## On the possibility of selecting molecules embedded in superfluid helium nanodroplets (clusters)

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Abstract. Methods for producing beams of nanometer-sized superfluid helium droplets and techniques for embedding single molecules and clusters in them open up many possibilities for spectroscopy, as well as providing insight into many physical and chemical processes occurring on the atomic and molecular level at extremely low temperatures ( $T \le 0.4$  K). In this paper, results of investigations into the possibility of selecting molecules embedded in superfluid helium nanodroplets (clusters) are reviewed. The method proposed starts with the selective vibrational excitation of cluster-embedded molecules by intense IR laser radiation (which greatly reduces the size of the excited clusters), followed by size-separating the clusters via scattering the cluster beam from a crossing molecular (atomic) beam. It is shown that molecules of a particular isotope (component) composition can be selected with this method. The advantages and disadvantages of the method are discussed. Methods for creating and doping helium nanodroplets and some other examples of their applications are also outlined.

### 1. Introduction

Many on-going experimental and theoretical investigations are carried out with the use of nanometer-sized superfluid helium nanodroplets (clusters) formed during gas outflow from cooled nozzle sources (see, for example, reviews [1-12]

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and recent publications [13-20]). The size of the clusters depends on the number N of helium atoms in a droplet and varies from dozens to  $N \sim 10^7$ . The available methods for producing beams of superfluid helium nanodroplets and embedding single molecules in these droplets make it possible to study molecular and cluster spectra in a new type of soft quantum matrix, namely, liquid superfluid helium [1-9, 12]. These methods are used not only to characterize spectra of single molecules and clusters at very low temperatures  $(T \sim 0.38 \text{ K})$  but also to gain an insight into many properties of superfluid helium nanodroplets themselves by spectroscopic techniques [5, 6, 9]. Moreover, experiments with helium nanodroplets open up many possibilities for investigations into various physical and chemical processes on the atomic and molecular levels at extremely low temperatures. By way of example, the method for embedding molecules in helium nanodroplets may be employed to produce long chains of definitely oriented polar molecules inside superfluid helium droplets [21]; this is of interest in the case of biologically important molecules. Also, helium nanodroplets may be used to realize high-spin states of alkali dimers and trimers [22, 23]. Unique conditions for cluster growth inside superfluid helium nanodroplets facilitate the production of high-energy isomers, such as cyclic water hexamers (tiny ice pieces) [24, 25]. Also evidenced were chemical reactions proceeding inside helium nanodroplets at very low temperatures [26] and orientation effects occurring during interaction between helium nanodroplets and molecules [27]. We have recently suggested [28, 29) and investigated [29-31] the possibility of selecting molecules embedded in helium nanodroplets in their isotope (component) composition. The objectives of the present review are to present the main results of these studies, comprehensively describe the proposed method, and thoroughly analyze its potential for the separation of isotopes in superfluid helium nanodroplets by the example of SF<sub>6</sub> molecules embedded in G N Makarov

helium nanodroplets. It will be demonstrated that the method of interest may be employed to select molecules in their isotope (component) composition. Its advantages and disadvantages are discussed in comparison with the well-known technique of isotopically selective infrared (IR) multiphoton dissociation of molecules in gasdynamically cooled jets and flows. Methods for creating and doping helium nanodroplets and the aforementioned examples of their applications are also briefly considered.

The paper outline is as follows. Section 2 is devoted to the methods for the production of helium nanodroplets (clusters) during gas outflow from cooled nozzle sources and their doping with single molecules and clusters. Also considered are the processes of formation of condensed and fragmented helium clusters and the interaction of uncontaminated helium clusters with particles, including the capture of foreign particles by the clusters. Results of the studies with helium droplets are presented to illustrate characteristic properties of these amazing nanometer-sized objects.

Section 3 considers selected applications of superfluid helium nanodroplets, first and foremost in the spectroscopy and synthesis of nonequilibrium structures. Methods and results of vibration-rotation (Section 3.1.1) and electron (3.1.2) spectroscopies of molecules (and atoms) inside and at the surface of helium droplets are discussed in brief. Manifestation of free molecular rotation in the spectra, i.e., direct spectroscopic confirmation of the superfluid nature of helium nanodroplets, is emphasized. Results of experimental studies demonstrating the presence of a dip (gap) in the phonon wing of electronic absorption spectra of glyoxal molecules  $(C_2H_2O_2)$  are presented, yielding one more spectroscopic confirmation of superfluidity of the helium droplets. Experiments are described on taking molecular spectra inside <sup>3</sup>He droplets and mixed <sup>3</sup>He/<sup>4</sup>He droplets, in which the threshold number of helium atoms in a droplet necessary for superfluidity to be apparent was determined. Formation of alkali dimers at the surface of helium nanodroplets and the results of experiments on the synthesis of cyclic water hexamers inside helium droplets are considered.

Section 4 (the central one in this review) expounds the results of studies designed to elucidate the possibility of selecting molecules embedded in superfluid helium nanodroplets (clusters). The selection method is described at length and an analysis is performed to evaluate its implications for the selection of molecules (such as  $SF_6$ ) embedded in helium clusters by means of their excitation under the action of intense CO<sub>2</sub>-laser radiation and angular splitting of the cluster beam on a beam of xenon atoms. The proposed method is shown to permit the selection of molecules of a different isotope (component) composition. This is compared with molecular selection by IR multiphoton dissociation of molecules in gasdynamically cooled jets and flows. The concluding Section 5 presents the main results of the studies being reviewed with reference to the merits and drawbacks of the proposed molecular selection technique.

# **2.** Production of helium nanodroplets (clusters) and doping techniques

#### 2.1 General remarks

Helium nanodroplets and their properties are being extensively investigated by both experimenters [1, 5-7, 11, 32-36] and theorists [10, 37, 38]. Methods for their production and

detection are most thoroughly reviewed in Ref. [11] (see also Ref. [9]). It is worthwhile to emphasize that the term 'droplets' is most properly applicable to helium because it is the sole substance that has no triple point. A liquid co-exists with vapor as the temperature decreases to absolute zero. Therefore, evaporative cooling of helium results in a liquid phase instead of a solid one.

An interesting feature of helium is the existence of its two stable isotopes: one (<sup>4</sup>He) being a boson, and the other (<sup>3</sup>He) a fermion. These two systems have quite different characteristics at low temperatures. In the temperature region where evaporative cooling is possible, <sup>3</sup>He usually behaves like an ordinary liquid, and <sup>4</sup>He as an ordered one with the property of superfluidity [39]. As far as helium nanodroplets are concerned, an interesting question is the meaning of such notions as 'liquid' and 'superfluidity' in application to a system so small with a not great number of atoms. Answers to this question are offered in part in Sections 3 and 4. More detailed information can be found in Refs [1, 5, 6, 9] (see also recent papers [13–20]).

It should be recalled that helium droplets were first observed by H Kamerlingh Onnes in his helium liquefaction experiments [40]. Considerable study is being given to the droplets of various sizes. We shall review only those experiments in which helium droplets are generated in active centers uniformly produced during expansion of helium in its outflow from a nozzle source. Their size varies from that of small clusters to micron-sized clusters. Such clusters, containing from  $N \sim 10$  to  $N \sim 10^7$  atoms (of micron diameter), are the main objects of ongoing studies. It is worth noting that these nanodroplets are more often referred to just as clusters. Therefore, no distinction is made below between helium nanodroplets and clusters: what is meant in either case is small helium droplets.

# 2.2 Formation of helium droplets during gas outflow from a nozzle

The most widespread method for the production of helium droplets consists in the homogeneous condensation of the gas expanding during its outflow from a nozzle [41–47]. The gas initially at rest above the nozzle at temperature  $T_0$  and pressure  $p_0$  expands as it outflows into a vacuum chamber through the nozzle outlet. The expansion is accompanied by adiabatic acceleration and cooling of the gas. If the local thermodynamic state of the gas passes through the gas/liquid co-existence region before internal interatomic collisions cease to be effective, phase separation occurs, resulting in the formation of a mixture of droplets and vapor in the jet.

Helium nanodroplets are frequently produced using nozzle sources cooled to a low temperature ( $T \leq 4$  K). When gas entropy above the nozzle is equal to or lower than that at  $\lambda$  point, a new mechanism of cluster formation associated with liquid phase fragmentation is feasible. In this case, the cluster beam in all probability also contains clusters of a 'different' type that form during condensation of the gaseous phase arising from fragmentation of liquid clusters. The identity of the properties of these two types of clusters remains to be elucidated. It appears that condensed and fragmented clusters are different, probably not only in size and velocity distributions but also in terms of the inner state (and possibly for clusters of the same size) since the mechanisms of their formation are also different. For example, clusters of these two types may have completely different angular momenta [11].

Because of low interatomic binding energy in small helium clusters (see Section 4.2), they are usually formed at high density and low temperature in the gas expansion zone [5]. These two parameters accounts for a large gas flux. Therefore, facilities for the production of liquid helium droplets are equipped with large pumps (ensuring high evacuation rates) and/or have very small nozzle outlets. A gas flux is proportional to the quantity  $p_0 d^2 T_0^{-1/2}$ , where d is the nozzle orifice diameter, and  $p_0$  and  $T_0$  are the gas pressure and temperature above the nozzle, respectively. The majority of facilities for the production of liquid helium nanodroplets have a nozzle orifice diameter between 5 and 20 µm, a pressure from 1 to 20 atm, and a temperature from 10 to 36 K. In experiments designed to produce fragmented clusters, the nozzle is sometimes cooled down to 3-4 K. In the ideal gas approximation, a nozzle with the orifice diameter 10 µm at  $T_0 \sim 20$  K and  $p_0 \sim 15$  atm makes it possible to produce the same gas flux as a nozzle with an orifice diameter of 50 µm operated at room temperature and gas pressure 2 atm [5]. Such a flux would run close to 4 atm cm<sup>3</sup> s<sup>-1</sup> ( $\sim 0.16$  mmol s<sup>-1</sup>).

Pumping out such gas flux is made possible by the use of diffusion pumps with an evacuation rate of roughly 10,000 l s<sup>-1</sup> for He ( $\cong$  4000 l s<sup>-1</sup> for nitrogen) at a limiting operating pressure of approximately  $3 \times 10^{-4}$  Torr [5]. Usually, such facilities produce helium nanodroplets containing a few thousand atoms each. It should be noted that sources operated at temperatures below 10 K for the production of large helium clusters ( $N \ge 10^5$ ) should either have a refrigerator with a low operating temperature or a nozzle directly cooled by liquid helium. A beam of clusters (droplets) is collimated by a skimmer located some 1-3 cm from the nozzle. In order to avoid beam scattering by the skimmer, the front edges of its walls must be as thin as possible. Skimmers for the purpose are usually manufactured by the electrophoretic deposition technique to have an inlet diameter of 0.5 - 1.0 mm.

#### 2.3 Doping of nanodroplets

Once a beam of helium clusters is formed using a skimmer, the clusters are doped with the chosen molecules or atoms. The two most widely applied doping techniques include (1) passing a cluster beam through a low-pressure gas cell, and (2) intersecting a cluster beam with another molecular or atomic beam. The former technique is the method of choice. The gas cell is normally as long as 10 cm. The intracell pressure is maintained such as to ensure production of a desired number of impurity particles per cluster. During the capture process, the particle's kinetic and internal energies, as well as solvation energy, are distributed throughout a droplet, which leads to evaporation of helium atoms. It was estimated [48] that around 200-250 atoms are evaporated when a small molecule, such as HCN, is captured; evaporation of a single atom requires an energy of 5.5-7 K. As a result, the microcanonical system in the case of <sup>4</sup>He and <sup>3</sup>He clusters is cooled down to 0.38 and 0.15 K, respectively [49]. These values are in fairly good agreement with the predictions of the theory [50, 51]. Also, evaporation of atoms is accompanied by a change in the angular momentum of the helium droplets.

Capture of particles by helium droplets follows a Poisson distribution for multiple capture [52]. This means that the probability of cluster formation [e.g.,  $(SF_6)_k$ ] inside a helium droplet depends on the probability  $I_k$  of the independent

capture of k SF<sub>6</sub> molecules, which is defined by the distribution [52]

$$I_k = k_{k0} \frac{(n\sigma L)^k}{k!} \exp(-n\sigma L), \qquad (2.1)$$

where  $k_{k0}$  is the amplitude factor, *n* is the gas density,  $\sigma$  is the capture cross section, and *L* is the cell length. In order to optimize the process by ensuring capture of a single particle per droplet, the gas column density must be roughly  $330N^{2/3}$  Torr cm [5]. Under typical conditions, efficacious doping of helium droplets is achieved when the vapor pressure amounts to  $10^{-4} - 10^{-5}$  Torr. This value is approximately four orders of magnitude smaller than that for the production of doped clusters in expanding jets with gascarriers. In other words, the method being considered can be used to study many substances that are impossible to observe in expanding jets. Molecules captured by one and the same droplet find one another inside it and form van der Waals complexes.

#### 2.4 Certain results of helium nanodroplet studies

Results of helium nanodroplet research (see Refs [9, 11]) indicate that the formation of <sup>4</sup>He<sub>N</sub> clusters during gasdynamic expansion from nozzle sources is due to the growth of smaller clusters, including He<sub>2</sub>, that play the role of condensation centers. The clusters are distributed in size and velocity, the velocity distribution being normally rather narrow. The cluster velocity is determined by the initial gas enthalpy in the source and the internal enthalpy of the system at a condensation point. The condensation point being dependent on several parameters, including the geometric characteristics of the nozzle, there is a marked distinction in size and velocity distributions between different production facilities even under similar conditions for the gas existence above the nozzle [11]. Conversion parameters specifying the formation of clusters of a desired size in nozzles with different dimensions are presented in Ref. [53]. The most useful information on the distribution of clusters with size and velocity has been obtained in particle scattering experiments [54] and time-of-flight measurements [55], respectively.

There is a substantial difference between  ${}^{4}\text{He}_{N}$  and  ${}^{3}\text{He}_{N}$  clusters. The former are bound complexes at any N, whereas small  ${}^{3}\text{He}$  droplets composed of at least 30 atoms each are highly unstable [56, 57]. The instability of small  ${}^{3}\text{He}_{N}$  droplets is attributable to the high zero-vibration energy and the small mass of isotope  ${}^{3}\text{He}$ . Hence the marked difference observed in experiments between the dependences of the mean droplet size  $\overline{N}$  on the gas temperature above the nozzle for these two isotopes. In the case of  ${}^{4}\text{He}$ , the mean size  $\overline{N}$  gradually increases with decreasing temperature, while the formation of  ${}^{3}\text{He}$  droplets has a threshold nature.

