, to u_s, l_s and M_s.

Anderson *et al.*[35] have compared the intensity of gasdynamic and effusion beams, assuming equal gas temperatures in the effusion source and in the nozzle and equal densities of the gas in the skimmer and in the effusion source:

$$\frac{I_{gd}}{I_{ef}} \approx \left(m\frac{c_P}{k}\right)^{1/2} \gamma \left(\frac{l_s}{l_1} M_1\right)^2, \tag{2.5}$$

where c_p is the specific heat at constant pressure. For a diatomic gas and $l_s M_1/l_1 = 10$ the intensity of the gasdynamic beam is a factor of 470 greater than the intensity of the effusion beam.

To obtain a high intensity in a gasdynamic beam it is necessary to create a flux in which a rather high Mach number is obtained ahead of the skimmer. To obtain high Mach numbers it is necessary to have a high rate of pumping of the gas from the volume between the nozzle and the skimmer. In Ref. 34 an estimate was made of the required ratio of the pressure P_0 in the nozzle chamber to the pressure P_b of the background gas ahead of the skimmer in order to obtain a flux with a Mach number M:

$$\frac{P_0}{P_b} \approx M^{2/(\gamma-1)}. \tag{2.6}$$

For $\gamma = 1.4$ and $M = 10$ the ratio is $P_0/P_b \approx 10^5$. It was because of the low pumping rate that the first experiments were unable to obtain gasdynamic beams of high intensity. The chamber into which the gas flows from the nozzle must be pumped out at a high rate to remove essentially all the gas except the small part that passes out through the skimmer. The role of the rate of pumping of the chamber has been established in Refs. 36–38. At the present time the problem of a high pumping rate has been effectively solved by the use of cryogenic and turbomolecular pumps.

In gasdynamic sources of molecular beams both converging and converging-diverging nozzles are used. However, in the diverging parts of the nozzle, calculated for the

production of fluxes with high Mach numbers and low densities, thick boundary layers are formed, and as a result the isentropic flow at the position of the nozzle frequently has completely disappeared. Such nozzles do not operate in the calculated regime.[32] Becker and Bier[32] have also observed that if the diverging part of the nozzle that they used was eliminated the intensity of the beam was unchanged. At the same time, viscous effects on the flow from the converging part of the nozzle are readily taken into account by choosing the effective diameter of the throat of the nozzle so that the theoretical expressions for nonviscous flow describe exactly the real situation.[39]

The skimmer usually has the shape of a cone with a vertex angle less than 60° and a diameter of the entrance aperture of the order of the mean free path in the arriving flux. The problem of the interaction between the free jet and the skimmer is very important, since the results of this interaction can lead to a large drop in the intensity of the molecular beam.[35,40] The geometric shape of the skimmer and the effect of the shape on the formation of the molecular beam have been discussed in Refs. 41–44.

The authors of Ref. 35 believe that a skimmer in the form of a slit should provide a beam of higher intensity than a conical skimmer. Such a skimmer allows a more economical use of the pumping capacity. Preliminary experiments carried by the authors of Ref. 35 with this kind of skimmer have supported this opinion. Kozlov and Shchebelin[45] have derived an expression for the density of a molecular beam beyond the slit skimmer. Let l_s be the distance from the nozzle to the skimmer, l_d the distance from the skimmer to the region of observation, l_1 the radius of the sphere of transition from isentropic gas flow to free molecular flow, S_1 the ratio of the velocity of the flux to the mean thermal velocity at the transition sphere, n_1 the concentration of gas molecules in the region of the transition sphere, y and z the coordinates of the plane of observation, $a=y/l_d$, $b=z/l_d$, and d_{sa} and d_{sb} the dimensions of the aperture of the skimmer in the corresponding directions. The skimmer is considered narrow rather than wide if the divergence of the beam beyond the skimmer is governed by the ratio of the velocity of the beam to the mean thermal velocity of the molecules in the beam, and not by the size of the aperture of the skimmer. The condition of narrowness of the skimmer is

$$\frac{d_s}{2l_1} \ll \frac{1}{S_1}. \tag{2.7}$$

For large distances from the skimmer to the region of analysis ($l_d \gg l_s$) the concentration n_d of molecules in the beam for the case of a narrow skimmer is given by the expression

$$n_d \approx n_1 \frac{d_{sa} d_{sb}}{l_d^2} \times \frac{S_1^2}{\pi} \exp\left[-S_1^2 \frac{l_s^2}{l_1^2} (a^2+b^2) \right]. \tag{2.8}$$

For a wide skimmer

$$n_d \approx \frac{l_1^2}{(l_s+l_d)^2} n_1, \tag{2.9}$$

if both $|a| \ll d_{sa}/2l_s$ and $|b| \ll d_{sb}/2l_s$, while

$$n_d = 0, \tag{2.10}$$

if $|a| \gg d_{sa}/2l_s$ or $|b| \gg d_{sb}/2l_s$. If the skimmer is narrow in the y direction and wide in the z direction, then for $|b| \ll d_{sb}/2l_s$

$$n_d \approx n_1 \frac{d_{sa} l_1}{l_d(l_s+l_d)} \times \frac{S_1}{\sqrt{\pi}} \exp\left(-S_1^2 \frac{l_s^2}{l_1^2} a^2 \right). \tag{2.11}$$

The ratio of the concentration of molecules on the axis of a beam produced by a narrow slit-type skimmer ($d_{sa} = d_{sb} = d$) and to the concentration on the axis of a beam produced by a skimmer that is wide in the z direction and has an entrance aperture $d_{sa} = d$, is $\sqrt{\pi} l_1/dS_1$, calculated for a distance l_d from the skimmer for $l_d \gg l_s$ by formulas (2.11) and (2.8). If $d=1$ mm, $S_1=10$, and $l_1=100$ mm, then the gain in the concentration of the beam when a skimmer wide in the z direction is used is ~ 18.

It is possible in jets of gasdynamic apparatuses used for the formation of molecular beams to obtain small aggregates of molecules—clusters. The formation of centers of condensation and coagulation were first observed in an apparatus with gasdynamic sources of molecular beams by Becker and his coworkers.[46,47] They determined the critical temperature at which there is a sharp increase in the intensity of the molecular beam, which they associated with the appearance of clusters in the beam. In Refs. 48 and 49 the presence of clusters was demonstrated for jets of carbon dioxide gas emerging from small nozzles. These investigators were able to measure the concentration of the clumps of particles of various sizes by a mass-spectrometric analysis of the cluster ions, obtained by electron bombardment of beam formed from a jet of CO_2. Cluster beams have been studied many times. A more detailed introduction to this topic can be found in the reviews of Refs. 34 and 40.

3. PULSED GASDYNAMIC SOURCES

As noted above, gasdynamic sources require considerable pumping capacity both for the nozzle chamber and for other parts of the apparatus. This problem can be solved effectively with the use of gasdynamic sources with intermittent operation. Pulsed gasdynamic sources have been used successfully.[50,51] Fast-acting valves have been developed for the control of the flux through the nozzle, so that it is possible to use large-diameter nozzles at high working gas pressures in the nozzle chamber. In this way it is possible to obtain molecular beams with a low level of condensation[52] and with an intensity two or three orders of magnitude above that of molecular beams obtained with continuous gasdynamic molecular beam sources. In this way the requirements on the pumping system of the gasdynamic source are considerably reduced. It has been pointed out[53] that with a pulsed gasdynamic source that gives 100 μs pulses with a repetition rate of 10 Hz, an instantaneous intensity is attained that is 100 times that of a continuous source. The time required to attain a steady-state flux is many times shorter than the pulse length, so

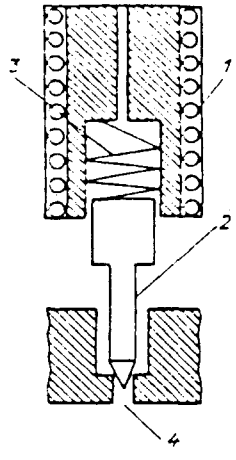

FIG. 5. Electromagnetic valve. *1*) Excitation coil; *2*) needle; *3*) return spring; *4*) nozzle.

that it is possible to use a pulsed source for those problems that employ a continuous source, but the pumping rate can be reduced by a factor of 10.

