Spectroscopy of single molecules and clusters inside helium nanodroplets. Microscopic manifestation of ⁴He superfluidity

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<u>Abstract.</u> Newly developed techniques for producing beams of superfluid helium nanodroplets and for embedding single molecules or unstable particles (clusters and radicals) in such droplets make it possible to study the spectra of molecules and clusters in a new type of gentle quantum matrix — liquid superfluid helium. This paper reviews research into the spectroscopy of single molecules and clusters inside helium nanodroplets. Methods used in producing and studying helium nanodroplets in molecular beams formed during gas outflow from a cooled expansion nozzle are described, as are methods for embedding single molecules and clusters into droplets and spectroscopy techniques for single molecules and clusters inside helium nanodroplets. It is shown that the properties of helium

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Received 5 June 2003, revised 3 December 2003 Uspekhi Fizicheskikh Nauk **174** (3) 225–257 (2004) Translated by E Yankovsky; edited by A Radzig nanodroplets themselves can be studied by performing spectroscopic measurements. Experiments on the synthesis of aligned molecular chains and those on the observation of chemical reactions inside helium nanodroplets are considered. Several properties of helium nanodroplets and trapped Bose – Einstein condensates are compared. The potential of the method and some unsolved problems are also discussed.

1. Introduction

One of the most vivid achievements of physics and chemistry in the last decade has been the development of a method for studying the spectra of single molecules inside superfluid helium nanodroplets (clusters) and the experimental findings obtained by this method. The method, which has come to be also known as helium nanodroplet isolation (HENDI) spectroscopy (see, e.g., Ref. [24]), makes it possible not only to obtain high-resolution spectra of single molecules (including unstable ones) at very low temperatures ($T \le 0.4$ K) but also opens up new possibilities for studying the properties of superfluid helium at the microscopic level and many physicochemical processes taking place on the atomic–molecular level at ultimately low temperatures. The method can be used to produce long chains of polar molecules aligned in a certain manner inside nanodroplets of superfluid helium, which is especially interesting in the case of biologically important molecules, and to do direct spectroscopic observations of elementary excitations in superfluid helium clusters.

There are two well-known ways of studying the spectra of molecules at low temperatures: the molecular beam spectroscopy and the molecular spectroscopy in solid matrices (e.g., neon or argon matrices) also known as matrix isolation spectroscopy. The molecular beam method [1, 2] is one of the most widespread methods used in studies of the spectra of molecules and unstable particles. The use of gasdynamically cooled molecular beams and jets [1-4] makes it possible not only to substantially simplify the absorption spectra of molecules due to the intensive cooling of the gas [5, 6] but also to perform all measurements in conditions where there are almost no collisions between the molecules, which markedly reduces all perturbing effects [1, 2, 7, 8]. Moreover, in gasdynamically cooled molecular beams one can achieve fairly high concentrations of unstable particles, such as van der Waals molecules [4, 9-14] and free radicals [15]. Note that the spectroscopy of van der Waals molecules and free radicals in molecular beams has lately attracted the attention of researchers (see Refs [9-15]).

In the molecular beam spectroscopy, perturbations are minimal because of the absence of particle collisions, but the possibility of producing various unstable particles is limited. On the other hand, using the matrix isolation spectroscopy, one can produce various unstable particles, but it is almost impossible to dispose of the inhomogeneous line broadening caused by the interaction between the solid matrix and the particles under investigation [16, 17]. However, despite these restrictions, both spectroscopic methods are widely used in physicochemical studies and have contributed to the striking development of many areas of physics and chemistry. The method of spectroscopy of molecules inside nanodroplets, which is examined in the present review, unites the aboveoutlined methods, so to say, and makes it possible to resolve the contradictions discussed previously. Indeed, one of the ways to reduce the perturbations introduced by the matrix is to use liquid or solid helium as the matrix. The main problem in this case is the implantation of the molecules under investigation into a cold matrix, since at very low temperatures the molecules condense or form aggregates on the walls of the container.

Actually, the method under discussion is a combination of the molecular beam method and the method of spectroscopy of molecules in matrices and essentially amounts to the following. A beam of noble-gas clusters in which each cluster consists of $10^3 - 10^5$ atoms either crosses a molecular (atomic) beam or passes through a low-pressure chamber with a molecular (atomic) gas. In their motion, the clusters capture one or several molecules (atoms). After that they are examined by laser spectroscopy methods [18].

The HENDI spectroscopy underwent rapid development after it was extended to liquid helium clusters [19] and especially after Toennies's group showed (see Ref. [20]) that the molecules embedded in liquid ⁴He clusters possess spectra similar to those of free molecules in the gaseous phase. Instead of diffusion bands expected in the spectra of molecules in the condensed phase and caused by the interaction between the molecules and the matrix, free rotation of molecules manifests itself in the spectra. Although light molecules with small anisotropy (e.g., H₂ and CH₄) were known to be able to freely rotate in the condensed phase, this was the first time that heavy molecules with large anisotropy (e.g., OCS, CF_3CCH , and $(SF_6)_2$) had been observed as freely rotating in a liquid surrounding medium, but only with a somewhat higher moment of inertia [21].

The possibility of recording spectra with a well-resolved rotational structure for molecules inside superfluid helium droplets placed this method at the foreground of research into unstable particles. In addition, the method made it possible to study the superfluidity of ⁴He at the nanoparticle level, which in itself is a very interesting area of the condensed matter physics. As a result, dozens of laboratories all over the world are working on these problems, and in the last decade or so several hundred papers have been published and the number is rapidly growing. The spectra of molecules in helium nanodroplets, the microscopic manifestation of the ⁴He superfluidity, and the properties of the helium clusters proper are being actively studied both experimentally and theoretically.