The results of completed studies suggest the capture (including the multiple capture) of particles by helium clusters and the formation of impurity clusters inside or at the surface of helium droplets. The distribution of impurity particles throughout helium droplets is consistent with the predicted Poisson distribution for multiple capture [52]. The phenomenon of capturing impurities by helium droplets opens up good prospects for their applications in spectroscopy and in the investigation of physical and chemical processes inside the helium droplets or at their surfaces. The results of such investigations are presented in Sections 3 and 4.

### 3. Application of helium nanodroplets

# 3.1 Spectroscopy of molecules and clusters inside helium nanodroplets

3.1.1 Vibration - rotation spectroscopy. Doubtlessly, the main sphere of applications of superfluid helium nanodroplets (clusters) is the spectroscopy of molecules, atoms, and clusters inside and at the surface of the droplets. This section is focused on the results of vibration-rotation spectroscopy of molecules and clusters inside helium nanodroplets. Data on electron spectroscopy will be considered in the next section. It should be recalled that the spectroscopy of molecules and clusters inside helium nanodroplets has been discussed at length in the reviews [5, 6, 9]. Here, we are dealing only with the most typical experimental results, bearing in mind that findings obtained by the spectroscopy of molecules inside helium droplets underlie the molecule selection technique described in the present communication. Therefore, the spectroscopic data discussed below may be helpful for understanding the essence of the proposed method and processes making up its basis.

The most noticeable feature of vibration – rotation spectroscopy of molecules inside <sup>4</sup>He droplets is pertinent to the manifestation of free molecular rotation in the spectra, regarded as direct and unquestionable proof of the superfluid nature of helium nanodroplets. The vibration – rotation spectrum of a molecule is  $\leq 0.26 \text{ cm}^{-1}$  wide when the steady-state droplet temperature equals 0.38 K. This value is smaller than the isotope shift in IR-absorption spectra of practically all molecules of interest for the laser-assisted separation of isotopes. This fact accounts for the possibility of highly selective laser excitation of the chosen molecules inside helium droplets (see Section 4).

The width of the vibration-rotation spectrum of a molecule inside a helium droplet is also smaller than the line shift induced by complex formation. Therefore, spectra of various small oligomers in helium droplets do not overlap, and the capture of more than one molecule by a droplet results in the decreased intensity of the spectrum of a single molecule without altering its shape. A different situation takes place in the case of large oligomers because spectral shifts tend to the asymptotic limit as the number of molecules in a cluster increases [21, 58]; hence the overlap of the spectra. Nevertheless, OCS-(H<sub>2</sub>)<sub>N</sub> complexes containing up to

17 hydrogen molecules were obtained under favorable conditions and their spectra were successfully resolved [4].

3.1.1.1 Experimental methods. Molecular spectroscopy inside helium nanodroplets is based on two methods [5, 9]: one being the molecular beam technique, and the other matrix isolation spectroscopy. This accounts for its advantages and disadvantages. Evidently, certain spectroscopic techniques are inapplicable to molecular beams. For example, it is practically impossible to obtain molecular absorption spectra when dealing with well-collimated beams by measuring the attenuation of exciting radiation. In this case, only the laserbolometric [59, 60] or pyroelectric [61-63] technique for the detection of the absorbed energy enables one to obtain molecular absorption spectra in a beam. The bolometric method is widely utilized in molecular beam research [41, 42] and is successfully used to study van der Waals complexes [45, 64-66] as well. When molecules are excited in a beam, a bolometer (or pyroelectric detector) detects a rise in the beam energy owing to the absorption of laser radiation [59-63]. In the case of cluster beams, these detectors usually record a fall in the beam energy because absorption of the laser radiation most frequently leads to cluster dissociation and the subsequent scattering of the resulting fragments from the beam [45, 64-66]. The outcome is the beam depletion (exhaustion) and a diminished total energy reaching the bolometer.

A typical experimental setup for studying molecular and cluster spectra inside helium nanodroplets is schematically depicted in Fig. 1. Large helium clusters (droplets) are formed during gas outflow from the nozzle. When passing through the scattering chamber, they capture a 'guest' (studied) molecule. During their further travel toward the mass spectrometer, the clusters are irradiated by frequency-tuned laser light. The laser being in resonance with the 'guest' molecule, the absorbed energy causes helium atoms to evaporate from the clusters and deteriorates the signal from the mass spectrometer. Molecular spectroscopy in helium clusters is a relatively new field of research. For this reason, the availability of an appropriate radiation source dictates the choice of the molecules to be studied. Earlier experiments [67, 68] were carried out with SF<sub>6</sub> molecules and included excitation of molecular vibration frequency v<sub>3</sub>. An SF<sub>6</sub> molecule has a rather large absorption cross section in the CO<sub>2</sub>-laser generation region. Powers of a few watts are readily achievable with cw tunable CO<sub>2</sub>-lasers. This transition in SF<sub>6</sub>





molecules was later investigated using a tunable diode laser with a view to resolving the rotational structure [69]. Diode lasers were also employed in experiments designed to study the OCS molecular spectra [4, 7, 70, 71].

The first experiments on helium clusters doped with HF,  $H_2O$  and  $NH_3$  molecules [72–74] were carried out with the use of pulsed lasers. Their advantages are high power and a wide tuning range, whereas drawbacks include a wide lasing line and field-induced broadening of molecular transitions under study. As a result, it is sometimes difficult to understand whether spectral line broadening is due to the interaction with the matrix or is related to the laser itself.

Also used in such experiments are powerful tunable gas lasers (pulsed or continuously operated; see, for instance, Ref. [75]). Due to a scanty set of frequencies being generated, such lasers are more suitable than others for studying small molecules with a small moment of inertia and well-separated spectral lines. Their high power allowed them to be widely employed in transition saturation experiments [35]. Most experimental spectra were obtained with color center lasers operating in the 3  $\mu$ m [21, 58, 75–77] and 1.5  $\mu$ m [35] regions. These lasers are characterized by a wide tuning range, relatively high power (30 and 250 mW, respectively), and high spectral resolution.

3.1.1.2 Infrared and microwave excitation. Infrared spectroscopy of molecules enclosed in helium droplets is of great interest because it may be applied to obtaining a resolved rotational structure even in the spectra of relatively large molecules and clusters. One such example is considered in the present section (more can be found in Ref. [9]). Figure 2 illustrates the IR-absorption spectrum of SF<sub>6</sub> in the neighborhood of molecular vibrational frequency  $v_3$  inside <sup>4</sup>He droplets with a well-resolved rotational structure. It needs to be emphasized that a rotational structure in 'classical' solvents can be observed only for molecules with a small moment of inertia. It is equally important that the presence of a resolved rotational structure in the spectrum makes it possible to measure the cluster temperature. Such a possibility deserves special emphasis because there had been no way to directly measure cluster temperature until these experiments came into laboratory practice. Moreover, researchers seemed to be unaware of any proposal to overcome this



**Figure 2.** IR-absorption spectrum of SF<sub>6</sub> in the neighborhood of molecular vibrational frequency  $v_3$  inside an <sup>4</sup>He droplet (N = 2700) (solid curve). For comparison, a calculated spectrum for a freely rotating molecule is also presented (dotted curve) [1].

impediment. Very soon thereafter, however, tunable narrowband lasers were utilized to resolve rotational structure in the spectra of molecules inside helium clusters and thus to measure their temperature [49, 69, 78].

In the course of time, the schemes devised for helium cluster beam excitation and detection were improved. Bolometers used in earlier experiments were substituted by mass-spectrometric detectors 'transparent' to cluster beams. In these experiments, a cluster and a laser beams spread in parallel but opposite directions. Owing to this, the interaction length between the cluster beam and laser radiation was increased to several dozen centimeters. Such geometry allowed for the use of low-power diode lasers. The beam depletion technique was employed to examine molecular spectra inside helium nanodroplets using both bolometers and mass spectrometers. It is worthwhile to note that even at a droplet temperature of 0.38 K, the mean scattering angle of helium atoms during evaporation was about  $10^\circ$  in the laboratory system of coordinates [5]. Due to this, the helium atoms being evaporated avoided the detector, which resulted in a decreased flux along the beam axis, i.e., to beam depletion.

When molecules are excited in a microwave region, radiation is usually localized inside the waveguide, part of which is co-linear with the cluster beam [5]. The intensity of radiation under such conditions can be increased and its entering the bolometer excluded. Otherwise, it can strongly influence the measured signal.

It should be noted that the rotation spectroscopy of molecules inside helium droplets is different from vibration and electron spectroscopies in that it is essentially a multiphoton technique. Energies of purely rotational transitions (0.5-70 GHz) are insufficient for the evaporation of even a single helium atom. Microwave spectroscopy of molecules inside helium droplets is based on the phenomenon of rotational relaxation in an isolated droplet that enables the molecules to absorb photons from time to time, with their energy being converted to the droplet energy. It was found in experiments that microwave excitation of molecules produces signals almost as strong as vibrational excitation does. This fact has been exploited in estimating the number of rotational relaxation cycles that each molecule must undergo while it remains (around 100  $\mu$ s) in the microwave field. In this way, the relaxation time of HCCCN molecules was obtained [79].

Powerful sources of microwave radiation (dozens of watts) and large dipole moments of molecular transitions in this spectral region make possible experiments on saturation spectroscopy [77, 79, 80]. The results of such experiments provide an insight into the nature and magnitude of inhomogeneous spectral broadening.

**3.1.1.3 Double resonance technique and Stark spectroscopy.** Molecular spectra inside helium clusters were also studied by MW-MW and MW-IR double resonance techniques and Stark spectroscopy. With the double resonance method, it is possible to single out a homogeneous line width against the background of inhomogeneous broadening. The first MW-MW double resonance experiments were carried out utilizing HCCCN molecules [79] and included excitation of rotational R(3) and R(4) transitions in molecules. Measurements under conditions of saturation of these transitions gave evidence that typical spectral lines were inhomogeneously broadened ones. Line broadening was interpreted as a sign of spectral diffusion. MW–IR double resonance experiments were made with HCCCN [77] and OCS [81] molecules. It is worth mentioning that MW–IR resonance spectroscopy provides an opportunity to study the entire set of rotational levels and to probe rotational states unrelated to pumping radiation. It was experimentally revealed [77, 81] that all rotational levels are to a certain extent populated by pumping radiation, which probably suggests rapid rotational diffusion. Indeed, rotational relaxation times of molecules inside helium droplets lie in the nanosecond range [79].

Experiments on the Stark spectroscopy of molecules inside helium clusters have shown that this method is potentially applicable to studying interactions of impurity molecules with the surrounding helium and deformation of molecules (and complexes, in particular) by a mild helium solvent [21, 82]. It should be emphasized that the mixing of rotational states appears as one of the manifestations of the Stark effect [83]. In helium droplets where helium atoms attach to intracluster molecules, it is possible to induce Q-branches(usually forbidden) in such linear molecules as HCN and HF having rather high rotational constants (which accounts for the presence of only R(0) lines in their rotational spectra within the helium droplets). Stark spectroscopy allows for the direct measurements of the band origin (zero line) and the rotational constant of a molecule [82]. In such experiments, a relatively weak electric field is usually employed to avoid inducing large line shifts. The shifts are measured with respect to the field strength, and the exact location of the Q-branch is determined by extrapolation toward the zero field.

It is worth noting that a rotational structure in the spectra is sometimes undesirable and needs to be suppressed (see Refs [5, 9]). To this effect, pendular state spectroscopy may be utilized in experiments with polar molecules in a gaseous phase [81, 84]. In this technique, a relatively strong static electric field is applied, which converts molecular rotation into dipole moment vibrations (precession) about the direction of the external field. In the strong static field limit (and under conditions of parallel constant and induced dipole moments), the entire rotational contour undergoes collapse to a single line coincident with the line of a purely vibrational transition. The integral intensity of this line is thrice that in the zero field. This method was employed in experiments with helium droplets in the works [21, 85] where it allowed obtaining resolved spectra of linear chains containing up to eight HCN [21] and twelve HCCCN [58] molecules. Molecular rotation inside helium droplets was also possible to suppress by substituting <sup>3</sup>He for <sup>4</sup>He [7, 70]. For instance, pendular state spectroscopy was used in studies [4, 71] where collapse of the absorption band of OCS- $(H_2)_N$  complexes was induced to determine N from measured band shifts. The method is also applicable to nonpolar molecules. However, the lines for <sup>3</sup>He clusters are not as narrow as for <sup>4</sup>He ones.

**3.1.1.4 Molecular spectroscopy inside** <sup>3</sup>He and <sup>3</sup>He<sup>-4</sup>He **droplets.** Interesting results were obtained in the studies of IR-spectra (using SF<sub>6</sub> [49, 86] and OCS [7, 87] molecules) inside <sup>3</sup>He droplets and mixed <sup>3</sup>He<sup>-4</sup>He droplets. Owing to the somewhat lower energy of <sup>4</sup>He zero vibrations, these atoms are largely located in mixed droplets around impurity molecules [88]. It leads to the formation of an <sup>4</sup>He cluster inside the <sup>3</sup>He cluster. When the number of <sup>4</sup>He atoms is small, the molecular spectra in <sup>3</sup>He clusters are inhomogeneously broadened due to the different content of <sup>4</sup>He atoms

within the <sup>3</sup>He clusters in a given beam. In other respects, the spectra resemble those in pure <sup>4</sup>He clusters with the sole exception that the droplet temperature is significantly lower ( $\sim 0.15$  K) by virtue of the evaporative cooling of <sup>3</sup>He clusters. As the concentration of <sup>4</sup>He atoms in the expanding mixture increases from 0.1 to 4%, the temperature rises to the limiting value (0.38 K) for <sup>4</sup>He droplets [5].

Studies of IR-spectra of OCS molecules in pure <sup>3</sup>He droplets demonstrated [7, 87] (see also Refs [1, 9]) that they undergo collapse to one broad band, as in the case of a classical liquid. At the same time, an <sup>4</sup>He droplet exhibits a well-resolved rotational structure. Interaction potentials of OCS molecules with <sup>3</sup>He and <sup>4</sup>He atoms being roughly identical, this discrepancy may be assigned to different droplet states, namely, superfluid for <sup>4</sup>He, and normal liquid for <sup>3</sup>He.

A study of OCS IR-absorption spectra [7] revealed a threshold for the formation of the superfluid state in <sup>4</sup>He clusters. Controlled numbers of <sup>4</sup>He atoms were added to large <sup>3</sup>He clusters containing OCS molecules (up to 100 atoms per cluster). As a result, the IR spectrum eventually exhibited a rotational structure suggesting gradual transition to the superfluid state. The superfluidity became virtually established when the number of <sup>4</sup>He atoms in a cluster was close to 60 (roughly equivalent to two solvate layers). A further rise in the number of <sup>4</sup>He atoms per cluster failed to bring about a qualitative change in the molecular spectrum [7] (see also Refs [5, 9]).