3.1. Pulsed gasdynamic sources with electromagnetic valves

A diagram of a pulsed gasdynamic source with an electromagnetic valve is shown in Fig. 5. When a current pulse passes through the excitation coil *1* the needle *2* is drawn in the direction of the coil and opens the nozzle *4*. When the current is cut off the spring *3* returns the needle to its initial position. Such a valve has been operated at a rate of 10–50 Hz, maintaining a pressure up to 10 MPa.[54] The diameter of the nozzle was 335 μm and the duration of the gas pulse was ~ 600 μs. The authors of Ref. 55 used an electromagnetic valve with a time of 0.3–300 ms in the open state to produce a source of halogen atoms. To suppress the sticking of the halogen atoms to the walls of the valve and prevent their catalytic recombination on the walls, all the parts of the valve were coated with Teflon. The halogens were dissociated by means of a microwave discharge. Typical instantaneous chlorine fluxes in the reactor were $\sim 10^{15}$ s^{-1}. In the work reported in Ref. 56 Bucher *et al.* described a valve that provides reliable sealing at the temperature of liquid nitrogen at a helium pressure of 8 to 10 atmospheres in the pressure reservoir ahead of the valve. The needle in this valve was made of Teflon with an iron core embedded in it. The valve produced helium pulses ~ 450 μs long with a repetition rate of 10 Hz. Reference 57 describes the design of a fast-acting pulsed electromagnetic valve that can operate with a repetition frequency up to 100 Hz, forming gas pulses with a full width at half maximum of ~ 100 μs. The valve can operate with a pressure of the working gas up to 20 atm. To make a fast-acting valve, the authors of Ref. 57 used a light plastic Bellville spring instead of the usual spiral spring, which is heavier for the same stiffness.

3.2. Pulsed Gasdynamic Sources with Piezoelectric Valves

Piezoelectric valves open and close as the result of the bending of a plate made of a piezoelectric material that is fastened to a metal membrane. Because of the high frequencies of the natural oscillations of the plate (several kHz) and the low power requirement, such valves can operate at high pulse repetition rates that are not attainable for valves of other design. The disadvantage of piezoelectric valves is related to the small deflection of the piezoelectric plate (a few tens of micrometers) and to its low strength. Usually, piezoelectric valves limit the gas supply when the diameter of the nozzle exceeds 0.1 mm.[58] The valve described in Ref. 58 forms a molecular beam with an intensity that is entirely determined by the nozzle for a nozzle diameter up to 1 mm. The piezoelectric plate used in the valve flexes 100 μm for a voltage of 1000 V. Tests have been made of a valve with a nozzle of diameter 0.2 mm and gas pressures above 3 MPa and with a nozzle of diameter 1 mm and a pressure of 0.6 MPa. The valve operated at pulse repetition frequencies above 150 Hz. Typical gas pulse lengths were 170 to 250 μs and depended on the diameter of the nozzle. Marinescu[59] has proposed a valve with which it is possible to obtain a high local gas density at the entrance to the vacuum chamber with a minimum total amount of gas admitted into the chamber. The exit fitting of the valve is a capillary with an inner diameter of 0.18 mm. However, the gas pulses obtained with this valve are long because of the scattering of gas on the walls of the capillary. The piezoelectric valve is used in pulsed gasdynamic sources of cold beams of atomic hydrogen.[60] The hydrogen is dissociated into atoms by a microwave discharge. From the nozzle of the dissociator the atoms are directed along a short Teflon connecting tube to an accommodator at the temperature of liquid helium. The cooled gas flows out into a vacuum, forming an intense molecular beam. The beam is detected by a calibrated residual gas analyzer placed a distance of ~ 70 cm from the accommodator. The highest pulse intensity of $2 \cdot 10^{15}$ cm^{-2}s^{-1} with the autocollimator at 5.8 K was obtained for a hydrogen beam with a velocity of 680 m/s. In this case the flux of atomic hydrogen through the accommodator was $9.4 \cdot 10^{18}$ sr^{-1}s^{-1}.

3.3. Pulsed gasdynamic sources with a "current loop" valve

Pulses of gasdynamic beams of short duration (less than 100 μs) are of interest for time-of-flight investigations with high time resolution. In 1968 Dimov[61] proposed a pulsed nozzle of the "current loop" type. Gentry and Giese[62] used a pulsed nozzle as a source of a gasdynamic molecular beam and obtained pulses with a duration of 10 μs. A diagram of the source is shown in Fig. 6. The seat of the valve is a metal plate *2* clamped on the two ends, while the center is fastened to an O-ring *3*. The body of the source is rigid, and the plate *2* is easily flexed, and the period of its natural oscillations is 10 μs. When current pulses are applied as shown in Fig. 6 the plate is deflected so that the seal is broken and the gas passes through the center of the O-ring, which acts as the nozzle. It was re-

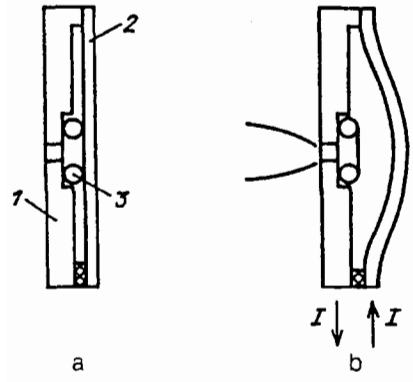

FIG. 6. Diagram (a) and principle of operation (b) of a pulsed gasdynamic source of the current-loop type. *1*) Body; *2*) metal plate; *3*) O-ring.

ported in Ref. 63 that with this valve operating at a frequency of ~20 Hz gas pulses were obtained with a duration of 7 μs. Pulsed nozzles of the current loop type have been used successfully in Refs. 64 and 65 for obtaining intense supersonic beams of metal clusters. Maruyama *et al.*[64] have noted that to obtain time reproducibility of the action of the valve the spring must not be overheated or overloaded.

A source that also belongs in this class is the one reported in Ref. 52, mentioned above, with which an atomic beam of helium was formed with an intensity of 10^{23} $sr^{-1}s^{-1}$, which is two or three orders of magnitude higher than that of beams generated by the continuous-action source of Compargue.[33] Beams have been formed with the device described in Ref. 52 with a rise and fall time in the density of 50 μs and with a time of constant density of 150 μs. The stagnation pressure of the gas was 20 atm. The source operated at a frequency of 5 Hz.

Saenger[66] has discussed the question of the lower limit of pulse duration τ of a gasdynamic molecular beam source, for which the supersonic free jet will be comparatively "colder" than the jet of a continuous-action source. The time τ consists of the intermediate times Δt_1, Δt_2, and Δt_3. In the time Δt_1 the gas is accelerated to the velocity of sound in the critical cross section of the nozzle,

$$\Delta t_1=\frac{2D}{(2kT_0/m)^{1/2}}\left(\frac{\gamma+1}{\gamma}\right)^{1/2}, \tag{3.1}$$

where D is the diameter of the nozzle, T_0 is the gas temperature in the nozzle chamber, and $\gamma=c_p/c_v$. The time Δt_2 is required for the formation of a buffer zone, which contains the molecule partners in the collision events during the time of expansion:

$$\Delta t_2=\frac{2Nl}{u}, \tag{3.2}$$

where

$$u=\left(\frac{\gamma}{\gamma-1}\right)^{1/2}(2kT_0/m)^{1/2}$$

is the flow velocity that is established during the expansion at a distance x from the critical cross section of the nozzle, l is the mean free path of the molecules, and N is the number of collisions required to establish equilibrium in the translational, rotational, and vibrational energies of the molecules in the flow. The time Δt_3 is necessary to form the pre-buffer zone, from which the molecules are supplied to the buffer zone as particles are lost from the latter by virtue of the components of velocity perpendicular to the axis of the beam

$$\Delta t_3=\frac{Cx}{u}, \tag{3.3}$$

where C is a constant, $0.05<C<0.5$.

As pointed out by Saegner,[66] the condition $\Delta t>\tau$, where Δt is the pulse length of the gasdynamic source, is satisfied by all known gasdynamic sources of molecular beams except the one described in Ref. 62.

Thus the existing pulse technology and arsenal of experimental methods provide a high peak flux for molecular beams that are then used for various measurements.

4. METHODS OF PRODUCING HIGH-ENERGY GASDYNAMIC MOLECULAR BEAMS

The maximum attainable particle energy in gasdynamic beams is determined by the temperature of the gas in the nozzle chamber.[35] Since the expansion is accompanied by the conversion of the enthalpy of the gas into the energy of directed motion of the molecular beam, for Mach numbers greater than 4 the final particle energies in the beam turn out to be above the mean thermal energy of the gas molecules in the nozzle chamber by a factor of about $2\gamma/3(\gamma-1)$. If the gas temperature in the nozzle chamber is 3000 K the particle energy reaches 0.5 eV. To increase further the energy of the particles in the beam it is necessary to use methods of heating the gas that do not cause destruction of the materials of the source components. The effects associated with the destruction can be avoided if pulsed heating of the gas is used. In 1961 a gasdynamic source was developed in which the gas was heated in a shock tube.[67] In this apparatus the ballistic pendulum method was used to study the transfer of momentum of the molecules to a solid surface for argon beams with energies of about 1.2 eV.[68] Takahashi and Teshima[69] used an apparatus of this type to achieve a velocity of 1.77 km/s in a neon beam with a gas temperature in the nozzle chamber of 3100 K and a pressure of 1660 torr. This is not the ultimate figure of merit, since a gas temperature of 10 000 K can be obtained in a shock tube.[69]

Another approach to the production of high-energy beams of particles is the use of cooled nozzles and heating of the initial gas in an electric arc. Knuth[70] has developed such a device and has carried out experiments with argon, generating beams with a particle energy above 1 eV. He points out the main disadvantage of a device of this type: the expanding gas is contaminated by the material of the electrodes. In Ref. 71 Young *et al.* have reported the development of a device for arc heating of a gas with a low

rate of erosion of the electrodes and improved stability of the arc, achieved by application of an axial magnetic field. Beams of argon atoms with energies of 1.52 eV have been produced in an apparatus with arc heating of the gas.[72]

Götting *et al.*[73] have used an arc source for producing beams of deuterium atoms. The source included a cooled nozzle, which acted as the anode and a cathode made of thoriated tungsten, fastened in a movable cooled holder in order to vary the anode-cathode spacing, which has a significant influence on the degree of dissociation of deuterium D_2 and the energy of the D atoms. With a diameter of 1.5 mm for the critical cross section of the nozzle, the optimum anode-cathode spacing was 0.1 mm. As in the case of the source described in Ref. 71, the arc was stabilized with a magnetic field of 0.1 T applied along the axis of the nozzle. At a voltage of 18–30 V the arc current was 130 A. The arc was struck with argon, which then was displaced by deuterium. The operating lifetime of the nozzle was ~50 h. With this device it was possible to generate beams of atomic deuterium with energies of 0.8 to 2.5 eV.