It is worthwhile to mention some recent experimental [17] and theoretical [13] studies aimed at determining the superfluidity threshold using small CO<sub>2</sub>-doped helium nanodroplets ( $N \le 17$ ). In Ref [17], rotational constants were measured with different numbers of helium atoms in the droplet. The two studies showed that superfluidity becomes microscopically apparent when the number of helium atoms in a droplet is  $N \ge 5-13$ , i.e., when even the first shell around the molecule is incompletely filled. At N = 30-50, the rotational constant *B* of the molecule acquires a value close to that in large helium nanodroplets [17].

3.1.2 Electron spectroscopy. Electron spectroscopy in helium droplets is considered at length in Ref. [6] (see also earlier reviews [8, 89, 90] and a recent publication [9]). Here, we shall briefly discuss electron spectroscopic techniques and the most characteristic findings of interest with respect to the proposed method for molecule selection. To recall, electronic excitation of molecules embedded in a cluster may lead to the excitation of helium degrees of freedom. This phenomenon is due to a considerable change in interaction potential between a molecule and helium atoms under electron excitation conditions, which accounts for the marked alteration of the equilibrium configuration of the helium solvation shell. Being very soft, liquid helium is highly susceptible to interaction with impurities. Electronic excitation is able to substantially change both the interaction force and its anisotropy. Moreover, in some extreme cases, it may even result in the replacement of an attractive interaction by a repulsive one and thus induce an ejection of excited particles from the droplet. In moderate cases, electronic excitation leads to a considerable change in rotational constants and gives rise to phonon wings in the spectra. Taken together, the above data indicate that electronic spectra of molecules and clusters inside helium droplets contain important information on the structure and dynamics of helium surrounding.

3.1.2.1 Methods. Experiments on the electronic excitation of molecules, as in the case of IR spectroscopy, may be conducted using detection methods based on signal measurements with the aid of a mass spectrometer [8, 32, 69, 91-93]. However, the results obtained in many studies indicate that some other detection techniques provide more advantages. It is worth mentioning the successful employment of surface ionization detectors, well known for their enhanced quantum efficiency in the spectroscopy of alkali metal atoms [94] and  $He_2^*$  eximers [95, 96]. When electronically excited, these particles become detached from the droplets, which results in a decreased ion current during detection in the beam plane. Another widely used method is the laser-induced fluorescence (LIF) technique [22, 92, 97-102]. For atoms and molecules with a quantum yield of fluorescence close to 10%, this method gives a signal-to-noise ratio one or two orders of magnitude higher than the method in which attenuation of the signal resulting from beam depletion is measured by a mass spectrometer. One more advantage of the LIF technique is its higher sensitivity versus that of the just mentioned alternative method when applied to large droplets containing over  $10^4$  helium atoms [103]. To recall, the multiphoton ionization technique combined with a quadrupole mass filter or time-of-flight measurements was successfully employed in experiments with helium clusters [104-109].

3.1.2.2 Spectroscopy of metal atoms at the surface of and inside

helium droplets. The binding energy between alkali and helium atoms is very low (the depth of potential well  $\varepsilon \le 1.5 \text{ cm}^{-1}$  [6, 110]). For this reason, the size and the shape of the helium solvation shell around a metal atom is first and foremost determined by the repulsive component of interaction, which is in turn described by Pauli repulsion between parallel electron spins of helium and metal atoms. This makes the region in a helium droplet occupied by a solvated metal atom look like a bubble around a free electron in liquid helium. However, the radius of such a bubble (5– 10 Å) is smaller because, in this case, electrons are not free but bound to the ion nucleus (even if not very tightly) [89, 90, 111–114]; therefore, the energy of their zero vibrations is lower.

Electronic absorption (emission) spectra may be utilized to find the position of a metal atom at the surface of or inside a helium droplet. It has been shown (see Refs [6, 9] and references cited therein) that atomic spectra of certain metals (Ag, Al, Eu, Mg) attached to helium clusters resemble spectra in bulk liquids. This means that metal atoms are enclosed in helium droplets. The blue shift and the width of these spectra are normally 300-500 cm<sup>-1</sup>, as predicted by the model taking into account bubble formation [89]. As mentioned above, electronic excitation of an atom sometimes leads to the replacement of its attractive interaction with a droplet by a repulsive one and the resulting ejection of the excited metal atom from the droplet [107, 108]. On the other hand, timeresolved fluorescence spectra of Mg atoms reveal that the majority of atoms remain in the droplet after electronic excitation [115].

The results of experiments indicate that all alkali atoms (Li, Na, K [98], Rb, Cs [109]) are located at the surface of helium droplets rather than inside them, as suggested by their much narrower spectra and smaller shifts ( $\approx 5-10$  cm<sup>-1</sup>) compared with those in bulk liquid helium [114, 116, 117]. At the same time, it is theoretically predicted that the atoms of alkali metals should lie 5-6 Å below the droplet surface [118]

(where the helium density is only 1/2 of the bulk density) and the helium surface around each atom is distorted by the presence of a sort of 'dimple'.

A different situation takes place with atoms of alkalineearth metals. Their location inside or at the surface of helium droplets cannot be definitely predicted from their interaction potential with helium. Magnesium is the sole metal of the group whose atoms were shown to be present inside helium droplets [115]. Ca, Sr, and Ba atoms attached to helium droplets cause much more prominent blue shifts in the spectra than alkali atoms [119]. This means that they are submerged in helium and form bubble states. However, the shifts said are much smaller than spectral shifts in bulk helium [99]. Evidently, this should be attributed to the subsurface location of the atoms, where the helium density is low. Indeed, results of calculations [120] confirm that Ca atoms lie in a deep 'cave' and are covered by a thin helium layer, the density of which is only 1% of the bulk density.

3.1.2.3 Spectroscopy of organic molecules inside helium droplets. A wealth of important information was obtained in research on electronic excitation of organic molecules (see, for instance, Refs [6, 9]). Experiments were designed to study electron transitions to the first excited singlet states for certain organic molecules inside helium droplets, such as glyoxal [3, 91, 103], polyaromatic hydrocarbons [92, 100, 121], indoles [56, 102], and porphyrines [122, 123]. In most cases, the spectra were measured by the LIF technique, though sometimes by the beam depletion method. The majority of spectra exhibited a sharp line corresponding to the onset of transition, which is accompanied by well-resolved vibrational bands on the highfrequency side. The zero transition and each vibrational band had sharp phononless lines followed by phonon wings (PWs). PW intensities markedly increased close to the zero phonon lines. Phonon wings extended approximately 20-50 cm<sup>-1</sup> towards the high-frequency side [6].

The spectra exhibit slightly shifted lines as opposed to large shifts of absorption lines characteristic of metal atoms in liquid helium where the repulsive part of the interaction potential predominates in the framework of the bubble model. The shifts of zero spectral lines arising from interactions with the helium matrix vary from 10 to  $100 \text{ cm}^{-1}$ . These values are almost 100 times greater than in vibrational transitions [5] (see Section 3.3.1) due to the stronger coupling of the helium matrix to the excited electronic states. It should be noted, however, that electronic excitation energies are almost an order of magnitude higher than vibrational transition energies.

**3.1.2.4 Zero phonon lines and phonon wings.** Zero phonon lines (ZPLs) constitute sharp bands of about  $0.2-1 \text{ cm}^{-1}$  in width, which are frequently restricted by the width of laser lines, when a pulsed laser serves as an excitation source. In other words, inhomogeneous line broadening in helium droplets is very small, in contrast to other matrices where the same transition lines are normally wider (by up to three orders of magnitude) [124, 125].

The interaction between a chromophore molecule and helium atoms being much stronger than between helium atoms themselves, the helium surrounding takes the form of a molecule even in the case of highly asymmetric particles, such as amino acids [102]. It facilitates the use of sharp ZPLs for the study of minor structural changes in a molecule usually associated with small spectral shifts.

Each zero phonon line for molecules has a phonon wing from the blue side [56, 91, 92, 100, 121, 122]. Phonon wings serve as indicators of vibrations of a compressed volume of the helium environment, induced by electronic excitation of a molecule. As shown in Ref. [91], the PW of a glyoxal molecule in an <sup>4</sup>He droplet is separated from the zero phonon line by a well-apparent dip (gap) about 5 cm<sup>-1</sup> in width. The theory elaborated for the explanation of phonon wings produced by impurities in solids [126] predicts that the PW intensity is proportional to the density of phonon states [91, 126]. This theory fairly well describes the phonon wing in glyoxal, taking advantage of the dispersion curve of elementary excitations in bulky superfluid helium [127-131]. Because the sharp phonon-roton curve is a characteristic of the superfluid helium state [130, 131], this result may be regarded as one more experimental evidence that <sup>4</sup>He droplets reside in a superfluid state.

The glyoxal spectrum in undoped nonsuperfluid <sup>3</sup>He droplets contains no gap separating ZPLs and PWs [2, 3, 132]; this fact confirms the above inference and is consistent with different patterns of elementary excitations in <sup>4</sup>He and <sup>3</sup>He. Roton dip evolution was examined in Ref. [88] after the addition of a known number of <sup>4</sup>He atoms to an undoped <sup>3</sup>He droplet containing a glyoxal molecule. Because of their low zero-vibration energy, <sup>4</sup>He atoms form a shell around the glyoxal molecule [128]. The results of the study indicate that a well-apparent dip (gap) between ZPLs and PWs evolves again when the number of <sup>4</sup>He atoms exceeds  $N \ge 120$  [2, 132]. Theoretical predictions for an undoped <sup>4</sup>He cluster [48, 133, 134] gave evidence of the gradual appearance of a roton minimum for clusters containing  $N \ge 100$  atoms. This finding was interpreted as an onset of superfluidity, in excellent agreement with available experimental data.

#### 3.1.2.5 Spectral changes related to the helium atom localization

close to a molecule. Large aromatic molecules strongly interacting with helium atoms (at a binding energy of  $\approx 100 \text{ cm}^{-1}$  per atom) cause these atoms to be localized within the first solvation shell. This leads to several spectral changes [6, 9] because the dense helium shell serves as a base for the formation of structural isomers. As a result, ZPLs may split and the shape of the phonon spectrum undergo modification reflecting more localized excitations of the compressed shell.

Certain molecules, such as indole [56] and tetracene [92], show ZPL multiplets when placed in helium. Lines in these multiplets lie approximately  $1-2 \text{ cm}^{-1}$  apart. Because such molecules have no isomers, splitting can be due only to certain nonequivalent configurations of the helium environment. The nature of line splitting was most thoroughly explored in tetracene molecules. Experiments involving burning dips in the spectra and measurement of radiation lifetime, reported in Refs [92, 121], confirmed that both the ground and the excited states of tetracene inside helium droplets are split into two components. Splitting can be explained by the localization of several helium atoms at the surface of a planar molecule; owing to this, the topology of the respective interaction potential determines the number and structure of isomers. The same experiments demonstrated the strong dependence of splitting patterns on the chromophore environment. By way of example, the addition of an Ar atom to a tetracene molecule inside a helium cluster completely eliminates the splitting of ZPLs [92]. It can be accounted for by the fact that the added atom raises the

internal temperature of the cluster and thereby changes the structure of the helium surrounding.

**3.1.3 Conclusion.** The most noticeable feature of vibration – rotation spectra of molecules embedded in helium nanodroplets is the appearance of free molecular rotation. The vibrational – rotational structure of molecular spectra inside helium nanodroplets is identical to the spectral structure of the same molecules in the gaseous phase (conservation of linearity, symmetry, and selection rules) even though rotational constants undergo significant alteration (see, for instance, Refs [5, 9]). It is the manifestation of free molecular rotation inside helium droplets that gives direct spectroscopic evidence of the superfluid nature of helium droplets.

IR spectroscopy of OCS molecules inside mixed  ${}^{3}\text{He}-{}^{4}\text{He}$  clusters demonstrated the existence of a threshold for the origin of the superfluid state in  ${}^{4}\text{He}$  clusters. It was shown that superfluidity fully develops when the number of  ${}^{4}\text{He}$  atoms in a cluster amounts to  $N \approx 60$ .

An attractive peculiarity of vibration-rotation spectroscopy in helium droplets is a very small shift in zero vibrational lines that does not normally exceed 0.1%. In contrast, spectroscopy in the conventional Ne or Ar matrices as a rule shows much greater band shifts. For example, matrixdependent band shifts in the case of HF molecules for He, Ne, and Ar are 0.067, 0.24, and 1.1%, respectively [135]. Small shifts in helium are largely due to its low density and polarizability. At the same time, experimental results frequently reveal efficacious mutual compensation of the effects, which accounts for the smaller-than-expected shifts [5].

Line widths of molecular electron transitions inside superfluid helium droplets do not exceed 0.1 cm<sup>-1</sup>; in other words, these lines are approximately three orders of magnitude narrower than observed during similar transitions in ordinary solid matrices. This means that electron transitions, as well as vibrational ones, may be used to highly selectively excite molecules inside helium droplets by laser radiation. Helium droplets have a negligible effect on the transition frequency. Shifts in electronic spectra induced by interaction with the matrix vary from ~ 30 to 50 cm<sup>-1</sup> for organic molecules embedded in helium droplets, and from ~ 5 to 6 cm<sup>-1</sup> for alkali dimers and trimers at the droplet surface. For comparison, shifts in ordinary solid matrices vary in the range from ~ 200 – 300 cm<sup>-1</sup> to ~ 1000 cm<sup>-1</sup>.

#### **3.2 Other applications of helium nanodroplets**

In what follows, we shall briefly consider other applications of helium nanodroplets. To begin with, they were employed to obtain dimers and trimers of alkali metal atoms at the droplet surface [22, 23], synthesize linear chains of polar molecules oriented in a certain way inside helium nanodroplets [21], conduct chemical reactions within droplets [26], and observe orientational effects [27]. These applications of helium nanodroplets have been discussed in great detail in a recent review [9]. Therefore, we shall only mention here a method for the production of alkali dimers and trimers at the surface of helium droplets. Another application of helium nanodroplets will instead be considered at greater length, namely, their use for the synthesis of water hexamers [24, 25].

**3.2.1 Production of alkali dimers at the helium droplet surface.** It needs to be emphasized that the production of atomic dimers and trimers of alkali metals is a challenging experimental problem. Alkali metal dimers arise either in the singlet

or the triplet electronic state. Electron spin pairing in the singlet state corresponds to the formation of a covalent bond (5943 cm<sup>-1</sup> for Na<sub>2</sub>). On the other hand, configuration of parallel valence electron spins provokes Pauli repulsion. For example, an evolving triplet state is characterized by a very weak van der Waals minimum (174 cm<sup>-1</sup> for Na<sub>2</sub>). In experiments with the gaseous phase in a heated tube, dimers are formed at high temperatures, and equilibrium concentration of triplet states is negligibly small. It is the use of molecular beams with gas-carriers that makes possible the production of molecules in a triplet state and the performance of the experiments on their excitation [136, 137].

The problem can be resolved by the application of helium droplets. Two or more metal atoms may sequentially occupy the droplet surface in a capture cell and freely move over the surface of or inside the droplet until they find one another and attach to form a molecule or a large cluster. The newly formed particle is rapidly cooled down to the droplet temperature, namely,  $T \sim 380$  mK. Because alkali dimers and trimers are loosely attached to the surface of helium droplets (the binding energy is less than 1 cm<sup>-1</sup>), relaxation of the energy of almost 6000 cm<sup>-1</sup> leads to the effective detachment of singlet molecules from the droplet [23]. Conversely, weakly bound triplet molecules accumulate at the droplet surface. It was found [23, 101] that fluorescence spectra of sodium-doped helium droplets mostly contain strong triplet bands  $(1^{3}\Sigma_{\sigma}^{+} - 1^{3}\Sigma_{\mu}^{+})$  in the 12,900-16,500 cm<sup>-1</sup> region, whereas singlet transitions are virtually absent in these spectra. This suggests a rise in the concentration of loosely bound triplet molecules at the droplet surface [22, 23]. Similar results were obtained in experiments with Li<sub>2</sub> and K<sub>2</sub> molecules.

It is worthwhile to note that both triplet and singlet molecules are localized at the droplet surface, which is confirmed by a very small spectral shift of electron transition frequencies (less than 5 cm<sup>-1</sup>). On the contrary, large spectral shifts (around 700 cm<sup>-1</sup>) were recorded for Na<sub>2</sub> singlet – singlet transitions in bulky liquid helium [117]. The localization of alkali molecules at the droplet surface is also confirmed by the results of computations based on the density functional [138] and of semiempirical calculations [139]. These calculations indicated that Na<sub>2</sub> and Li<sub>2</sub> molecules, similar to atoms, occupy dimples at the droplet surface. Electron spectroscopy data for alkali dimers and trimers at the surface of helium droplets were analyzed in Refs [23, 101] (see also the reviews [6, 9]).

**3.2.2 Synthesis of cyclic water hexamers.** An interesting application of helium droplets was reported in Refs [21, 24, 25, 58]. The authors demonstrated the possibility of using very cold helium droplets for the synthesis of strongly non-equilibrium structures that cannot be obtained by any other method. They synthesized linear chains of HCN molecules [21] (see also Refs [5, 9]) and cyclic water hexamers [24, 25] inside helium droplets. In this section, we shall consider the preparation of high-energy isomers inside helium droplets, which is exemplified by the synthesis of cyclic water hexamers.

The cyclic water hexamer is a higher-energy isomer compared with the hexamer having a cage structure and being observed in the gaseous phase in earlier studies [140, 141]. Experimental evidence reported in Refs [24, 25] indicates that cyclic hexamers arise when water molecules are inserted into preformed cyclic complexes of a smaller size and the resulting complex is rapidly cooled inside a helium droplet. The rapid cooling prevents complex rearrangement to a more stable cage structure.

It should be emphasized that studies of water clusters are of great interest because their results are essential in describing the properties of bulky liquid and ice at the molecular level. The structural landscape associated with large water clusters is highly diverse. The theory predicts the existence of numerous local minima at the potential energy surface, each corresponding to a specific isomer. Many of these isomers resemble transient (short-lived) structures arising in liquid water and tetrahedral ice [24]. Therefore, investigations into the structure of water clusters may shed light on the properties of bulk liquid water.

Despite the possibility, in principle, of preparing different structural isomers, experiments with small water clusters indicate that only one — the most stable — isomer forms for each cluster size. This finding substantially restricts configuration space for experimentation with structural isomers. The employment of superfluid helium nanodroplets as a medium for growing water clusters allows this space to be expanded. As a result, the authors of Refs [24, 25] observed formation of cyclic water hexamers. This observation is of special interest in light of computer simulations indicating that cyclic water and in ice [142, 143]. The structure of a cyclic water hexamer is shown in Fig. 3a together with that of





**Figure 3.** (a) Cyclic and cage isomers of the water hexamer calculated in Ref. [147]. (b) Infrared spectra of O-H vibrations of water clusters formed in a gaseous phase (top curve) and in liquid helium droplets (bottom curve). Numerals correspond to the cluster size. The question-mark refers to a weak band, the frequency of which coincides with that of a water hexamer having the cage structure [24].

a cage isomer [144–146] previously investigated in Refs [140, 141].

A detailed description of the experimental setup used in these studies can be found in Ref. [148]. Helium droplets were formed during expansion of highly purified helium gas outflowed from a nozzle orifice 5  $\mu$ m in diameter; the nozzle was cooled to 19–22 K. The droplets traversed a capture chamber filled with water vapor. The pressure within the chamber could be varied to optimize capture efficiency per molecule. The capture of several molecules by one helium droplet resulted in the formation of water clusters inside it due to the stronger interaction between water molecules than between them and the helium atoms. Vibrational excitation of the molecules was effected by a color center laser, and the molecular beam was detected using a bolometer.

It appears opportune, before presenting experimental results, to clarify why processes of cluster growth resulting from homogeneous condensation during gas outflow from the nozzle and in helium droplets are substantially different and end in the formation of clusters with different structures. Condensation in a free jet occurs at an earlier stage of gas expansion and the clusters thus formed are cooled then by double collisions. Such cooling is a slow process compared with that inside helium droplets; it promotes cluster transition to the lowest-energy configuration. In contrast, a helium droplets captures water molecules with an interval of a few dozen microseconds. This interval is large enough even compared with the relatively slow relaxation time of intramolecular vibrations of complexes in the gaseous phase [149]. It may be supposed, then, that water molecules are completely cooled between their sequential captures by helium clusters. In this way, for example, a water trimer forms as a water molecule cooled down to 0.38 K [69] attaches to a similarly cold dimer. Larger clusters are formed in the same manner. It was shown by the example of HCN clusters [21] that such a mechanism of cluster growth leads to the formation of only linear chains, where each molecule is captured by a droplet, cooled inside it, and oriented in the course of long-range interactions. Because of cooling inside liquid helium droplets, the condensation energy released during cluster formation is rapidly removed from the cluster. Due to this, the system remains in a local minimum when barriers exist in the intermolecular interaction potential between the geometry associated with particle approaching and the global minimum geometry. As soon as the initial structural rearrangement is completed, further restructuring is hampered by the deficit of thermal energy in a helium droplet.

The structures of water dimers and trimers previously observed in liquid helium [73] are the same as in the gas phase. In particular, trimers are shown to have the most stable cyclic structure. The spectra of these two types of clusters are in excellent agreement with those reported in earlier studies (Fig. 3b). It is well known that a trimer with an open, chain-like structure has minimal energy [150]. Nevertheless, the intensities of O-H bonds in this isomer are lower than the intensities of hydrogen bond modes in cyclic trimers, making its detection by absorption spectra very difficult.

Let us consider now a situation where the fourth water molecule approaches a cyclic trimer. Studies of methanol cluster formation in helium demonstrated [151] that the insertion of the fourth molecule into the ring immediately after the cyclic methanol trimer was formed is hampered for lack of the energy necessary for ring cleavage. The resulting structure is a tetramer in the form of a cyclic trimer with the fourth methanol molecule attached from the outside by the hydrogen bond. A different situation is realized in the case of water clusters. Figure 3b presents spectra of O-H bonds within water clusters formed in liquid helium and spectra of the respective complexes formed in an expanding free jet. As mentioned above, dimer and trimer vibrational bands are completely identical in these two cases, barring the fact that the bands in liquid helium are narrower because of lower temperature. The authors of Refs [24, 25] report seeing absorption bands similar to tetramer and pentamer transition bands in the gaseous phase at 3416 and 3360  $\text{cm}^{-1}$ , respectively [152], meaning that water molecules, unlike methanol [151], cleave the ring and enter the cyclic trimer in the low-energy environment of the helium droplets. Evidently, there are channels with a low-energy barrier for the insertion of water molecules into cyclic trimers and tetramers. The above difference between the two situations probably lies in the fact that the ring readily opens for water clusters as a result of hydrogen atom tunneling through the existing potential barriers, whereas the opening is hindered in the case of methanol, where heavier atoms are involved in the motion.

A most interesting feature of helium droplet spectra is the presence of an additional peak on the red side from the pentamer (denoted by the arrow in Fig. 3b). This peak is lacking in the spectra obtained in the gaseous phase. The authors of the work [24] demonstrated that the peak of interest corresponds to the cyclic isomer of a water hexamer. Because water molecules are embedded in smaller cyclic structures, as shown in Ref. [24], the further growth of a cluster obviously leads to the formation of a cyclic hexamer. Transformation of the cyclic structure of a water hexamer into a hexamer with the cage structure proceeds via numerous rearrangements of hydrogen bonds that are hindered in liquid helium (Fig. 3a) due to the lack of energy necessary for the formation of a three-dimensional cage. At the same time, several other local minima lie below the cyclic hexamer energy. This means that the authors of Refs [24, 25] not only observed the formation of a high-energy isomer of the water hexamer but also used the process of water cluster growth in a helium droplet to control the kinetic system so as to obtain the desired structural isomer.

**3.2.3 Conclusion.** Results of the studies reviewed indicate that helium nanodroplets can be utilized to produce high-spin molecular states of alkali metal atoms and synthesize strongly nonequilibrium structures that are impossible to obtain by any other method. In the synthesis of linear molecular chains inside helium nanodroplets, the cluster diameter places the fundamental limit on the chain length [21]. Also shown is the possibility of using supercooled helium droplets as small-sized reactors possessing catalytic activity for the examination of multistage reactions [26] (see also Refs [5, 9]). Quantum effects, such as tunneling, predominate at low temperatures. Low-temperature reactions constitute a new line of research in selective chemistry, opening up new possibilities for the synthesis of previously unavailable products.

# 4. Selection of molecules embedded in helium nanodroplets

#### 4.1 General remarks

In what follows, we shall consider results of research [28-31] on the possibility of selecting molecules embedded in super-

fluid helium nanodroplets (clusters). The consideration will be focused on the applicability of this method to the laserassisted separation of isotopes. It is worth noting in this context that the isotopically selective infrared (IR) multiphoton dissociation (MPD) of molecules is currently the most widely used technique of all other processes induced by highpower IR laser radiation. The selective dissociation of CF<sub>2</sub>HCl (Freon-22) molecules provided a basis for the largescale separation of carbon isotopes in this country (see, for example, recent review [153] and references cited therein). The potential possibility of applying the same technique to the separation of isotopes of heavier elements (e.g., Si, U, W, Os) gave incentive to numerous studies on IR multiphoton excitation (MPE) and dissociation of molecules in gasdynamically cooled jets and flows [43, 154]. The point is that isotope shifts in IR-absorption spectra of molecules containing the aforementioned elements are relatively small  $(\Delta v_{is} \leq 5-10 \text{ cm}^{-1} \text{ in the case of silicon-containing mole-}$ cules, and  $\Delta v_{is} \leq 1 \text{ cm}^{-1}$  for such molecules as UF<sub>6</sub>, WF<sub>6</sub>, OsO<sub>4</sub>). As a result, linear and multiphoton absorption (MPA) spectra of molecules containing different isotopes strongly or totally overlap. In these conditions, the gain in selectivity of dissociation can be achieved only by cooling molecules in gasdynamic jets and flows. Cooling of a gas leads to a marked narrowing of linear [155, 156] and multiphoton [62, 157, 158] IR absorption bands, structure formation in MPA spectra [159-164], and, as a consequence, the gain in selectivity of dissociation. Selective processes of IR excitation and dissociation of molecules in gasdynamically cooled jets and flows have been considered at length in Ref. [153]. We think that another challenging problem is the development of alternative techniques for the laser separation of isotopes. The possibility of considerably narrowing the IR-absorption spectra of the molecules embedded in helium nanodroplets looks very promising in that it provides a tool for their selective excitation and laser isotope separation. Moreover, processes underlying the selection of molecules inside helium nanodroplets are certainly very interesting by themselves.

#### 4.2 Fundamentals of the method

Experimental [1, 2, 88, 103] and theoretical [48, 133, 134, 165] studies have demonstrated (see also Sections 3.1.1 and 3.1.2) that <sup>4</sup>He nanodroplets (clusters) containing  $N \ge 100$  particles possess the property of superfluidity [39]. Molecules embedded in them freely rotate inside the droplet and have very narrow IR absorption spectra owing to the very low droplet temperature ( $T \sim 0.37$  K [1-3, 6-9]). For example, the total absorption bandwidth of  ${}^{32}SF_6 v_3$  vibrations in a droplet of superfluid helium is only  $\simeq 0.25$  cm<sup>-1</sup> [49, 69, 166] (see Fig. 2). This means that IR absorption spectra are perfectly well 'separated' not only in the case of molecules with relatively large (  $\geq 5-10 \text{ cm}^{-1}$ ) isotope shifts (e.g., SF<sub>6</sub>, SiF<sub>4</sub>) but also for molecules containing heavy elements and characterized by isotope shifts  $\leq 1 \text{ cm}^{-1}$  in IR absorption spectra (OsO<sub>4</sub>, WF<sub>6</sub>, UF<sub>6</sub>, etc.). In other words, the sharp narrowing of linear absorption spectra of molecules embedded in superfluid helium nanodroplets creates prerequisites for their highly selective excitation by IR laser radiation inside these droplets. In fact, this permits exciting only those helium clusters in a beam that contain molecules of the desired isotope composition.

Absorption of radiation by a molecule embedded in a helium nanodroplet heats the droplet and causes a number of atoms to evaporate from it [1-9, 166]. By way of example,



Figure 4. Schematic of a molecule selection experiment [28, 30].

absorption of one quantum of radiation emitted by a CO<sub>2</sub>laser ( $\lambda \sim 10 \mu$ m,  $\hbar \omega \sim 0.12 \text{ eV}$ ) results in the evaporation of almost 200 atoms from a helium droplet [1, 5, 9, 166]. Evaporation of atoms cools the droplet and its temperature becomes stable again at  $T \sim 0.37$  K [1, 7, 9, 51]. Both heating and evaporation occur very soon after photon absorption (in a time  $\leq 10^{-8} - 10^{-9}$  s [51, 166 – 168]). Taken together, these findings may constitute a basis for the selection of molecules embedded in superfluid helium nanodroplets and differing in terms of isotope and component composition.