Arc sources are frequently used for creating metastable atoms and radicals. A simple device has been proposed in Ref. 74, in which a pulsed gasdynamic source is combined with an electric arc discharge. At the time that the valve is opened a mixture of gases containing H_2O, NH_3, CH_3CN, and C_2N_2 at a pressure of 3 to 4 atm is admitted into a Teflon chamber with built-in metal electrodes on which a potential of 1000 V is applied. A dc electric arc is struck in the entering mixture, which leads to the formation of beams of radicals OH, NH, CN, and C_2.

Gasdynamic sources with gas heating in an electric arc offer promise as a means of forming beams of atoms, radicals and metastable atoms and radicals. Their main drawback is the erosion of the electrodes, which contaminates the beams.

A gasdynamic source for the formation of atomic beams of xenon with an intensity above 10^{15} $cm^{-2}s^{-1}$ with the energy of the atoms above 1 eV has been described in Ref. 75. The gas is heated in a continuous optical discharge maintained in the region of the critical cross section of the nozzle by focused radiation of a cw CO_2 laser at a power of 70 W ($\lambda = 10.6$ μm). According to the calculations of these investigators the operation of this source provides beams of atomic helium with a velocity up to 10 km/s; however, in this case a laser with the high power of 1.3 kW is required. A diagram of this source is shown in Fig. 7.

Anderson *et al.*[35] have discussed the gasdynamic means of obtaining molecular beams from mixtures of gases. If the mixture consists of light and heavy components with a low relative concentration of the heavy component, then in the gasdynamic beam that is obtained the heavy particles move with a velocity corresponding to the average mass. In this way it is possible to obtain heavy particles of higher energy than in the case of a beam containing only the pure heavy gas. Moreover, since the heavy particles at the entrance to the skimmer have high Mach numbers, they are focused on the axis of the gasdynamic source, with the intensity of the beam of heavy particles exceeding the intensity of the effusion beam by a factor of

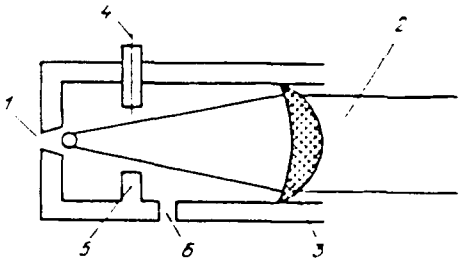

FIG. 7. Gasdynamic source with gas heated in an optical discharge. *1*) nozzle; *2*) laser beam; *3*) lens; *4*) high-voltage electrode; *5*) grounded electrode; *6*) feed line for admitting the gas.

10 to 100. For example, measurements by Becker and Henkes[76] have shown that the velocity of argon atoms in a beam formed of an argon-hydrogen mixture is of the order of the mean-mass velocity. In investigations with a working mixture of hydrogen with 1% argon at room temperature[77] it was observed that the velocity of the argon atoms reached 2100 m/s, corresponding to approximately 1 eV. The measured argon concentration in the beam was about 40%. Hydrogen with an admixture of nitrogen was used in the work reported in Ref. 78 and it was found that the nitrogen concentration increases near the axis of the beam when a detached shock wave is set up ahead of the skimmer. If the shock wave becomes attached or is "swallowed", then the composition of the beam corresponds to that of the mixture in the nozzle chamber. A gasdynamic source has been reported[79] in which hydrogen with a 0.15% admixture of xenon was used to produce a xenon beam with a translational energy of 7.2–13 eV at a mixture temperature of 460–1100 K in the chamber. A beam of xenon was produced in a similar way in the work reported in Ref. 33, in which the translational energy reached 37.5 eV at a temperature of 3000 K in the nozzle chamber.

With the use of the gasdynamic method it is possible to form beams of the liquid[34] or the solid phase. Sosnowski *et al.*[80] have described the design of a gasdynamic source of a gallium beam. This source has a two-filament electron gun used for controlled heating the graphite crucible containing the working material (Ga). A multigrid electron trap removes impurity ions and the electron background from the beam. The beams produced by this source contain accelerated clusters in addition to Ga atoms. A different type of source of beams of atoms and clusters, based on the evaporation of material by laser radiation, has been developed by Smalley.[81] A beam of high-intensity radiation from a pulsed laser is focused on a rod of the material. In the interaction of the laser radiation a small amount of the material is evaporated into a flux of an inert carrier gas, in which the vapor partially condenses into clusters. The mixture formed in this way then expands into a vacuum. The region of heating is limited to a small area of the target, so that thermal shields and cooling are not required for normal functioning of the source. The use of a pulsed source of the carrier gas beam allows one to use a pump of moderate throughput. Tembruell and Lubman[83] have improved the

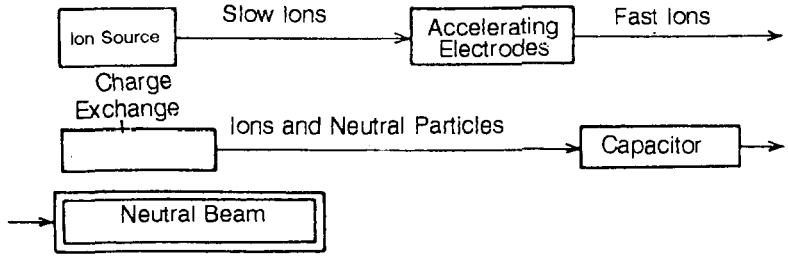

FIG. 8. Block diagram of device of obtaining a high-energy beam of neutral particles.

laser evaporation source by providing it with a cavity of a size chosen so as to minimize the interaction the plasma cloud with the walls, reduce the accumulation of material deposited on the walls, and optimize the transfer of heat from the inert gas to the walls of the cavity. With the use of a fast-acting "current loop" valve Maruyama *et al.*[64] were able to obtain a high velocity in the carrier gas at the time of the laser pulse for the acceleration of clusters to the final velocity of the supersonic beam. Those investigators believed that this source could be used for investigations of large biomolocules by the method of laser evaporation.[83–85]

A device for the formation of beams of aluminum dimers by laser evaporation[86] also had an evaporation cavity. Those investigators[86] note that the sudden expansion of the channel in the evaporation region causes enrichment of the beam in aluminum dimers. To improve the stability of the characteristics of the beams, the evaporation source, fashioned in the form of a rod, is rotated so that each pulse of laser radiation will interact with a fresh aluminum surface.

The method of laser evaporation is a promising means of obtaining beams of atoms and clusters of refractory metals. It is clear that in connection with the rising interest in the structure of clusters (e.g., Ref. 87), devices such as those described above will be extensively developed.

After the discussion of effusion and gasdynamic sources of molecular beams it is worth while to make a comparative analysis of them.

1. Effusion sources form molecular beams of low intensity ($\sim 10^{16}$ $sr^{-1}s^{-1}$), whereas continuous gasdynamic beams reach intensities up to $\sim 10^{21}$ $sr^{-1}s^{-1}$ (Ref. 33), and pulsed sources go as high as 10^{23} $sr^{-1}s^{-1}$ (Ref. 52).

2. The energy of the particles of an effusion beam is on the average equal to $kT/2$. Thus at a source temperature of 3000 K it is possible with velocity selectors to separate out particles in the tail of the Maxwell–Boltzmann distribution, with a maximum useful energy of 0.5 eV (Ref. 35). The intensities corresponding to the highest energy of the particles are extremely low. The energies of the particles of gasdynamic beams, as indicated above, can substantially exceed 1 eV.