The essence of the method is as follows (see Fig. 4). A beam of superfluid helium nanodroplets (clusters) containing embedded molecules of a chosen isotope composition is irradiated by intense IR laser radiation resonant with molecular vibrations at a distance  $\Delta x_0$  from the nozzle. In this situation, only those helium clusters that contain resonantly excitable molecules are excited in the beam; in contrast, clusters with molecules that fail to absorb laser radiation remain unexcited. The absorbed energy heats the droplet and causes helium atoms to evaporate. The atoms being evaporated escape from the cluster isotropically. The binding energy per atom (in kelvins) within a helium cluster as a function of *N* is given by the relation [37, 48]

$$\frac{E}{N} = -7.21 + 17.71N^{-1/3} - 5.95N^{-2/3}.$$
(4.1)

In large clusters (with  $N \ge 10^6 - 10^7 \text{ atoms}$ ), the atomic binding energy roughly equals the binding energy in bulk liquid helium ( $\sim 7.2$  K [48]) and decreases with decreasing cluster size (Fig. 5). For example, the atomic binding energy in clusters with  $N \leq 10^3$  and 200 atoms is  $E/N \leq 5.5$  K and 4 K, respectively [48]. In doped clusters, the atomic binding energy is larger than in undoped ones [48]. The interaction between an impurity particle and helium atoms in a given cluster is stronger than between the helium atoms themselves. Therefore, the difference between the binding energies strongly depends on the type of impurities and is especially large in small clusters ( $N \le 100$ ) [48]. Suffice it to say that the atomic binding energy in a helium cluster with  $N \sim 100$ atoms, containing an embedded SF<sub>6</sub> molecule, is  $E/N \sim 10$  K [48] and increases to  $E/N \sim 20$  K in clusters with  $N \sim 40$ .

When a cluster being excited absorbs 5-10 quanta from the field of laser radiation with a wavelength of around 10 µm, its size is diminished by 1000-2000 atoms. If the sizes of molecule-doped helium clusters in a beam amount to  $(2-3) \times 10^3$  atoms, the absorption of IR photons will result in a substantial decrease in their sizes. Conversely, when the



**Figure 5.** Helium cluster energies deduced from the diffusion Monte Carlo theory (crosses) and the Euler – Lagrange theory (circles). The solid line is the approximation derived from relation (4.1) [48].

cluster size is smaller than  $10^3$  atoms, the excitation may result in their complete fragmentation and the formation of free (totally 'stripped') SF<sub>6</sub> molecules. In other words, IR excitation will lead to a significant change in the size distribution of cluster molecules compared with that in the initial beam. In this case, selectively excited clusters will be of substantially smaller size than unexcited ones.

The next step involves the selection of clusters in terms of size [28-31] by means of scattering the cluster beam of interest from a secondary molecular (or atomic) beam [36, 52, 54] that intersects it following laser excitation at a distance of  $\Delta x_0 + \Delta x_1$  from the nozzle (see Fig. 4). A beam of xenon or krypton atoms may be employed for the purpose. Scattering from a secondary beam results in angular splitting of the cluster beam [54] — that is, in a different angular deflection of differently sized constituent clusters. As helium clusters are scattered from a secondary beam, the particles are captured by the droplets with which they collide [36, 52, 54]. The angular momentum of a captured particle is transferred to the droplet. The droplet is heated and losses, through evaporation, a number of atoms depending on the energy of a captured particle (as under the action of laser excitation). In the case of a monatomic gas, as many as 100-200 atoms are evaporated from one cluster; more than 600 atoms may evaporate from a single droplet containing polyatomic molecules, such as  $SF_6$  [52]. The smaller the helium clusters, the larger their angular deflection during scattering from a crossing beam, meaning that selective excitation of molecules inside helium clusters by high-power IR laser radiation and subsequent differential angular deflection of differently sized clusters may be used to select the desired molecules embedded in helium nanodroplets. In what follows, we shall consider the computational procedure [28-30] and analyze the implications of the proposed method for the selection of molecules in terms of their isotope composition using  $SF_6$  as an example.

## 4.3 Size distribution of clusters and computational procedure

The size distribution of clusters within a beam is logarithmically normal [46, 52, 54, 169]:

$$f(N) = \frac{1}{N\sigma\sqrt{2\pi}} \exp\left(-\frac{(\ln N - \mu)^2}{2\sigma^2}\right).$$
(4.2)

It is actually a Gaussian distribution in a frame of reference with a logarithmic abscissa axis.

The mean value  $\bar{N}$  and its standard deviation S are given by the expressions

$$\bar{N} = \exp\left(\mu + \frac{\sigma^2}{2}\right), \quad S = \bar{N}\sqrt{\exp\sigma^2 - 1},$$
 (4.3)

where

$$\mu = \ln\left(\frac{\bar{N}^2}{\sqrt{S^2 + \bar{N}^2}}\right), \quad \sigma^2 = \ln\left(\frac{S^2}{\bar{N}^2} + 1\right)$$

Distribution maximum  $N_{\text{max}}$  and functional dependence  $f(N_{\text{max}})$  are defined as [46, 54]

$$N_{\max} = \exp(\mu - \sigma^2), \quad f(N_{\max}) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(\frac{\sigma^2}{2} - \mu\right).$$
(4.4)

The half-width of an asymmetric distribution is defined as follows

$$\Delta N_{1/2} = \exp\left(\mu - \sigma^2 + \sigma\sqrt{\ln 4}\right) - \exp\left(\mu - \sigma^2 - \sigma\sqrt{\ln 4}\right).$$
(4.5)

It is roughly equal to the mean cluster size [54].

Let us take as the starting point of computations the log normal distribution f(N) with interrelated parameters  $N_{\text{max}} = 1800$ ,  $\bar{N} = 2846$ , and S = 1701. For simplicity, the distribution is normalized to unity:

$$\int f(N) \, \mathrm{d}N = 1 \,. \tag{4.6}$$

This distribution is rather close to the experimental one reported in Ref. [54]. Such a relatively narrow distribution was chosen for obtaining a higher degree of selectivity (see Section 4.5). Let us analyze the transformation of cluster size distribution in the following processes: (1) the capture of molecules in a chamber for cluster doping, (2) selective laser excitation, and (3) the capture of atoms from a scattering beam. Afterwards, we shall derive a relation for the assessment of the selectivity and efficiency of the separation process.

Probabilities of molecular and atomic captures are proportional to the cluster cross section  $\sigma_N$  or  $N^{2/3}$  (because  $\sigma_N \sim N^{2/3}$ ). Let us first consider transformation of the size distribution in the doping process. The size distribution fs(N)for clusters doped with single molecules has the form

$$fs(N) = f(N) \left(\frac{N}{\bar{N}}\right)^{2/3} \left[ \int f(N) \left(\frac{N}{\bar{N}}\right)^{2/3} \mathrm{d}N \right]^{-1}.$$
 (4.7)

The last multiplier in relation (4.7) is introduced in order to restore normalization. In the simplest case, evaporation of m atoms from each cluster due to cluster doping with single molecules leads to the 'displacement' of cluster size distribution:

$$fs1(N) = fs(N+m).$$
 (4.8)

Following laser excitation of the clusters and evaporation of L molecules from each of them, the distribution takes the

form

$$fs1L(N) = fs1(N+L).$$
 (4.9)

Now, we have

$$fs1L\,\mathrm{d}N\neq 1\,.\tag{4.10}$$

When L = 1200, the integral

$$\int fs L \,\mathrm{d}N = I L \tag{4.11}$$

roughly equals 0.95. This distribution will be distorted again in the course of scattering by the deflecting atomic beam. As a result, we obtain

$$fs1Ls(N) = fs1L\left(\frac{N}{\bar{N}}\right)^{2/3} \int fs1L \, dN$$
$$\times \left[\int fs1L\left(\frac{N}{\bar{N}}\right)^{2/3} \, dN\right]^{-1}.$$
(4.12)

A similar transformation takes place in the case of unexcited clusters as well. The last factor in relation (4.12), as in formula (4.7), is introduced to restore normalized distribution. We do not consider here a change in the cluster size distribution accompanying evaporation of helium atoms, caused by the capture of atoms from the deflecting beam, because this change has no effect on the angle of cluster deflection.

Figure 6 demonstrates transformation of cluster size distribution in the above processes. It shows the log normal distribution prior to the capture of molecules (curve 1), after the capture of molecules with zero energy (m = 0, curve 2), and after the capture of molecules and atoms from the deflecting atomic beam (curve 3). Curve 4 describes the distribution of cluster sizes after the capture of molecules and laser excitation, while curve 5 describes the same after the capture of molecules, laser excitation, and the capture of atoms. The total value of the laser-induced effect can be assessed by comparing distributions 3 and 5. It follows from Fig. 6 that, in the ideal case (when m = 0), the difference between distributions 3 (without laser excitation) and 5 (under laser excitation) is very large, especially in the region of small N values. Figure 7 presents the log normal distribution (curve 1) and cluster size distributions (curves 2



**Figure 6.** Transformation of helium cluster size distribution in a beam [28, 29] (see the text for details).



**Figure 7.** Log normal distribution of helium clusters by size (curve 1) and their distribution after the capture of mobile molecules (m = 680) and atoms from the deflecting beam (curve 2). Curve 3 is the size distribution after the capture of mobile molecules (m = 680), laser excitation, and the capture of atoms from the deflecting beam [29, 30].

and 3, respectively) analogous to distributions 3 and 5 in Fig. 6 for the case of SF<sub>6</sub> capture (m = 680). Evidently, the laser-induced effect in this case is not so prominent. Nevertheless, the difference between distributions 2 and 3 is quite large.

The angle of deflection of a cluster beam (with the cluster momentum  $Nm_{\text{He}}v_1$ ) by a monochromatic atomic beam (with the atom momentum  $m_2v_2$ ) equals (see Section 4.4)

$$\theta \approx \frac{m_2 v_2}{N m_{\rm He} v_1}, \quad N = \frac{m_2 v_2}{\theta m_{\rm He} v_1} = \frac{k_0}{\theta}, \quad k_0 = \frac{m_2 v_2}{m_{\rm He} v_1}.$$
 (4.13)

The transformation of cluster size distribution to that by angles can be represented as

$$f(N) dN \to f\left(\frac{k_0}{\theta}\right) \frac{k_0}{\theta^2} d\theta = G(\theta) d\theta.$$
 (4.14)

This implies the fulfillment of the relationship

$$\int f(N) \, \mathrm{d}N = \int G(\theta) \, \mathrm{d}\theta \,. \tag{4.15}$$

In order to obtain a relation for the evaluation of selectivity and efficiency of the process, the following transformations need to be taken into consideration:

$$fs1Ls(N) \to G1L(\theta),$$
 (4.16)

$$fs1s(N) \to G1(\theta)$$
. (4.17)

When clusters are doped with single molecules, angular (differential) selectivity is determined by the relationship

$$S1(\theta) = \frac{G1L(\theta)}{G1(\theta)}.$$
(4.18)

Let us introduce, for simplicity, integral functions of the type

$$IG(\theta) \,\mathrm{d}\theta \equiv \int_{\theta}^{1} G(\varsigma) \,\mathrm{d}\varsigma \,. \tag{4.19}$$

If all doped clusters deflected through the angles larger than  $\theta$  are taken together, integral selectivity may be introduced,



**Figure 8.** Angular distributions of doped helium clusters (where m = 0) in the absence of laser excitation (curve *I*) and under laser-induced excitation (curve *2*). Curves *3* and *4* are the differential and integral selectivities, respectively [29, 30].

which is defined as

$$IS1(\theta) = \frac{IG1L(\theta)}{IG1(\theta)}.$$
(4.20)

The efficiency of the process is possible to find in the following way:

$$E1(\theta) = \frac{IG1L(\theta)}{IG1L(0)}.$$
(4.21)

We also made similar calculations [29, 30] to take into account the influence of the capture of two molecules on the selectivity and efficiency of the process. Selected results will be presented in Section 4.5.4. Figure 8 depicts angular distributions of doped clusters (for m = 0) with laser excitation (curve 2) and without it (curve 1). Also, the figure illustrates differential selectivity (curve 3) and integral selectivity (curve 4). It follows from Fig. 8 that in the limiting (ideal) case (when m = 0) the selectivity is rather high.

#### 4.4 Application to SF<sub>6</sub> molecules

A concrete example is provided by helium clusters containing  $SF_6$  molecules. Natural  $SF_6$  gas contains the following amounts of sulfur isotopes: <sup>32</sup>S — 95.02%, <sup>33</sup>S — 0.75%,  $^{34}$ S — 4.2%, and  $^{36}$ S — 0.017% [170]. The isotope shift in the vibrational band  $v_3$  equals approximately 8.5 cm<sup>-1</sup> per atomic mass unit [171]. The absorption spectrum of  ${}^{32}SF_6 v_3$ vibrations inside helium droplets is fairly well known [49, 69, 166]. The center of the band lies at 946.55  $\text{cm}^{-1}$ , and its total width is around  $0.25 \text{ cm}^{-1}$  [49, 69, 166]. This absorption band matches the 10.6-µm generation band of a CO<sub>2</sub> laser. In particular, the 10R(50) line of a <sup>13</sup>CO<sub>2</sub> molecular laser  $(946.54 \text{ cm}^{-1})$  and the 10R(35) line of a  ${}^{16}\text{O}{}^{13}\text{C}{}^{18}\text{O}$  molecular laser (946.64 cm<sup>-1</sup>) are sufficiently resonant with the absorption band of <sup>32</sup>SF<sub>6</sub> molecules located inside superfluid helium droplets. Certain lines of CO2-laser radiation are resonant with  $v_3$  vibrations of other SF<sub>6</sub> isotopomers inside helium droplets. At the same time, it should be noted that frequencytuned IR lasers, in particular, high-pressure CO<sub>2</sub> lasers with smooth frequency tuning and color center lasers, are optimal for the selective molecular excitation in superfluid helium clusters.

It should be borne in mind that the effective excitation of clusters requires rather high radiation intensity at which the excitation rate is commensurable with the energy relaxation rate, namely

$$\sigma I \tau_{V-T} \sim 1 \,, \tag{4.22}$$

where  $\sigma$  is the absorption cross section of SF<sub>6</sub> molecules in a helium cluster in cm<sup>2</sup>, *I* is the radiation intensity in photons cm<sup>-2</sup> s<sup>-1</sup>, and  $\tau_{V-T}$  is the excitation energy relaxation time in s. Moreover, to enable each cluster to absorb 5 quanta on average, the duration  $\tau_p$  of an exciting pulse must satisfy the condition

$$\tau_{\rm p} \ge 10\tau_{V-T} \,. \tag{4.23}$$

Suppose that the absorption cross section of SF<sub>6</sub> molecules inside a helium cluster equals the gas-kinetic cross section of a molecule ( $\sigma \sim 2.4 \times 10^{-15}$  cm<sup>2</sup> [172]), and that the energy relaxation time  $\tau_{V-T}$  in the cluster is 0.56 ns [166]. Then, the intensity of laser radiation must be  $I \ge 7 \times 10^{23}$  photons (cm<sup>2</sup> s)<sup>-1</sup>, in accordance with relationship (4.22). This condition (4.22) is easy to fulfill if helium clusters are excited by a CO<sub>2</sub> laser with a pulse energy of  $E \ge 10^{-2}$  J and a pulse length of about 100 ns.

Let us consider in more detail the process of cluster deflection during scattering by a molecular (atomic) beam. As mentioned above, a molecule is captured by the superfluid helium cluster with which it collides and its momentum is transferred to the cluster [36, 52, 54]. When a helium cluster with mass  $m_1 = Nm_{\text{He}}$  and velocity  $v_1$  collides with a beam particle of mass  $m_2$  and velocity  $v_2$  and the angle between the primary and secondary beams is  $\alpha$ , the angle  $\theta$  of cluster deflection is given by the relation

$$\tan \theta = \frac{\sin \alpha}{m_1 v_1 / m_2 v_2 + \cos \alpha} \,. \tag{4.24}$$

Let a beam of xenon atoms  $(m_2 = 131.3 \text{ a.m.u.}, v_2 \sim 300 \text{ m s}^{-1})$  serve as the scattering beam. In this case, i.e., when  $m_1 \ge m_2$   $(m_1 = 8,000 \text{ a.m.u.})$ ,  $v_1 \sim 1.6v_2$   $(v_1 \sim 480 \text{ m s}^{-1} \text{ [54]})$  and angle  $\theta$  is small, it is possible to obtain, with quite a high precision, the following relationship

$$\theta = \frac{m_2 v_2}{Nm_{\rm He} v_1} \sin \alpha = \frac{1}{N} \frac{m_2}{m_{\rm He}} \frac{v_2}{v_1} \sin \alpha \,. \tag{4.25}$$

When the angle between the beams of helium clusters and xenon atoms equals  $\alpha = 90^{\circ}$ , it follows from relationship (4.25) that helium clusters containing  $N \sim 2000$  atoms are deflected through the angle  $\theta \sim 0.56^{\circ}$  (0.01 radian). In the above estimates, the mass of SF<sub>6</sub> molecules was considered negligible compared with the mass of the helium droplet into which they were embedded. The selectivity of separation, e.g., between <sup>32</sup>SF<sub>6</sub> and <sup>34</sup>SF<sub>6</sub> molecules, described by the relationship

$$s = \frac{[{}^{32}\text{SF}_6]^* / [{}^{34}\text{SF}_6]^*}{[{}^{32}\text{SF}_6]^0 / [{}^{34}\text{SF}_6]^0}, \qquad (4.26)$$

exceeds unity in the region of angles  $\theta \ge 0.01$  rad, and is below unity in a region of smaller angles (curve 3 in Fig. 8). The square brackets in relationship (4.26) denote the concentrations of molecules deflected through the angle  $\theta$  (indicated by asterisks) and concentrations of molecules in the initial gas.

It is worth noting that free SF<sub>6</sub> molecules resulting from the excitation and subsequent evaporation of small doped helium clusters are deflected by xenon atoms through the angle  $\theta \cong 30^{\circ}$  (in the case of direct collisions). At the same time, the probability of the SF<sub>6</sub> molecule scattering by xenon atoms is considerably smaller than that of cluster scattering because cross sections of these particles are significantly different ( $\sigma_{\text{SF}_6} \sim 2.4 \times 10^{-15} \text{ cm}^2$  [172],  $\sigma_N = \sigma_0 N^{2/3}$  [48], where  $\sigma_0 \sim 2.2 \times 10^{-15}$  cm<sup>2</sup> [48] is the effective cross section of a helium atom in a cluster, and  $\sigma_N$  is the helium cluster cross section). For example, the cross sections of helium clusters containing N = 1000 and N = 100 atoms are  $\sigma_N \sim 2.08 \times$  $10^{-13}$  cm<sup>2</sup> and  $\sigma_N \sim 6 \times 10^{-14}$  cm<sup>2</sup>, respectively [48]. For this reason, the major part of SF<sub>6</sub> molecules are not deflected by a beam of xenon atoms and remain within the straight cluster beam. The majority of the bigger clusters ( $N \ge 10^4$ ) that are deflected through very small angles ( $\theta \leq 0.1^{\circ}$ ), as apparent from relationships (4.24) and (4.25), are also preserved within the same beam; hence, the advantage of performing experiments with the beams of clusters of intermediate size,  $\bar{N} \sim (1-3) \times 10^3$ , that can be deflected through relatively large angles  $\theta \ge 2-3^\circ$ . Also, small clusters tend to more readily evaporate due to their lower atomic binding energy. A beam of small-sized clusters also has a narrower distribution width [54] that permits enhancing the selectivity of their separation by size when the cluster beam is deflected by a secondary beam. Because the scattering beam deflects heavy enough helium clusters through rather small angles  $(1-2^{\circ})$ , experiments should be carried out using wellcollimated cluster beams [54]. Moreover, flight distances after crossing the deflecting and cluster beams must be sufficiently large ( $\Delta x_2 \ge 50$  cm) if a high angular resolution is to be achieved (see Fig. 4). It needs to be emphasized that the use of pulsed IR lasers requires that experiments be conducted with modulated cluster beams in order to realize comparable relative pulse durations for laser and cluster beams and, thus, reach better contrast in molecule selection.

# 4.5 Factors affecting the selectivity and efficiency of the process

4.5.1 The effect of particle velocity distribution in a scattering beam. One of the factors responsible for impaired separation selectivity is the finite width of the velocity distribution of xenon atoms in the scattering beam. We examined [29, 30] the dependence of selectivity on the 'degree of monochromaticity' of the scattering atomic beam. A measure of the 'degree of monochromaticity' was the ratio  $\eta$  of the average atomic velocity in the beam to the spread in velocity, i.e.,  $\eta = \bar{v}/\Delta v$ . The results are presented in Fig. 9 showing that selectivity for  $\eta \ge 5$  is hardly different from that in the case of a monochromatic beam (compare curves 1 and 2). It is significantly (almost thrice) lower than that for a monochromatic beam only when the spread in atomic velocity is very large ( $\eta \leq 2$ ). The values of  $\eta \ge 5$  being easily realized under experimental conditions, it may be assumed that the velocity distribution of atoms within a beam has no appreciable effect on the selectivity of the process. It should also be noted that helium cluster beams themselves are characterized by very narrow velocity distributions ( $\eta \ge 50$ ; see, for instance, Refs [36, 52, 54]). Therefore, the influence of this parameter on selectivity may be neglected.



**Figure 9.** Angular dependences of differential selectivity for a monochromatic deflecting atomic beam ( $\eta = \infty$ , curve *I*) and atomic beams characterized by the parameters  $\eta = 5$  (curve 2) and  $\eta = 2$  (curve 3) (see the text) [30].

4.5.2 The effect of nonselective evaporation of helium atoms. The main factor responsible for impaired selectivity is the nonselective thermal evaporation of atoms resulting from the capture of energy-carrying molecules. This effect is illustrated by Fig. 10 showing angular dependences of integral selectivity and efficiency for three different numbers of helium atoms evaporating from clusters involving captured molecules (m = 0, 200, and 600). It can be seen that selectivity drops sharply with a rise in the number of evaporating helium atoms. This observation implies the necessity of cooling gas in a capture chamber in the case of large molecules (such as SF<sub>6</sub>, OsO<sub>4</sub>, and UF<sub>6</sub>). Indeed, the capture of an SF<sub>6</sub> molecule at 150 K causes evaporation of only 160-170 atoms from a cluster. Then, as follows from Fig. 10, the integral selectivity for the angles  $\theta \ge 0.04$  rad is almost one order of magnitude larger than that in molecule capture at room temperature.



**Figure 10.** Angular dependences of efficiency (curves 1-3) and integral selectivity (curves 1S-3S) for different numbers of helium atoms evaporating from clusters with captured molecules (m = 0, 200, and 680). Curves 4 and 4S are angular dependences of efficiency and integral selectivity for the case of a cluster beam containing singly and doubly doped clusters in the ratio 2:1 (m = 200) [30].

It should be emphasized here that the finite length  $\Delta x_{int}$  of the interaction region for a cluster beam and a scattering atomic beam ( $\Delta x_{int} \cong 1 \text{ cm}$ ) may also contribute to the impairment of the process selectivity. However, this impairment is insignificant (on the order of  $\Delta x_{int}/\Delta x_2$ ) when the distance between the interaction region and the detector (or the slit) is relatively large ( $\Delta x_2 \ge 50 \text{ cm}$ ); it becomes even smaller with increasing  $\Delta x_2$ .

4.5.3 The effect of Poisson distribution of molecules inside droplets. Let us consider the factors important in terms of efficiency of the separation process. Impaired efficiency (and selectivity, too) is first and foremost related to the fact that the probability of capturing impurity particles by helium clusters follows the Poisson distribution [52] [see relationship (2.1)]. For this reason, only part of the helium clusters in a beam is doped with single molecules. Under different experimental conditions (such as gas pressure and the interaction length in the capture chamber), a cluster beam may contain quite a few helium droplets which captured two or more SF<sub>6</sub> molecules that in turn form SF<sub>6</sub> clusters inside each droplet. Helium clusters that capture more than one molecule are smaller in size than singly doped clusters because they lose more atoms through evaporation. When the cluster beam is scattered from the atomic beam, such clusters are deflected through larger angles, which may result in the essentially impaired selectivity of the process. Therefore, experiments should be carried out with a minimal fraction of helium clusters containing several SF<sub>6</sub> molecules. In this case, the total number of doped helium clusters in the beam also decreases, naturally affecting process efficiency. As is apparent from Fig. 10, the two calculated parameters, selectivity and efficiency (for the angles  $\theta \ge 0.02$  rad), in the case of singly doped clusters are approximately twice as large as in the case when the number of clusters that capture two molecules each amounts to 50% of those containing a single molecule.

### 4.5.4 The effect of double collisions between clusters and atoms.

Let us also consider the influence of double collisions between helium clusters and atoms of a crossing beam on the efficiency and selectivity of a separation process. Secondary collisions of helium clusters with atoms are quite possible at a sufficiently high particle density (and/or interaction length  $\Delta x_{int}$ ) in the deflecting atomic beam. Naturally, such collisions influence both the efficiency and selectivity of the process. In fact, double collisions must have the same effect as double scattering of a cluster beam by the same atomic beam. Therefore, calculations should be made bearing in mind the evaporation of about 200 helium atoms ( $m \sim 200$ , when a xenon atom is captured from the beam [51]) from a cluster following the capture of the first atom from the scattering beam and transformation of the size distribution (multiplication by  $N^{2/3}$ ) resulting from the capture of the second atom.

Cumbersome formulas describing sequential transformation of the above distributions are not presented here. Instead, we shall analyze a more pessimistic result [30] obtained directly from the transformation of cluster size distributions, determined with regard to the aforementioned factors, into the angular distribution. However, the quantity  $2k_0$  is inserted instead of  $k_0$  in relationships (4.13) and (4.14) because the total angle through which the clusters are deflected in consequence of double collisions is approximately twice as big. Data on the selectivity and efficiency of



**Figure 11.** Angular dependences of integral selectivity (curves *IS* and *2S*) and efficiency (curves *I* and *2*) for the case of single (curves *IS* and *I*) and double (curves *2S* and *2*) collisions between helium clusters and atoms of the deflecting atomic beam. The number of helium atoms evaporating from clusters with captured molecules and atoms is m = 200 and  $m_1 = 200$ , respectively [30].

the separation process taking into account all the above factors [29, 30] are summarized in Fig. 11 (curves 2S and 2) together with the results for single collisions (curves 1S and 1). It appears from the figure that double collisions substantially decrease the selectivity and slightly enhance the efficiency of the process as compared with single ones. Specifically, the efficiency being equal (E = 0.1), selectivity in the case of single collisions is almost 2.5 times that in double collisions. This means that a higher selectivity of the process can be achieved by conducting experiments under conditions of small double-collision events, when the atomic number density in the deflecting beam is relatively low.

#### 4.6 Evaluation of the yield of enriched products

Since the process being considered has potential implications for the practical separation of isotopes, it is interesting to evaluate the yield of 'enriched' products. True, only rough estimates are feasible. Therefore, the values below cannot be used as the initial data for the calculation of the real capacity of the process; it can only be deduced from experimental findings. Nevertheless, we believe that even an approximate assessment of the yield of the final products is expedient.

What follows will be based [30] on the intensities of real helium cluster beams and the throughput of the diffusion pumps used for their production [5, 9]. As mentioned in Section 2.2, a gas flux in 'standard production units' with helium nanodroplets is around 4 atm  $cm^3 s^{-1}$ (~ 0.16 mmol s<sup>-1</sup>). This value (4 atm cm<sup>3</sup> s<sup>-1</sup>), corresponding to approximately 10<sup>20</sup> particles per second, is taken as the initial one for further estimations. Let the mean cluster size in a beam be  $\overline{N} = 10^3$ . Were each cluster in the beam doped with a single SF<sub>6</sub> molecule, the SF<sub>6</sub> flux would be  $10^{17}$  molecules per second. Let us consider now factors responsible for the decrease in this number. Let a gas flow be formed by a twodimensional (slotted) nozzle with a slot width of 50 cm. We should recall that exactly such nozzles are employed, for instance, in studies of excitation and isotopically selective IR multiphoton dissociation of UF<sub>6</sub> [173] and SF<sub>6</sub> [163, 164] molecules. Slot type nozzles appear to be most suitable for the selection of molecules by this method (see Section 4.5). It is possible to extract about 10% of the clusters from a jet by forming a pencil beam. Not more than 20% of the clusters can be doped with single molecules. We will consider a process with a continuous cluster beam in which clusters are excited by a pulsed CO<sub>2</sub> laser with a pulse repetition rate  $f \sim 500$  Hz. Notice that CO<sub>2</sub> lasers operating at such a pulse repetition rate are employed for the large-scale separation of carbon isotopes [174, 175].