3. For the same state of the gas in the chambers of gasdynamic and effusion sources, the width of the kinetic energy range in the gasdynamic source is narrower. This is a consequence of the adiabatic cooling of the gas in the gasdynamic sources. For example, in an effusion beam only about 11% of the particles have velocities within a 5% interval near the mean. In a gasdynamic beam with a Mach number of 10, about 47% of the molecules have a velocity inside a 5% interval near the mean.[35]

4. In effusion beams the state of the particles is identical with their state in the source chamber and equilibrium exists among all the degrees of freedom. In gasdynamic beams the energy distribution function of the internal degrees of freedom of the particles and the composition of the beam are in general not in equilibrium and must be measured in every instance.[34]

5. Gasdynamic sources of molecular beams require much more capacity in the pumping system than do effusion sources. This results in a complicated design and a high cost for the gasdynamic sources.

5. SOURCES BASED ON CHARGE-TRANSFER WITH ACCELERATED IONS

In recent years interest has arisen in the study of atom-molecule collisions by the method of low-angle collisions of beams of high-energy particles (of the order of 100 eV and above), during which the short-range forces of interaction of the particles are studied. Investigations of this type provide information for the description of the behavior of matter in extremal conditions.[88] Conventional gasdynamic sources cannot be used in experiments on high-energy scattering, since they do not provide beams of particles with energies in the required range.

There is a completely different approach to solving the problem of obtaining beams of high-energy particles, in which a neutral beam is produced by charge exchange of electrostatically accelerated ions. This method has been described in detail in Ref. 89. A block diagram of the method is shown in Fig. 8.

Amdur *et al.*[90] have described a molecular beam source of this type. The principal part of the source is shown in Fig. 9. A low-voltage arc is struck between the grounded oxide-coated filament *1* and the copper anode *2* at a pressure of ~ 0.1 torr. The copper cathode *3*, with a negative potential of from 0 to 100 V applied to it extracts the ions from the discharge. The ions, drifting in the direction of the aperture in the lower part of the cathode, are focused with a hemispherical grid onto an aluminum accelerating electrode *4*, whose negative potential can be varied from 150 to 2000 V. Some of the positive ions pass through an aperture of diameter 0.5 mm in the electrode, and as a result of charge exchange are converted into fast neutral particles. The ions are deflected by the electric field

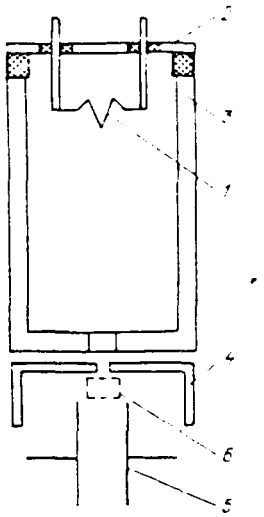

FIG. 9. Device for preparing a high-energy beam of neutral particles. *1*) grounded filament; *2*) copper anode; *3*) copper cathode; *4*) accelerating electrode; *5*) capacitor; *6*) region of charge exchange of the fast ion beam.

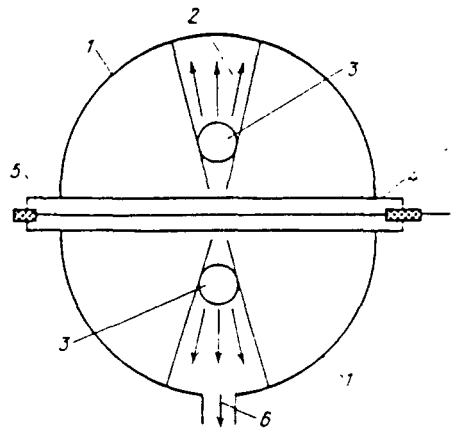

FIG. 10. Diagram of source with saddle field. *1*) Cathode; *2*) ions; *3*) oscillating electrons; *4*) shield electrodes; *5*) anode; *6*) beam of ions and atoms.

of the capacitor *5* with a potential difference of about 1000 V on the plates.

Amdur and Miller[91] have described an improved device with a different ion source. In this ion source the gas at a pressure of $\sim 10^{-3}$ torr is fed into a copper cylinder with a diameter of 12.7 mm and a length of 76 mm, with a magnetic field of a few hundred gauss applied along its axis. Electrons emitted by a tungsten filament move along the axis of the cylinder in helical trajectories under the action of this field and are reflected from the ends of the cylinder because of the negative potential applied to the ends, and in this way the path length of the electrons increases, with a consequent increase in the ionization probability. It is thus possible to maintain an arc at a considerably lower pressure than without the magnetic field. The ions that are formed are extracted from the discharge through one of the ends of the cylinder by means of the electrode that is used for reflecting the electrons, and they are accelerated to the desired energy in the low-pressure region.

The method based on charge exchange with fast ions allows one in principle to boost the final energy of the particles of a beam to any desired value. However, because of the spreading of the beam induced by the space charge, the beam intensity rapidly falls off as the energy of the beam is reduced. Therefore in the majority of experiments the particle energy in the beam has been above 100 eV.

A device for obtaining molecular beams has been developed[92,93] for which the particle energy can be varied in the range 5 to 1000 eV. The nitrogen molecules are ionized in the device by electron impact, and the ions are accelerated and focused into a beam. The beam is neutralized by charge exchange. The beam intensity in this device is from $10^8\ s^{-1}$ at low energies to $10^{11}\ s^{-1}$ at high energies. The energy width of the beam is less than 0.5 eV. However, such a low intensity in the molecular beam is insufficient for carrying out most experiments, since a highly sensitive detection apparatus is required.

Franks[94,95] has reported the development of a source for a beam of neutral particles with an electric field that has a saddle point. In this source the electrons are set into oscillation between two sectors of the cathode by a dc electric field. A diagram of this source is shown in Fig. 10. The electrons that are generated in one sector of the cathode pass the region of the anode in the direction of the other sector; they are slowed, turned around, and caused to oscillate in the potential field around the central saddle point. Therefore, the electrons travel over a long trajectory before they are captured by the anode. If a gas is introduced, the probability of its ionization is enhanced because of the long electron path. The positive ions formed in this discharge travel radially in the direction of the cathode and exit through the aperture in the latter from the source region along straight trajectories. The source[94] generates beams of particles with energies 2.5–8.5 keV with a potential of 3–10 kV on the anode.

The mechanism for the formation of the beam in sources with saddle-shaped fields by itself makes it possible to obtain practically neutral beams without neutralization of the beam outside the region of the source by some means. Unlike the sources described previously, where the ions are formed in the plasma and are extracted by an external field, in a source with a saddle field the internal electric field both provides the energy to the ionizing electrons and also impels the ions along straight trajectories. In this case any mechanism of neutralization of the accelerated ions that happens to operate in the source region results in the formation of a neutral beam of particles. An analysis of an argon beam[94] showed that it contained both ions and atoms. By means of an electrode with a potential of +300 V, located 2 cm from the cathode the concentration of atoms in the beam was reduced to 5%, and conversely, with a careful shielding of the region of the cathode to decrease the internal field at the cathode the ion component could be reduced to less than 1%. Neutraliza-

tion can occur as a result of charge exchange or by capture of an electron by the ion. Franks[94] believes that the neutralization is mainly due to electron capture, because when an electric field sufficient to remove the electrons from the vicinity of the cathode is present the beam can be made almost entirely ionic.

Among the advantages of this method are its universality from the point of view of obtaining beams of various particles (atoms, molecules, radicals) and the wide range of particle energy. A serious drawback of this means of generating beams is the low intensity of the beams for particle energies lower than 100 eV. However, the possibility of using commercially available technology makes this method widely used.[88]

6. MECHANICAL SOURCES

In 1948 Marshall *et al.*[96] proposed a simple method of forming molecular beams, based on the acceleration of gas molecules by collision with the blades of a rapidly rotating rotor. In order that the molecules acquire as high a velocity as possible it is necessary to obtain a high rate of rotation of the rotor. A rapidly rotating object is subject to destruction, with the maximum rate of rotation of the object depending only on the shape of the object and the material of which it is made. It was shown[96] that the optimum form of the object is a relatively thin rotor, with the cross section of the blades decreasing with the distance r from the axis of rotation as $\exp(-ar^2)$. The velocity of the tips of the metal rotor blades used by Bull and Moon[97] for accelerating a beam of CCl_4 was 700 m/s. By the use of plastic materials, strengthened by graphite fibers, a rotor with a diameter of 15 cm reached a tip velocity of 2 km/s.[98] The velocity of the molecular beams produced by this rotor exceeded 2 km/s, which corresponds to energies of 0.42 eV for Ne and 0.84 eV for Ar. Nutt *et al.*[99] have shown that for a rotor of diameter 15 cm the duration of a pulse detected at a distance of 30 cm is $\sim 20\ \mu$s. At a pressure of 10^{-4} torr in the rotor chamber each pulse consists of 10^9–10^{10} molecules. Those investigators[99] believe that an increase in the gas concentration in the region of the rotor blades by means of a multichannel effusion source of a molecular beam would increase by a factor of 1000 the intensity of the molecular beam produced by this mechanical source.

It has been pointed out that such a molecular beam source can be improved in the following ways: In the first method the working material is affixed to the blades of the rotor, and as the temperature of the rotor increases the evaporating particles of the working material form a molecular beam; in the second, the working gas, introduced through an aperture in the hub of the rotor, is brought to the tips of the blades through special apertures.

Despite the complexity of making the device, this method of generating molecular beams will probably be further developed, since it has a number of advantages: a broad range of molecule velocities in the beam and a high pulse frequency.[1] There exists doubt, however, about the possibility of obtaining beams of chemically active particles by means of a mechanical source.

7. GENERATION OF BEAMS OF ATOMIC OXYGEN

The methods described above are universal: they can provide beams composed of a variety of atoms and molecules. There also exist special methods by which one can obtain beams of molecules (or atoms) of a particular type. For example, Friichtenicht[100] has produced beams of fast fluorine atoms (1–10 eV) by the irradiation of a thin (~ 1 μm) film of BiF_3 with a focused beam of a ruby laser. As shown in Ref. 100, the beam of F atoms is characterized by a broad particle energy range (up to 14 eV). At a distance of 0.6 m from the focus the intensity of the flux of F atoms with an energy ~ 5 eV is $\sim 10^7$ cm^{-2}s^{-1}. The energy of the atoms in the beam can be controlled by changing the energy density of the laser radiation at the focus of the lens.

It has been proposed that the sputtering of solid samples by fast particles might be used to form beams of potassium atoms.[101] In the action of a focused beam of 6 keV A^+ ions on the potassium sample (cross-sectional area of the laser beam ~ 0.2 mm^2) a beam of potassium atoms was generated with an energy of 0.2–45 eV. The maximum sputtering rate was observed for an angle of incidence of the ion beam of 70°. By means of a velocity selector it was possible to select potassium beams of intensity $4.7 \cdot 10^8$ cm^{-2}s^{-1} with a velocity of 1660 m/s, of intensity $9.5 \cdot 10^8$ cm^{-2}s^{-1} with a velocity of 3700 m/s, and of intensity $5 \cdot 10^8$ cm^{-2}s^{-1} with a velocity of 9660 m/s.

Of particular interest in physico-chemical investigations (including studies of the gas-surface interaction) are intense beams of atomic oxygen with energies from a fraction of an electron volt to several electron volts. Below, methods of obtaining such beams are described.

7.1. Thermal dissociation of oxygen

The authors of Ref. 102 have produced atomic oxygen by means of thermal dissociation of pure oxygen O_2, at a pressure of ~ 1 torr in an iridium oven heated to 2100 K. A degree of dissociation of 6 to 8% and a velocity of the O atoms up to 1.5 km/s were obtained with this source.[102] In Ref. 103 a new type of oven for the dissociation of oxygen has been proposed, with which a beam of particles of density $\sim 10^{11}$ cm^{-3} has been produced with a degree of O_2 dissociation exceeding 70%. This oven[103] is a narrow iridium tube, one end of which is heated to 2150 K by a beam of electrons emitted from an iridium cathode coated with thorium oxide. A small-diameter tube placed in an oxygen reservoir made it possible to obtain a directed beam of atoms if the mean free path of the particles near the heated end of the tube was greater than the diameter. In order to keep the oxygen molecules out of the atomic beam emanating from the heated part of the tube, its central part was shielded with a tab of metal. The authors of Ref. 103 state that this oven design is distinguished by its long lifetime, which is important for sources of beams of chemically active particles.

7.2. Dissociation of oxygen in rf and microwave discharges

Sibener *et al.*[104] have developed a gasdynamic source of beams of atomic oxygen, in which the dissociation of the

O_2 molecules occurs in a microwave discharge in the nozzle chamber. With this source[104] beams of oxygen atoms have been obtained with translational energies of 0.14–0.5 eV and an intensity above 10^{18} $sr^{-1}s^{-1}$. These investigators[104] note that when the working gas is helium and oxygen the beam contains $O(^3P)$ and $O(^1D)$ oxygen atoms, while with a mixture of oxygen and argon the beam contains only $O(^3P)$ oxygen atoms. In the work reported in Ref. 105, Siebener *et al.* supplied to the source a mixture of oxygen and helium (1:9), with a pressure in the chamber of 110 torr and a discharge power of 130 W. The velocity of the oxygen atoms in the beam was 1.95 km/s, which corresponds to a translational energy of 0.3 eV for the oxygen. Buss *et al.*[106] used the apparatus of Ref. 104 to obtain a beam of excited oxygen atoms with a velocity of 2.37 km/s (energy 0.44 eV). With an apparatus similar to the one used in the work of Ref. 11 a beam of oxygen atoms was obtained with a translational energy of 0.7 eV.

The authors of Ref. 108 obtained a 35% oxygen dissociation in a microwave discharge with a power of 100 W. In these experiments a mixture of oxygen and helium (15% O_2) was used. With a pressure in the nozzle chamber of 80 torr the velocity of the O atoms in the beam was 2.2 km/s (0.38 eV).

The gasdynamic installation "Surfatron" with a surface microwave discharge in oxygen has provided an atomic beam of oxygen with an intensity of 10^{17}–10^{18} $cm^{-2}s^{-1}$ with an energy of 1.5–5 eV in the beam of O atoms.[109] However the beam contained a considerable amount of excited atoms and products of erosion of the nozzle.

7.3. Dissociation of oxygen in a dc electric arc

Silver *et al.*[110] have described a source of atomic oxygen in which the dissociation of O_2 occurs when a jet of oxygen is injected into a helium (or argon) flow heated in a dc plasmatron. The degree of dissociation of oxygen in the mixture of argon and oxygen (2% O_2) at a power of 9 kW fed to the arc was close to unity. At a pressure close to atmospheric in the nozzle chamber the intensity of the oxygen beam was $3 \cdot 10^{17}$ $sr^{-1}s^{-1}$. The velocity of the oxygen atoms in the beam was 1.5–4 km/s, which corresponds to energies of 0.2–1.3 eV. The power of the dc arc, which could be varied in the range 4 to 12 kV, and also the concentration of oxygen in the mixture with the gas carrier, had a significant effect on the degree of dissociation of oxygen. When a mixture of argon with a 2% admixture of oxygen was used the degree of dissociation of oxygen was close to unity with a power of 9 kW to the arc. This high degree of dissociation was achieved because the residence time of the oxygen in the nozzle chamber (0.15–0.5 μs) was long enough for the dissociation of the O_2 molecules, but too short for the recombination of the O atoms.

7.4. Dissociation of oxygen by an optical discharge

In the work reported by Cross *et al.*[111] a gasdynamic source of beams with heating of the gas by a continuous optical discharge[75] was used to create beams of atomic oxygen. A mixture of oxygen and argon (1:1) was used as the working mixture. The continuous optical discharge in the region of the critical cross section of the nozzle was maintained with the use of a focused CO_2 laser beam with a power of 500 W, which provided a high degree of dissociation of oxygen and heated the oxygen atoms to $T = 8000$ K. At the exit from the nozzle a beam of oxygen atoms was obtained with an intensity from 10^{16} to 10^{17} $cm^{-2}s^{-1}$ and a velocity of the atoms of 3 to 4 km/s.

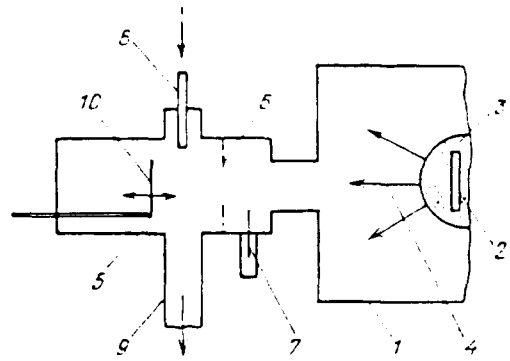

FIG. 11. Preparation of a beam of oxygen atoms from the peripheral plasma of the tokamak ACT-1. *1*) Chamber of the tokamak ACT-1; *2*) limiter; *3*) peripheral plasma *4*) beam of atomic oxygen; *5*) drift chamber; *6*) diaphragm; *7*) valve; *8*) feedline for admitting the gas; *9*) pumpout line; *10*) movable target.

In Ref. 9 a pulsed source of fast oxygen atoms based on the action of a pulsed CO_2 laser on oxygen admitted to the expanding part of the nozzle was developed for the study of the processes of destruction of various materials by atomic oxygen. During the experiment, which was described in Ref. 9, 10^{-4} g of oxygen was admitted to the expanding part of the nozzle through a pulsed valve (100 μs). The gas entering the nozzle was ionized by a laser pulse ($\lambda = 10.6$ μm, pulse energy 5 J, pulse length 2.5 μs). The high-pressure plasma formed in this way underwent expansion accompanied by the formation of a shock wave which propagated in the direction of the exit end of the nozzle and heated the gas within the nozzle, forming a high-temperature plasma. By virtue of the special construction of the nozzle electron-ion recombination occurred in the plasma. There was virtually no recombination of oxygen atoms with the formation of O_2. As the gas expanded the kinetic energy of the oxygen atoms increased. According to Ref. 9, more than 10^{18} oxygen atoms with a kinetic energy of 5 eV were formed in a single pulse.