The fraction of irradiated clusters in the beam (relative pulse duration) is given by

$$c_{\rm f} = \frac{\Delta x_{\rm irr} f}{v_1} \,. \tag{4.27}$$

Here,  $\Delta x_{irr}$  and  $v_1$  are the length of the irradiated volume and the velocity of the cluster beam, respectively. The beam speed is about 500 m s<sup>-1</sup> [52, 54]. If the laser pulse energy is, for instance, 2 J and the laser beam is perpendicular to the cluster beam velocity, an irradiated path of length  $\Delta x_{\rm irr} \sim 20$  cm (or laser beam cross section  $20 \times 1$  cm<sup>2</sup> in the irradiation area) is easy to realize. In this case, the energy flux is around  $0.1 \,\mathrm{J}\,\mathrm{cm}^{-2}$ or one order of magnitude higher than the energy flux density needed to efficiently excite clusters [see relationship (4.22)]. Hence, the irradiation relative pulse duration is  $c_{\rm f} \sim 0.2$ . Finally, it should be taken into consideration that only 20% of the clusters at most can be deflected by the scattering atomic beam as a result of single collisions. This quantity is equivalent to approximately  $10^{-3}$  parts of the total number of clusters in the beam, or  $10^{14}$  SF<sub>6</sub> molecules per second. Bearing in mind that the efficiency of the process  $E \sim 0.1$ when the integral selectivity  $IS \sim 10$  (see Fig. 10, curves 2S and 2 at m = 200), the yield of the enriched product (SF<sub>6</sub>) is about  $10^{13}$  molecules per second or  $3.6 \times 10^{16}$  molecules per hour, which is an equivalent to approximately 0.01 mg  $h^{-1}$ . Certainly, it is a very low capacity even if the above estimates refer to a single small production unit equipped with one diffusion pump.

# 4.7 Comparison with the technique of IR multiphoton dissociation of molecules

Let us now compare the results obtained by the method of interest and the well-known technique of IR multiphoton dissociation of molecules [63, 153]. It is worthwhile to note that the latter approach is also characterized by the low yield of enriched products when applied to the multiphoton dissociation of SF<sub>6</sub> and UF<sub>6</sub> molecules in gasdynamically cooled jets and flows [63, 153]. For example, the laser-assisted separation of uranium isotopes by means of IR multiphoton dissociation of  $UF_6$  molecules is accomplished using rather a poor mixture (the concentration ratio of UF<sub>6</sub> to gas-carrier molecules is below 0.01 [173, 176]) in order to increase the efficiency of gas cooling in gasdynamic flows. At the same time, effective excitation and dissociation of molecules require rather high laser energy flux densities (at least  $\ge 1 \text{ J cm}^{-2}$  for the dissociation of previously excited molecules) resulting in a decrease in the irradiation relative pulse duration (to  $c_{\rm f} \leq 0.001$ ). High selectivities ( $S \sim 3-5$ ) appear feasible only in association with low yields (  $\leq 0.01$ ). However, isotope separation by IR multiphoton dissociation of molecules in gasdynamic flows is admissible at a pressure two orders of magnitude higher in the chamber (about  $10^{-2}$  Torr) and equally more intense gas flows (i.e., around  $10^{22}$  particles per second). These estimates (taking into account all the aforementioned factors) indicate that the

product yield may be as large as 10<sup>15</sup> molecules per second or  $3.6 \times 10^{18}$  molecules per hour. These values are two orders of magnitude higher than the ones obtained with cluster beams. At the same time, the high selectivity of dissociation in the case of molecules with small isotope shifts is achievable only in multifrequency IR fields, which markedly complicates the isotope separation process. Moreover, it requires realization of high energy flux densities and a much greater (by two orders of magnitude) contribution of laser photons to the dissociation of molecules because the process is characterized by a high dissociation energy and low selectivity (the majority of laser photons being utilized to excite molecules containing a nontarget isotope). In contrast, selective excitation and dissociation of clusters in cluster beams require only moderate single-frequency laser radiation. Therefore, larger volumes can be irradiated by one laser in comparison with the case of molecular dissociation. Finally, higher selectivities are attainable with the helium cluster method under consideration.

It needs to be noted in connection with the above estimates that the building of industrial production units for the laser-assisted separation of uranium isotopes by IR multiphoton dissociation of UF<sub>6</sub> molecules is deemed to be lacking in cost-effectiveness (at the modern level of laser technologies) [177]. Further studies on currently available experimental facilities are needed to elucidate the entire set of issues pertaining to both the development of laser systems and optimization of gasdynamic flows. Therefore, the methods described in this review can presently find practical applications only for laser separation of exotic molecules and/or small amounts of substances. At the same time, their wider use in the future cannot be excluded.

To conclude this section, it should be noted that an advantage of the method of interest is the possibility of using microwave radiation to selectively excite molecules embedded in droplets. Experimental results (see, for instance, Refs [5, 9] and references cited therein) indicate that the application of high-power microwave radiation for excitation of molecules inside helium droplets and their evaporation produces the same effects as IR laser radiation. The efficiency of the process can be enhanced by forming a cluster beam during gas outflow through a slot type nozzle and/or diaphragm. This approach makes it possible to substantially increase the beam cross section and, consequently, the number of helium clusters in it. The main shortcomings of the method are the technical difficulties in its realization and relatively low capacity.

### 5. Conclusions

Research completed thus far has demonstrated considerable opportunities for using helium nanodroplets for the spectroscopy and investigations into the properties of superfluid helium at the microscopic level and into many atomic and molecular physico-chemical processes at ultralow temperatures. Spectroscopic techniques for the detection of molecules embedded in helium nanodroplets has provided evidence that liquid helium constitutes a soft and practically nonperturbing ultracold matrix. An advantage of such a matrix lies in the fact that all 'hot' vibrational states and the majority of rotational states of the particles are frozen at the temperature of a liquid droplet. Due to its softness, the helium matrix adapts its structure near a molecule to the latter's structure. These properties of a quantum liquid comprising helium droplets makes them a unique medium for high-resolution spectroscopy. Molecules embedded in droplets exhibit very narrow IR-absorption spectra (bandwidth  $\leq 0.3 \text{ cm}^{-1}$ ) by virtue of the ultimately low temperature of helium droplets, creating prerequisites for highly selective laser excitation of the desired molecules inside helium droplets.

Spectroscopic techniques have made it possible to elucidate and understand many properties of atoms and molecules located inside and at the surface of liquid superfluid helium droplets, as well as the nature of their interactions with the surrounding helium atoms. Moreover, these methods provide a deeper insight into the properties of small liquid helium droplets themselves. Specifically, the spectroscopic methods were used to study elementary excitations in helium droplets and measure their temperature.

It was shown that helium nanodroplets are possible to employ for obtaining high-spin molecular states of alkali metals and for the synthesis of strongly non-equilibrium structures that cannot be prepared by any other method. Helium nanodroplets are small-sized isothermal reactors. They may be utilized to examine chemical reactions supported by tunneling with minimal perturbations of the solvent. Low-temperature reactions are a new line of research in selective chemistry, opening up prospects for the synthesis of new products.

The available results of investigations indicate that the selective excitation of superfluid helium clusters containing embedded molecules by intense IR laser radiation and their subsequent size-dependent angular deflection by a scattering atomic beam allows for the selection of molecules in isotope (component) composition.

Important advantages of superfluid helium droplets (clusters) for the selection of molecules by the method under consideration include the low atomic binding energy ( $\leq 7.2$  K [48]) and free molecular rotation within clusters, as well as low cluster temperature and the resulting narrow absorption spectra of the molecules enclosed in them. The first factor accounts for the fact that absorption of a single IR photon leads to a significant decrease in the cluster size. As a result, the atomic binding energy also falls (see Fig. 5); this, in turn, moderates pumping energy requirements.

Unlike isotopically selective IR multiphoton dissociation of molecules (see, for instance, Refs [63, 153, 178–181] and references cited therein), applicable only to polyatomic molecules, selection of molecules embedded in helium nanodroplets is also suitable for small, e.g., diatomic molecules. Owing to free molecular rotation, IR-absorption spectra of small molecules (including diatomic and triatomic ones) inside superfluid helium nanodroplets exhibit separate narrow vibrational – rotational lines [1, 5, 9], which provides a basis for the highly selective excitation of such molecules. Moreover, doping helium clusters with small molecules does not lead to as marked a distortion of their size distribution as in the case of large molecules, with the result that better selectivities are attained during cluster excitation by laser radiation (see Fig. 10).

To conclude, further experiments with helium nanodroplets can be expected to bring to light many new interesting effects and open up possibilities for the examination of physico-chemical processes on the atomic and molecular levels at ultimately low temperatures.

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#### References

- 1. Toennies J P, Vilesov A F, Whaley K B Phys. Today 54 (2) 31 (2001)
- 2. Lugovoj E et al., in *Atomic and Molecular Beams: The State of the Art 2000* (Ed. R Campargue) (Berlin: Springer-Verlag 2001) p. 755
- 3. Grebenev S et al. *Physica B* **280** 65 (2000)
- 4. Grebenev S et al. *Science* **289** 1532 (2000)
- 5. Callegari C et al. J. Chem. Phys. 115 10090 (2001)
- 6. Stienkemeier F, Vilesov A F J. Chem. Phys. 115 10119 (2001)
- 7. Grebenev S, Toennies J P, Vilesov A F Science 279 2083 (1998)
- 8. Toennies J P, Vilesov A F Annu. Rev. Phys. Chem. 49 1 (1998)
- Makarov G N Usp. Fiz. Nauk 174 225 (2004) [Phys. Usp. 47 217 (2004)]
- 10. Kwon Y et al. J. Chem. Phys. 113 6469 (2000)
- 11. Northby J A J. Chem. Phys. 115 10065 (2001)
- 12. Toennies J P, Vilesov A F Angew. Chem., Int. Ed. 43 2622 (2004)
- 13. Paesani F, Kwon Y, Whaley K B Phys. Rev. Lett. 94 153401 (2005)
- 14. Paesani F, Whaley K B J. Chem. Phys. 121 4180 (2004)
- 15. Paesani F, Whaley K B J. Chem. Phys. 121 5293 (2004)
- 16. Lehnig R et al. J. Chem. Phys. 121 9396 (2004)
- 17. Tang J et al. Phys. Rev. Lett. 92 145503 (2004)
- 18. Zillich R E, Kwon Y, Whaley K B Phys. Rev. Lett. 93 250401 (2004)
- 19. Çarçabal P et al. J. Chem. Phys. **120** 6792 (2004)
- 20. Hoshina H et al. Phys. Rev. Lett. 94 195301 (2005)
- 21. Nauta K, Miller R E Science 283 1895 (1999)
- 22. Stienkemeier F et al. Phys. Rev. Lett. 74 3592 (1995)
- 23. Stienkemeier F et al. J. Chem. Phys. 102 615 (1995)
- 24. Nauta K, Miller R E Science 287 293 (2000)
- 25. Burnham C J et al. J. Chem. Phys. 117 1109 (2002)
- 26. Lugovoj E, Toennies J P, Vilesov A J. Chem. Phys. 112 8217 (2000)
- 27. Pörtner N, Vilesov A F, Havenith M Chem. Phys. Lett. 368 458 (2003)
- Lokhman V N, Makarov G N, in Sbornik Dokladov IX Vserossiiskoi (Mezhdunarodnoi) Nauchnoi Konf. "Fiziko-khimicheskie Protsessy pri Selektsii Atomov i Molekul", g. Zvenigorod, 2004 (Collected Reports at the IX All-Russian (Intern.) Conf. "Physico-chemical Processes in Selection of Atoms and Molecules", Zvenigorod, 2004) (Ed. Yu A Kolesnikov) (M.: TsNIIatominform, 2004) p. 121
- 29. Lokhman V N, Makarov G N Chem. Phys. Lett. 398 453 (2004)
- Lokhman V N, Makarov G N Zh. Eksp. Teor. Fiz. 127 570 (2005) [JETP 100 505 (2005)]
- Lokhman V N, Makarov G N, in *Tezisy Dokladov XVII Simpoziuma* "Sovremennaya Khimicheskaya Fizika", g. Tuapse, 18–29 Sentyabrya 2005 (Abstracts of XVII Symp. "Modern Chemical Physics", Tuapse, 18–29 September 2005) p. 42
- 32. Hartmann M et al. *Science* **272** 1631 (1996)
- 33. Lehmann K K, Scoles G Science **279** 2065 (1998)
- 34. Nauta K, Miller R E J. Chem. Phys. 115 10254 (2001)
- 35. Callegari C et al. J. Chem. Phys. 113 10535 (2000)
- 36. Gspann J Z. Phys. B 98 405 (1995)
- 37. Dalfovo F, Stringari S J. Chem. Phys. 115 10078 (2001)
- 38. Dalfovo F et al. Rev. Mod. Phys. 71 463 (1999)
- 39. Kapitza P L Zh. Eksp. Teor. Fiz. 11 1, 581 (1941)
- 40. Kamerlingh Onnes H Commun. Phys. Lab. Univ. Leiden 105 3 (1908)
- 41. Scoles G (Ed.) *Atomic and Molecular Beam Methods* Vol. 1 (New York: Oxford Univ. Press, 1988)
- 42. Scoles G (Ed.) *Atomic and Molecular Beam Methods* Vol. 2 (New York: Oxford Univ. Press, 1992)
- Anderson J B "Molecular beams from nozzle sources", in *Molecular Beams and Low Density Gasdynamics* (Gasdynamics, Vol. 4, Ed. P P Wegener) (New York: M. Dekker, 1974) p. 1
- Hagena O F "Cluster beams from nozzle sources", in *Molecular Beams and Low Density Gasdynamics* (Gasdynamics, Vol. 4, Ed. P P Wegener) (New York: M. Dekker, 1974) p. 93
- Kappes M, Leutwyler S "Molecular beams of clusters", in *Atomic and Molecular Beam Methods* Vol. 1 (Ed. G Scoles) (New York: Oxford Univ. Press, 1988) p. 380
- 46. Pauly H Atom, Molecule, and Cluster Beams II Cluster Beams, Fast and Slow Beams, Accessory Equipment, and Applications (Springer

Ser. on Atomic, Optical, and Plasma Physics, Vol. 32) (New York: Springer, 2000)