7.5. Generation of oxygen atoms by neutralization of the peripheral plasma of a tokamak

For the simulation of the conditions occurring in the impact of the flux of the ionosphere on the surface of a spacecraft in orbital motion at altitudes of 150 to 300 km, Langer *et al.*[112] proposed a method in which the peripheral plasma of a tokamak is reflected and neutralized in its interaction with the surface of a metal limiter. Figure 11 shows a diagram of the experiment carried out on the tok-

amak ACT-1 (Ref. 112). The flux of neutral oxygen atoms reflected from the cooled limiter, a gold plate with a potential of 0 to 150 V relative to the plasma, entered a differentially pumped chamber (10^{-4} Pa) and bombarded the target positioned there. By changing the potential of the limiter it was possible to control the energy of the neutralized atoms. The intensity of the oxygen atoms with an energy of 5 eV bombarding a target located at a distance of 1 m was $5 \cdot 10^{14}$ $cm^{-2}s^{-1}$. An admixture of the gases NO, CO, N_2 or He could be admitted into the drift chamber. The investigators were able to observe surface fluorescence at the target, but its spectrum differed from the emission spectrum from the surface of the space shuttle[8] and corresponded to the gas-discharge emission by oxygen with the corresponding admixtures.

7.6. Sputtering sources of atomic oxygen

Ferrieri *et al.*[113] have described a novel method of obtaining atomic oxygen by ion sputtering the surface of Ta_2O_5. A beam of argon ions with an energy of 40 keV and a current of 15 μa was incident on the target at an angle of 30° to the surface normal. A quadrupole residual gas analyzer was used to study the kinetic energy distribution of the oxygen atoms emerging at angles between $+60°$ and $-60°$ to the normal. These distributions were similar in shape, with a maximum located at ~ 7 eV, but stretching out beyond 20 eV. The yield of atomic oxygen by sputtering (the number of atoms per incident ion) was determined quantitatively by the yield of water as the product of the reaction of O with n-butane by means of gas chromatography in which the thermal conductivity was used to detect the products. The results of the measurements showed that in the case of fresh Ta_2O_5 the yield of atomic oxygen reached 72 atoms per ion, which gives a beam of $\sim 10^{15}$ $cm^{-2}s^{-1}$ from the surface of the target. It is possible that by increasing the mass and energy of the ions of the incident beam or by the use of other oxides one might obtain higher flux densities of atomic oxygen.

7.7. Dissociation of oxygen behind an intense shock wave

A description has been published in Refs. 114 and 115 of a source of a beam of atomic oxygen by pulse-periodic action based on an electromagnetic shock tube with a skimmer at the end. The electromagnetic shock tube was used as the means of obtaining a gasdynamic flux with a high enthalpy and was fabricated in the manner recommended in Ref. 116.

A diagram of the apparatus is shown in Fig. 12. The shock tube consists of a conical discharge chamber connected with a cylindrical working section. A microsecond spark discharge is struck in the discharge chamber between the annular and the central electrode (discharge energy ~ 1 kJ), and as a result an intense shock wave is formed in the gas filling the working chamber. The operating section of the shock tube is connected to a damping cylinder with a skimmer in the end of it. The skimmer has the form of a long cone with an apex angle of 60° and an entrance aperture with a diameter of 1 mm, comparable with the mean

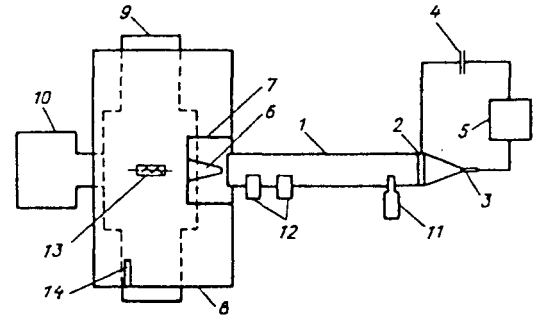

FIG. 12. Diagram of a source of an intense beam of atomic oxygen. *1*) electromagnetic shock wave; *2*) ring electrode; *3*) central electrode; *4*) capacitor bank; *5*) ignitron discharge; *6*) skimmer; *7*) damping volume; *8*) vacuum chamber; *9*) turbomolecular pump; *10*) forepump; *11*) movable-electrode tube; *12*) piezoelectric pressure gauge; *13*) ionization density gauge; *14*) ionization vacuum gauge.

free path of the particles in the accompanying flow behind the shock wave. The lip at the vertex of the skimmer is sharpened so as to separate the molecular beam from the accompanying flow without partial slowing of the flow. The expansion of the flow in the damping cylinder reduces the gasdynamic perturbations associated with the reflection of the shock wave from the end and prevents the approach of the gasdynamic perturbations towards the opening of the skimmer during the time of steady-state conditions behind the incident shock wave. The molecular beam propagates in a vacuum chamber that is continuously pumped by a turbomolecular pump. The pulse-periodic operation of the shock tube is achieved with steady-state feeding of the gas into the working section by means of a needle valve. The necessary pressure drop between the working section and the vacuum chamber is maintained at the entrance aperture of the skimmer. The electrical and the vacuum-gas designs of the apparatus were calculated for a pulse repetition rate up to 5 Hz. With air as the working gas a molecular beam was obtained with an intensity up to 10^{18} $cm^{-2}s^{-1}$, with the translational energy of the oxygen atoms reaching 5 eV. The concentration of atomic oxygen in the beam obtained from the air reaches 30%, and is therefore of interest in use as a source for studying the mechanisms of chemical reactions with the participation of fast oxygen atoms.[10] In pulse-periodic operation the source provides an accumulated irradiation dose of 10^{18} cm^{-2} to the sample surface in a time of 1 hour. It is of interest to apply the source to a laboratory simulation of the interaction of an impinging ionosphere flux with the surface of spacecraft.[8]

7.8. Source of atomic oxygen beams based on the neutralization of $O^-(^2P)$ ions by photodetachment of electrons

The source of oxygen atom beams described in Ref. 107 is based on the neutralization of pre-accelerated $O^-(^2P)$ ions by photodetachment of an electron. The O^- ions are formed by dissociative attachment to NO of electrons emitted by a tungsten filament. Then the ions and the

electrons are accelerated to the required energy (5 eV) by an electric field. A static magnetic field of 6 T directed along the axis of the beam is used to prevent the expansion of the beam of charged particles caused by the Coulomb forces of repulsion. The ions and the electrons are separated by an electric field perpendicular to the axis of the beam. The radiation of an argon-ion laser, reflected by a system of mirrors, intersects the trajectory of the ion beam many times, interacting with the $O^-(^2P)$ ions to form oxygen atoms in the ground state. With a laser power of 20 W, 100 intersections of the beam with the laser beam, and an ion kinetic energy of 5 eV, the efficiency of electron detachment was about 15%. To obtain a beam of oxygen atoms one can use a perpendicular electric field deflecting the O^- ions, or a target charged negatively to reflect the ions. With the source of Ref. 107 one can form a beam of oxygen atoms with an angular divergence of 20° and an atom energy of 5 eV. The ion current for these conditions was $\sim 5\ \mu$A and the efficiency of electron detachment was 15%. The data reported permit an estimate of the intensity of a beam produced by the device described in Ref. 107. It is easy to show that the intensity of the beam was $2 \cdot 10^{12}$ s^{-1}, which is four orders of magnitude higher than the intensity of beams of atoms with the same kinetic energy and obtained by the source based on the charge exchange with ions.[92,93]

8. CONCLUSIONS

The method invented in 1911 by Dunoyer[14,15] for producing molecular beams has proved to be extremely productive in science and technology. The method allows one to make precise measurements of the characteristics of nuclei, atoms, and molecules.[24] The development of gasdynamic sources,[30] which provide beams with intensities far above those of effusion sources, was an important step in the development of the method. The low temperatures that are relatively easy to achieve in gasdynamic molecular beams, have made it possible to carry out accurate experiments in the field of molecular spectroscopy.[117,118] The broad range of kinetic energies of particles of gasdynamic beams, plus the narrow velocity distribution functions of the atoms and molecules in the beams combination with the high intensities of the beams make gasdynamic beams an important means of studying the scattering of particles at solid surfaces[117] and the mechanism of elementary chemical reactions in the gas phase.[1]

Sources of molecular beams based on charge-exchange of rapidly moving ions are widely used in the investigations of atom-molecule collisions by the small-angle scattering of beams of particles, in which are studied the short-range forces of interaction of the particles, inelastic molecular transitions, and nonadiabatic electronic transitions. The information obtained in the experiments on high-energy scattering is the basis for the description of the behavior of matter at high temperatures and ultrahigh compression.[88]

In addition to the conventional sources of molecular beams, new ones have appeared: mechanical sources,[96] the method of sputtering a target,[101] and the method of laser evaporation.[100] The method of mechanical acceleration of a beam, while not yet in widespread use, will probably be improved and used in laboratory experiments, since it has an important advantage—the simplicity of controlling the velocity of the particles. An interesting suggestion is that of Nutt *et al.*[99] to use multichannel effusion sources for increasing the concentration of the gas near the tips of the rotor blades so as to increase the intensity of the beam of mechanically accelerated particles. The use of sources based on the sputtering of solid surfaces by beams of fast ions is hindered by the fact that the beams of this sort have a broad angular divergence and a broad range of particle energy. However, the use of this type of source is of interest as a method of applying coatings and making epitaxial films. The method of laser evaporation even now is widely used in the laboratory as a means of forming beams of clusters and atoms of refractory metals, as well as a method of generating beams of macromolecules and biomolecules.

In connection with the rising interest in the interaction between solid surfaces and fast chemically active particles with an energy comparable to the energies of the chemical bonds, we can expect an increase in the number of investigations into the development of new sources and the improvement of presently existing sources of beams of such particles. In particular, the necessity of studies of the oxidation-induced destruction of materials exposed to the action of fast beams of atomic oxygen is evident from observations of the destruction of coating materials of spacecraft flying in low, near-Earth orbits, and stimulates the interest of scientists in the development of effective sources of fast beams of atomic oxygen. As this review has shown, there exist at present a large number of different and very promising approaches to the solution of this problem.

We believe that this review has basically covered both the historical aspects of the development of the methods of generating molecular beams, and has described their present-day state. Particular attention was focused on the methods of forming fast intense beams of atomic oxygen, for which interest has increased in recent years.

[1] L. Yu. Rusin, *Kinetics and Catalysis. Progress in Science and Technology* [in Russian], VINITI, Academy of Sciences of the USSR, Vol. 18 (1988), p. 109.
[2] D. F. Padowitz and S. J. Sibener, J. Vac. Sci. Technol. A **9**, 2289 (1991).
[3] C. R. Arumainayagam, M. C. McMaster, and R. J. Madix, J. Vac. Sci. Technol. A **9**, 1581 (1991).
[4] M. P. D'Evelyn, A. V. Hamza, G. E. Gdowski, and R. J. Madix, Surf. Sci. **167**, 451 (1986).
[5] A. Boschetti, A. Cagol, C. Corragi, R. Jacobs, M. Mazzola, and S. Iannotta, Chem. Phys. **163**, 179 (1992).
[6] H. Vach, J. Häger, and H. Walter, Chem. Phys. Lett. **133**, 279 (1987).
[7] G. D. Billing, Computer Phys. Rep. **12**, 383 (1990).
[8] H. B. Garret, A. Chutjian, and S. B. Gabriel, J. Spacecraft Rockets **25**, 321 (1988).
[9] G. E. Caledonia, R. H. Krech, and B. D. Green, AIAA J. **25**, 59 (1987).
[10] V. S. Voitsenya, S. K. Guzhova, and V. I. Titov, *The Action of a Low-Temperature Plasma and Electromagnetic Radiation on Materials* [in Russian], Énergoatomizdat, Moscow (1991).
[11] J. R. Engstrom, D. J. Bonser, M. M. Nelson, and T. Engel, Surf. Sci. **256**, 317 (1991).
[12] R. J. Madix and A. A. Susu, Surf. Sci. **20**, 377 (1970).
[13] M. A. Herman and H. Sitter, *Molecular Beam Epitaxy. Fundamentals*