- Makarov G N Usp. Fiz. Nauk 176 121 (2006) [Phys. Usp. 49 117 (2006)]
- 48. Chin S A, Krotscheck E *Phys. Rev. B* **52** 10405 (1995)
- 49. Harms J et al. J. Mol. Spectrosc. 185 204 (1997)
- Gspann J, in *Physics of Electronic and Atomic Collisions: Invited Papers of the XII Intern. Conf., Gatlinburg, Tenn., USA, 1981* (Ed. S Datz) (Amsterdam: North-Holland, 1982) p. 79
- 51. Brink D M, Stringari S Z. Phys. D 15 257 (1990)
- 52. Lewerenz M, Schilling B, Toennies J P J. Chem. Phys. 102 8191 (1995)
- 53. Knuth E L J. Chem. Phys. 107 9125 (1997)
- Lewerenz M, Schilling B, Toennies J P Chem. Phys. Lett. 206 381 (1993)
- 55. Buchenau H et al. J. Chem. Phys. 92 6875 (1990)
- 56. Lindinger A et al. Z. Phys. Chem. 215 401 (2001)
- 57. Close J D et al. Chem. Phys. Lett. 276 393 (1997)
- 58. Nauta K, Moore D T, Miller R E Faraday Discuss. 113 261 (1999)
- 59. Gough T E, Miller R E, Scoles G Appl. Phys. Lett. 30 338 (1977)
- 60. Bassi D et al. J. Chem. Phys. **74** 2221 (1981)
- 61. Apatin V M et al. Appl. Phys. B 29 273 (1982)
- Apatin V M, Makarov G N Zh. Eksp. Teor. Fiz. 84 15 (1983) [Sov. Phys. JETP 57 8 (1983)]
- Makarov G N Usp. Fiz. Nauk 173 913 (2003) [Phys. Usp. 46 889 (2003)]
- 64. Miller R E J. Phys. Chem. 90 3301 (1986)
- 65. Huisken F Adv. Chem. Phys. 81 63 (1992)
- 66. Bacic Z, Miller R E J. Phys. Chem. 100 12945 (1996)
- 67. Goyal S, Schutt D L, Scoles G Phys. Rev. Lett. 69 933 (1992)
- 68. Goyal S, Schutt D L, Scoles G J. Phys. Chem. 97 2236 (1993)
- 69. Hartmann M et al. Phys. Rev. Lett. 75 1566 (1995)
- 70. Grebenev S et al. J. Chem. Phys. 114 617 (2001)
- 71. Grebenev S et al. Faraday Discuss. 118 19 (2001)
- 72. Blume D et al. J. Chem. Phys. 105 8666 (1996)
- 73. Fröchtenicht R et al. J. Chem. Phys. 105 6128 (1996)
- 74. Huisken F et al. J. Chem. Phys. **111** 2978 (1999)
- 75. Behrens M et al. J. Chem. Phys. 109 5914 (1998)
- 76. Nauta K et al. Science 292 481 (2001)
- 77. Callegari C et al. J. Chem. Phys. 113 4636 (2000)
- 78. Fröchtenicht R, Toennies J P, Vilesov A Chem. Phys. Lett. 229 1 (1994)
- 79. Reinhard I et al. *Phys. Rev. Lett.* **82** 5036 (1999)
- 80. Conjusteau A et al. J. Chem. Phys. 113 4840 (2000)
- 81. Friedrich B, Pullman D P, Herschbach D R J. Phys. Chem. 95 8118 (1991)
- 82. Nauta K, Miller R E Phys. Rev. Lett. 82 4480 (1999)
- Townes C H, Schawlow A L *Microwave Spectroscopy* (New York: Dover Publ., 1975)
- 84. Loesch H J, Remscheid A J. Chem. Phys. 93 4779 (1990)
- Nauta K, Miller R E, in *Atomic and Molecular Beams: The State of the Art 2000* (Ed. R Campargue) (Berlin: Springer-Verlag, 2001) Pt. VI. 3, p. 775
- 86. Harms J et al. J. Chem. Phys. 110 5124 (1999)
- 87. Grebenev S et al. J. Chem. Phys. 112 4485 (2000)
- 88. Pi M, Mayol R, Barranco M Phys. Rev. Lett. 82 3093 (1999)
- Tabbert B, Günther H, zu Putlitz G J. Low. Temp. Phys. 109 653 (1997)
- 90. Kanorsky S I, Weis A Adv. Atom. Mol. Opt. Phys. 38 88 (1998)
- 91. Hartmann M et al. Phys. Rev. Lett. 76 4560 (1996)
- 92. Hartmann M et al. J. Phys. Chem. A 105 6369 (2001)
- 93. Close J D et al. Chem. Phys. Lett. 276 393 (1997)
- 94. Callegari C et al. J. Phys. Chem. A 102 95 (1998)
- 95. Kim C et al. J. Low Temp. Phys. 113 1097 (1998)
- 96. Yurgenson S et al. Eur. Phys. J. D 9 153 (1999)
- 97. Harms J, Toennies J P J. Low Temp. Phys. 113 501 (1998)
- 98. Stienkemeier F et al. Z. Phys D 38 253 (1996)
- 99. Stienkemeier F, Meier F, Lutz H O Eur. Phys. J. D 9 313 (1999)
- 100. Hartmann M et al. Chem. Phys. 239 139 (1998)
- 101. Higgins J et al. J. Phys. Chem. A 102 4952 (1998)
- 102. Lindinger A, Toennies J P, Vilesov A F J. Chem. Phys. 110 1429 (1999)
- 103. Pörtner N, Toennies J P, Vilesov A F J. Chem. Phys. 117 6054 (2002)

- 104. Stienkemeier F et al. Phys. Rev. Lett. 83 2320 (1999)
- 105. Diederich T et al. Phys. Rev. Lett. 86 4807 (2001)
- 106. Döppner T et al. Eur. Phys. J. D 16 13 (2001)
- 107. Federmann F et al. Eur. Phys. J. D 9 11 (1999)
- 108. Federmann F et al. Phys. Rev. Lett. 83 2548 (1999)
- 109. Schulz C P, Claas P, Stienkemeier F Phys. Rev. Lett. 87 153401 (2001)
- Kleinekathöfer U, Lewerenz M, Mladenović M Phys. Rev. Lett. 83 4717 (1999)
- 111. Hansen J P, Pollock E L Phys. Rev. A 5 2214 (1972)
- 112. Wisdom J, Hartquist T W, Lane N F Phys. Rev. B 14 4205 (1976)
- 113. Kanorsky S I et al. Phys. Rev. B 50 6296 (1994)
- 114. Kinoshita T, Fukuda K, Yabuzaki T Phys. Rev. B 54 6600 (1996)
- 115. Reho J et al. J. Chem. Phys. 112 8409 (2000)
- 116. Beijersbergen J H M, Hui Q, Takami M Phys. Lett. A 181 393 (1993)
- 117. Takahashi Y et al. Phys. Rev. Lett. 71 1035 (1993)
- 118. Ancilotto F et al. Z. Phys. B 98 323 (1995)
- 119. Bauer H et al. *Phys. Lett. A* **146** 134 (1990)
- 120. Lewerenz M (unpublished)
- Lindinger A, Toennies J P, Vilesov A F Phys. Chem. Chem. Phys. 3 2581 (2001)
- 122. Hartmann M et al. Phys. Chem. Chem. Phys. 4 4839 (2002)
- 123. Slenczka A et al. J. Chem. Phys. 115 10199 (2001)
- Personov R I, in Spectroscopy and Excitation Dynamics of Condensed Molecular Systems (Modern Problems in Condensed Matter Sci., Vol. 4, Eds V M Agranovich, R M Hochstrasser) (Amsterdam: North-Holland, 1983) p. 555
- Almond M J, Downs A J Spectroscopy of Matrix-Isolated Species (Adv. in Spectroscopy, Vol. 17, Eds R J H Clark, R E Hester) (Chichester: Wiley, 1989)
- Pryce M H L, in *Phonons in Perfect Lattice and in Lattices with Point Imperfections* (Ed. R W H Stevenson) (Edinburgh: Oliver & Boyd, 1966)
- 127. Wilks J, Betts D S *An Introduction to Liquid Helium* 2nd ed. (Oxford: Clarendon Press, 1987)
- Bennemann K H, Ketterson J B, in *The Physics of Liquid and Solid Helium* (Interscience Monographs and Texts in Physics and Astronomy, Vol. 29, Eds K H Bennemann, J B Ketterson) (New York: Wiley, 1976)
- 129. Keller W E Helium-3 and Helium-4 (New York: Plenum Press, 1969)
- 130. Landau L J. Phys. USSR 11 91 (1947)
- Landau L D Zh. Eksp. Teor. Fiz. 11 592 (1941); Usp. Fiz. Nauk 93 495 (1967); J. Phys. USSR 5 71 (1941)]
- 132. Pörtner N, Toennies J P, Vilesov A F J. Chem. Phys. 117 6054 (2002)
- 133. Casas M et al. Z. Phys. D **35** 67 (1995)
- 134. Rama Krishna M V, Whaley K B J. Chem. Phys. 93 746 (1990)
- Huisken F, Kaloudis M, Vigasin A A Chem. Phys. Lett. 269 235 (1997)
- 136. Li L, Rice S F, Field R W J. Chem. Phys. 82 1178 (1985)
- 137. Diemer U, Gress J, Demtröder W Chem. Phys. Lett. 178 330 (1991)
- 138. Dalfovo F Z. Phys. D 29 61 (1994)
- 139. Lerner P B, Cole M W, Cheng E J. Low Temp. Phys. 100 501 (1995)
- 140. Liu K et al. Nature 381 501 (1996)

143.

144.

145.

146.

148.

149.

153.

154.

(1987)

1988) p. 14

141. Liu K, Brown M G, Saykally R J J. Phys. Chem. A 101 8995 (1997)

Speedy R J, Madura J D, Jorgensen W L J. Phys. Chem. 91 909

Xantheas S S, Dunning T H (Jr.) J. Chem. Phys. 99 8774 (1993)

Pedulla J M, Kim K, Jordan K D Chem. Phys. Lett. 291 78 (1998)

Makarov G N Usp. Fiz. Nauk 175 41 (2005) [Phys. Usp. 48 37 (2005)]

Miller D R "Free jet sources", in Atomic and Molecular Beam

Methods Vol. 1 (Ed. G Scoles) (New York: Oxford Univ. Press,

Applications of Lasers Vol. 11 (Ed. C B Moore) (New York:

156. Levy D H, Wharton L, Smalley R E, in Chemical and Biochemical

142. Belch A C, Rice S A J. Chem. Phys. 86 5676 (1987)

Mhin B J et al. Chem. Phys. Lett. 176 41 (1991)

Nauta K, Miller R E J. Chem. Phys. 111 3426 (1999)

152. Huisken F, Kaloudis M, Kulcke A J. Chem. Phys. 104 17 (1996)

147. Xantheas S S J. Chem. Phys. 102 4505 (1995)

Miller R E Science 240 447 (1988)

150. Xantheas S S Philos. Mag. B 73 107 (1996)

155. Jensen R J et al. Laser Focus 12 (5) 51 (1976)

Academic Press, 1977) p. 1

151. Behrens M et al. J. Chem. Phys. 111 2436 (1999)

- 157. Apatin V M, Makarov G N Appl. Phys. B 28 367 (1982)
- 158. Radloff W, Stert V, Ritze H-H Appl. Phys. B 38 179 (1985)
- 159. Borsella E et al. Chem. Phys. Lett. 93 523 (1982)
- Alimpiev S S et al. Kvantovaya Elektron. 10 562 (1983) [Sov. J. Quantum Electron. 13 331 (1983)]
- 161. Bassi D et al. Laser Chem. 5 143 (1985)
- 162. Apatin V M, Lokhman V N, Makarov G N Opt. Spektrosk. 63 762 (1987) [Opt. Spectrosc. 63 452 (1987)]
- 163. Makarov G N et al. Appl. Phys. B 65 583 (1997)
- Makarov G N, Lokhman V N, Ronander E Opt. Spektrosk. 83 232 (1997) [Opt. Spectrosc. 83 215 (1997)]
- 165. Sindzingre P, Klein M L, Ceperley D M Phys. Rev. Lett. 63 1601 (1989)
- 166. Hartmann M et al. J. Chem. Phys. 110 5109 (1999)
- 167. Nauta K, Miller R E J. Chem. Phys. 115 8384 (2001)
- 168. Madeja F et al. J. Chem. Phys. 116 2870 (2002)
- 169. Harms J, Toennies J P, Dalfovo F Phys. Rev. B 58 3341 (1998)
- Lide D R (Ed.-in-Chief) CRC Handbook of Chemistry and Physics 74th ed. (Boca Raton: CRC Press, 1993–1994)
- 171. McDowell R S et al. Spectrochim. Acta A 42 351 (1986)
- 172. Burak I, Steinfeld J I, Sutton D G J. Quant. Spectr. Rad. Trans. 9 959 (1969)
- 173. Okada Y et al. Appl. Phys. B 59 475 (1994)
- 174. Baranov V Yu, Dyad'kin A P, in *Izotopy: Svoistva, Poluchenie, Primenenie* (Isotopes: Properties, Preparation, Applications) (Ed. V Yu Baranov) (Moscow: IzdAT, 2000) p. 343
- 175. Dyad'kin A P et al., in Sbornik Dokladov VIII Vserossiiskoi (Mezhdunarodnoi) Nauchnoi Konf. "Fiziko-khimicheskie Protsessy pri Selektsii Atomov i Molekul", g. Zvenigorod, 2003 (Pod red. Yu A Kolesnikova) (Collected Reports at the VIII All-Russian (Intern.) Conf. "Physico-chemical Processes in Selection of Atoms and Molecules", Zvenigorod, 2003) (Ed. Yu A Kolesnikov) (Moscow: TsNIIatominform, 2003) p. 121
- 176. Takeuchi K et al. J. Nucl. Sci. Technol. 26 301 (1989)
- Baranov V Yu et al., in *Izotopy: Svoistva, Poluchenie, Primenenie* (Isotopes: Properties, Preparation, Applications) (Ed. V Yu Baranov) (Moscow: IzdAT, 2000) p. 357
- 178. Bagratashvili V N et al. *Multiple Photon Infrared Laser Photophysics* and Photochemistry (Chur: Harwood Acad. Publ., 1985)
- Cantrell C D (Ed.) Multiple-Photon Excitation and Dissociation of Polyatomic Molecules (Topics in Current Physics, Vol. 35) (Berlin: Springer-Verlag, 1986)
- 180. Makarov G N, Petin A N Zh. Eksp. Teor. Fiz. **119** 5 (2001) [JETP **92** 1 (2001)]
- 181. Makarov G N, Petin A N Chem. Phys. 266 125 (2001)