and Current Status. Springer Series in Materials Science, Vol. 7 (1989).
[14] L. Dunoyer, C. R. Acad. Sci. (Paris) **152**, 592 (1911).
[15] L. Dunoyer, Le Radium **8**, 142 (1911).
[16] V. S. Troitskii, Zh. Eksp. Teor. Fiz. **41**, 389 (1961) [Sov. Phys. Usp. **14**, 281 (1961)].
[17] H. Lew, Phys. Rev. **76**, 1086 (1949).
[18] N. I. Osipov, Prib. Tekh. Eksp. No. 5, 199 (1984) [Instrum. Exp. Tech. (USSR) **27**, 1265 (1984)].
[19] V. A. Pribytkov, O. I. Matveev, and A. K. Dubrova, Prib. Tekh. Eksp. No. 3, 218 (1987).
[20] J. M. B. Kellog, I. I. Rabi, and J. R. Zacharias, Phys. Rev. **50**, 472 (1936).
[21] L. Davis, B. T. Feld, C. W. Zabel, and J. R. Zacharias, Phys. Rev. **76**, 1076 (1949).
[22] D. E. Nagle, R. S. Julian, and J. R. Zacharias, Phys. Rev. **72**, 971 (1947).
[23] K. F. Smith, *Molecular Beams* [Russian Translation], Fizmatgiz, Moscow (1959).
[24] N. F. Ramsey, *Molecular Beams*, Clarendon Press, Oxford (1956).
[25] J. G. King and J. R. Zacharias, Adv. Electron and Electron Phys. **8**, 1 (1956).
[26] Y. Ota, *Thin Solid Films*, **106**, 3 (1983).
[27] Y. Ota, J. Electrochem. Soc. **124**, 1795 (1977).
[28] J. T. Cheung and J. Madden, J. Vac. Sci. Technol. B **5**, 705 (1987).
[29] J. T. Cheung, G. Niizawa, J. Moyle, N. P. Ong, B. M. Paine, and T. Vreeland, Jr, J. Vac. Sci. Technol. A **4**, 2086 (1986).
[30] A. Kantrowitz and J. Grey, Rev. Sci. Instrum. **22**, 328 (1951).
[31] G. B. Kistiakowski and W. P. Slichter, Rev. Sci. Instrum. **22**, 333 (1951).
[32] E. W. Becker and K. Bier, Z. Naturforsch. A **9**, 975 (1954).
[33] R. Camparque, A. Lebehot, J. C. Lemonnier, D. Marettee, and J. Pebay, Proceedings of the 5th International Symposium on Molecular Beams, April 7–11, 1975, Nice, France (1975).
[34] M. L. Aleksandrov and Yu. S. Kusner, *Gasdynamic Molecular, Ion, and Cluster Beams* [in Russian], Nauka, Leningrad (1989).
[35] J. B. Anderson, R. P. Andres, and J. B. Fenn, Ad. At. Mol. Phy. **1**, 345 (1965).
[36] K. Bier and O. Hagema, in *Rarefied Gas Dynamics*, J. A. Laurmann (ed.), Vol 1, Academic Press, New York, (1963), p. 478.
[37] J. B. Fenn and J. B. Anderson, in *Rarefied Gas Dynamics*, J. H. de Leeuw (ed.), Academic Press, New York (1966), p. 311.
[38] J. B. Anderson, R. P. Andres, J. B. Fenn, and G. Maise, *ibid*, p. 106.
[39] V. H. Reis and J. B. Fenn, J. Chem. Phys. **39**, 3240 (1963).
[40] P. P. Wegener (ed.), *Molecular Beams and Low Density Gasdynamics*, Vol. 4, Dekker, New York (1974).
[41] U. Bossel, Entropie No. 42, 12 (1971).
[42] U. Bossel, Report No. AS-63-6, Aeronaut. Sci. Division. University of California, Berkeley (1968).
[43] G. A. Bird, Phys. Fluids **19**, 1486 (1976).
[44] U. Bossel, Deutsche Luft- und Raumfahrt Forschunbsbericht No. 74–28 (1974).
[45] B. N. Kozlov and V. G. Shchebelin, Zh. Tekh. Fiz. **62**(1), 197 (1992) [Sov. Phys. Tech. Phys. **37**, 104 (1992)].
[46] E. W. Becker, K. Bier, and W. Henkes, Z. Phys. **146**, 333 (1956).
[47] E. W. Becker, R. Klingelhöfer, and P. Lohse, Z. Naturforsch. A **17**, 432 (1962).
[48] P. G. Bentley, Nature **190**, 432 (1961).
[49] W. Henkes, Z. Naturforsch. A **16**, 842 (1961).
[50] O. Hagena, Z. Angew. Phys. **16**, 183 (1963).
[51] K. Bier and O. Hagena, *Rarefied Gas Dynamics*, J. H. de Leeuw (ed.), Academic Press, New York (1966), p. 260.
[52] M. G. Liverman, S. M. Beck, D. L. Montes, and R. E. Smalley, J. Chem. Phys. **70**, 192 (1979).
[53] R. L. Beyer and M. D. Duncan, J. Chem. Phys. **74**, 2174 (1981).
[54] C. E. Otis and P. M. Johnson, Rev. Sci. Instrum **51**, 1128 (1980).
[55] W. Müller-Markgraf and M. J. Rossi, Rev. Sci. Instrum. **61**, 1217 (1990).
[56] J. P. Bucher, D. C. Douglass, P. Xia, and L. A. Bloomfield, Rev. Sci. Instrum. **61**, 2374 (1990).
[57] E. J. Corat and V. J. Trava-Airoldi, Rev. Sci. Instrum. **61**, 1068 (1990).
[58] D. Proch and T. Trickl, Rev. Sci. Instrum. **60**, 713 (1989).
[59] D. Marinescu, Rev. Sci. Instrum. **61**, 1749 (1990).
[60] A. Hershcovitch, A. Kronou, and T. O. Niinikoski, Rev. Sci. Instrum. **58**, 547 (1987).
[61] G. I. Dimov, Prib. Tekh. Eksp. No. 5, 168 (1968) [Instrum. Exp. Tech. (USSR) No. 4, 1193 (1968)].
[62] W. R. Gentry and C. F. Giese, Rev. Sci. Instrum. **49**, 595 (1978).
[63] W. R. Gentry, in *Atomic and Molecular Beam Methods*, G. Scoles (ed.), Oxford University Press, Oxford (1988).
[64] S. Maruyama, L. R. Anderson, and R. E. Smalley, Rev. Sci. Instrum. **61**, 3686 (1990).
[65] O. Cheshnovsky, K. J. Taylor, J. Conceicao, and R. E. Smalley, Phys. Rev. Lett. **64**, 1785 (1990).
[66] K. L. Saenger, J. Chem. Phys. **75**, 2467 (1981).
[67] G. T. Skinner, Phys. Fluids **4**, 1172 (1961).
[68] G. T. Skinner and B. H. Fetz, in *Rarefied Gas Dynamics*, J. H. de Leeuw (ed.), Academic Press, New York (1966), p. 536.
[69] N. Takahashi and K. Teshima, Thirteenth International Symposium on Rarefied Gas Dynamics, Novisibirsk, July 5–9, 1982, Abstracts, Vol. 1, p. 261.
[70] E. L. Knuth, Report No. 63-30, Department of Engineering, University of California at Los Angeles (1963).
[71] W. S. Young, W. E. Rodgers, and E. L. Knuth, Rev. Sci. Instrum. **40**, 1346 (1969).
[72] D. H. Winicur and E. L. Knuth, J. Chem. Phys. **46**, 4318 (1967).
[73] R. Götting, H. R. Mayne, and J. P. Toennies, J. Chem. Phys. **85**, 6396 (1986).
[74] R. Schlachta, G. Lask, S. H. Tsay, and V. E. Bondybey, Chem. Phys. **155**, 267 (1991).
[75] J. B. Cross and D. A. Cremers, Nucl. Instrum. Methods Phys. Res B **13**, 658 (1986).
[76] E. W. Becker and W. Henkes, Z. Phys. **146**, 320 (1956).
[77] R. Klingelhöfer and P. Lohse, Phys. Fluids **7**, 379 (1964).
[78] V. H. Reis and J. B. Fenn, J. Chem. Phys. **39**, 3240 (1963).
[79] V. M. Akimov, L. Yu. Rusin, and F. A. Tsyganov, Prib. Tekh. Eksp. No. 1, 164 (1991) [Instrum. Exp. Tech. (USSR) **34**, 166 (1991)].
[80] M. Sosnowski, S. Krommenhoek, J. Sheen, and R. H. Cornely, J. Vac. Sci. Technol. A **8**, 1458 (1990).
[81] R. E. Smalley, Laser Chem. **2**, 167 (1983).
[82] P. Milani and W. A. de Heer, Rev. Sci. Instrum. **61**, 1835 (1990).
[83] R. Tembruell and D. M. Lubman, Anal. Chem. **59**, 1003 (1987).
[84] J. R. Cable, M. J. Tubergen, and D. H. Levy, J. Amer. Chem. Soc. J. **110**, 7349 (1988).
[85] M. Karas, A. Ingendoh, U. Bahr, and F. Hillenkamp, Biomed. Environ. Mass Spectrom. **18**, 841 (1989).
[86] M. F. Cai, T. P. Dzugan, and V. E. Bondybey, Chem. Phys. Lett. **155**, 430 (1989).
[87] M. F. Cai, C. C. Carter, T. A. Miller, and V. E. Bondybey, Chem. Phys. **155**, 233 (1991).
[88] V. B. Leonas and I. D. Rodionov, Usp. Fiz. Nauk **146**, 7 (1985) [Sov. Phys. Usp. **28**, 332 (1985).
[89] I. Amdur and J. Jordan, "Elastic scattering of high-energy beams" [Russian translation], in *Research with Molecular Beams* [in Russian], MIr, Moscow (1969), p. 39.
[90] I. Amdur, J. E. Jordan, and S. O. Colgate, J. Chem. Phys. **34**, 1525 (1961).
[91] J. E. Jordan and I. Amdur, J. Chem. Phys. **46**, 165 (1967).
[92] N. G. Utterback and G. H. Miller, Rev. Sci. Instrum. **32**, 1101 (1961).
[93] N. G. Utterback and G. H. Miller, Phys. Rev. **124**, 1477 (1961).
[94] J. Franks, J. Vac. Sci. Technol. **16**, 181 (1979).
[95] J. Franks, Vacuum **34**, 259 (1984).
[96] D. G. Marshall, P. B. Moon, J. E. S. Robinson, and J. T. Stringer, J. Sci. Instrum. **25**, 348 (1948).
[97] T. H. Bull and P. B. Moon, Disc. Faraday Soc. **17**, 54 (1954).
[98] P. B. Moon and M. P. Ralls, Proc. R. Soc. London Ser. A **423**, 361 (1865).
[99] C. W. Nutt, T. J. Bale, P. Cosgrove, and M. J. Kirby, Proceedings of the Fifth International Symposium on Molecular Beams, April 7–11, 1975, Nice, France (1975).
[100] J. V. Friichtenicht, Rev. Sci. Instrum. **45**, 51 (1974).
[101] J. Politiek, P. K. Pol, J. Los, and P. K. Ikelaar, Rev. Sci. Instrum. **39**, 1147 (1968).
[102] J. Geddes, P. N. Clough, and P. L. Moore, J. Chem. Phys. **61**, 2145 (1974).
[103] B. van Zyl and M. W. Gealy, Rev. Sci. Instrum. **57**, 359 (1986).
[104] S. J. Sibener, R. J. Buss, C. Y. Ng, and Y. T. Lee, Rev. Sci. Instrum. **51**, 167 (1980).

[105]S. J. Sibener, R. J. Buss, P. Casavecchia, T. Hirooka, and Y. T. Lee, J. Chem. Phys. **72**, 4341 (1980).
[106]R. J. Buss, P. Casavecchia, T. Hirooka, S. J. Sibener, and Y. T. Lee, Chem. Phys. Lett. **82**, 386 (1981).
[107]O. J. Orient, A. Chutjian, and E. Murad, Phys. Rev. A **41**, 4106 (1990).
[108]P. A. Gorry, C. V. Nowikow, and R. Grice, Chem. Phys. Lett. **49**, 116 (1977).
[109]D. Morrison, R. C. Tennyson, and J. B. French, Fourth European Symposium on Spacecraft Materials in Space Environment, CERT. Sept. 6–9 1988, Toulouse, France (1988), pp. 435–452.
[110]J. A. Silver, A. Freedman, C. E. Kolb, A. Rahbee, and C. P. Dolan, Rev. Sci. Instrum. **53**, 1714 (1982).
[111]J. B. Cross, D. A. Cremers, and D. F. Tucker, AIAA paper No. 85-1068 (1988), p. 1.
[112]W. D. Langer, S. A. Cohen, D. M. Manos *et al.*, Geophys. Res. Lett. **13**, 337 (1986).
[113]R. A. Ferrieri and Y. Y. Chu, Rev. Sci. Instrum. **59**, 2177 (1988).
[114]V. M. Doroshenko, N. N. Kudryavtsev, and A. M. Sukhov, Eleventh All-Union Conference on the Dynamics of Rarefield Gases [in Russian], June 8–13, 1991. Abstracts. Leningrad (1991), p. 116.
[115]V. M. Doroshenko, N. N. Kudryavtsev, O. A. Mazyar, A. M. Sukhov, and O. V. Yatsenko, Preprint No. 8-340 [in Russian], Institute of High Temperature, Russian Academy of Sciences, Moscow (1992).
[116]R. W. Ziemer, ARS J. **29**, 642 (1950).
[117]J. B. Fenn, Thirteenth International Symposium of Rarefield Gas Dynamics, Novosibirsk, July 5–9, 1982, Abstracts, Vol. 1, p. 214.
[118]S. Svanberg, *Atomic and Molecular Spectroscopy. Basic Aspects and Practical Applications.* Springer Series on Atoms and Plasmas, Vol. 6 (1991).
[119]R. Campargue, J. Phys. Chem. **88**, 4466 (1984).

Translated by J. R. Anderson