The main goal of the present review is to give a brief picture of the method mentioned above, of the most interesting and important (from the author's viewpoint) experimental results achieved by this method, of some of its possible applications, and of problems that require further studies. We note immediately that the review in no way claims to provide a full picture of the results of the research in this field, which is practically impossible to do in a single review because of the large number of research papers and the broad spectrum of problems involved. As we proceed, references to works in which the material pertaining to the topic under discussion is covered in greater detail will be given. The starting point in preparing this review was review articles [21-29] and recent papers [30-33].

The outline of the review is as follows. Section 2 is a brief overview of works on generating helium droplets in the gas outflow from cooled nozzle sources and the methods used in studies of such droplets. The formation of both condensation and fragmentation helium clusters is examined. The results of studies of the size, density, and structure of helium clusters and the processes of capture of impurity particles by helium clusters are given. We discuss the results of investigating the structure and stability of positive and negative cluster ions of helium, including ³He, and processes of excitation of helium clusters by electrons and photons. The interaction between uncontaminated helium clusters and particles, including the process of capture of impurity particles by clusters, are discussed in greater detail in that section. Thus, Section 2 is like a guided tour through the physics of helium nanodroplets and forms a base for the sections that follow.

In Sections 3 and 4, which are the key sections of this review, we examine the results of research into the spectroscopy of molecules and clusters inside superfluid helium droplets. We describe an experimental facility and the methods utilized in generating helium nanodroplets doped with isolated molecules or clusters. The methods of rovibrational spectroscopy and electronic spectroscopy of molecules (atoms) that are inside helium nanodroplets or on the surface of such droplets are discussed. We present the results of studies concerning the vibrational–rotational (Section 3) and electronic (Section 4) spectra of molecules inside helium droplets. The free rotation of molecules (which is direct spectroscopic confirmation of the superfluid nature of helium nanodroplets) and the elementary excitations in the helium matrix during electronic excitation of the molecules are to manifest themselves in the spectra. We also present the results of studies of the effect of the helium surroundings on the rotational constants of molecules and on the width and shift of the spectral lines. Here, we examine the results of investigating the localization of atoms and molecules in a helium droplet. It is shown that particle localization directly affects their spectra. We describe experiments in which the dip (gap) in the phonon wing of the electronic absorption spectrum of a glyoxal molecule $(C_2H_2O_2)$ was observed. The presence of such a dip served as another spectroscopic confirmation of the superfluid nature of helium nanodroplets. We also analyze several models proposed in an attempt to explain the mechanism of variation of the rotational constants of molecules inside superfluid helium droplets. A description is given of the experiments in which the spectra of molecules inside ³He droplets and mixed ³He-⁴He droplets were recorded. These experiments made it possible to establish the threshold number of helium atoms in a droplet, which is needed for superfluidity to manifest itself. Finally, we examine the problems associated with formation of molecules, in particular, alkali metal dimers, on the surface of helium nanodroplets, and with the localization of helium atoms around an impurity molecules in a droplet.

In Section 5 we discuss several applications of superfluid helium nanodroplets, primarily for synthesizing nonequilibrium structures. In particular, we examine the results of recent experiments in which specially oriented chains of polar molecules were produced in helium nanodroplets (the example of HCN molecules is used). The experimental evidence of chemical reactions running inside helium nanodroplets is furnished (the example of the interaction of Ba atoms and N_2O molecules is used). The observation of orientational effects involving helium nanodroplets is also made. Finally, the example of small doped helium clusters is used to study the effect of the helium surroundings on molecular spectra.

Section 6 is devoted to a description of several properties of superfluid helium droplets and dilute gases of alkali metal atoms in traps, these two well-known Bose condensates. The properties of these quantum systems comprising interacting particles of limited dimensions, i.e., their ground states, sizes, densities, temperatures, and elementary excitations, are also explored. By comparing the properties of these systems we show that there is a profound analogy between the two. Finally, in the concluding Section 7 we present the main results of the research discussed in the review and list the most important achievements and promises, from the author's viewpoint.

2. Production of helium nanodroplets (clusters) and the methods used to study them

Helium nanodroplets and their properties have been intensively studied both experimentally [21, 23-26, 29-34] and theoretically [22, 27, 28]. The most comprehensive review of the methods of generation and detection of helium nanodroplets is the one written by Northby [23]. Note that the term 'droplet' in this case is very accurate, since helium is the only substance that has no triple point: the liquid coexists with the vapor as the temperature is lowered to absolute zero. Hence, when helium is cooled by the evaporation method, it transforms into the liquid phase rather than into the solid. Of course, there is always the question of the meaning of the term 'liquid', when the number of atoms in the system becomes small and when the droplet is charged, thus having a dense core. A partial answer to this question is given in Sections 2.1 - 2.7 and 6.

An interesting feature of helium is the existence of two stable isotopes, one of which (⁴He) is a boson, and the other (³He) a fermion. These two isotopes have very different characteristics at low temperatures. In the temperature range where cooling by evaporation is possible, ³He behaves basically like an ordinary liquid, while ⁴He behaves like an ordered liquid whose characteristic feature is superfluidity [35]. In this connection, it would be highly interesting to establish what precisely superfluidity means when we are dealing with so small a system as a helium nanodroplet.

In Sections 2.2-2.7 we briefly discuss the most widespread methods of detecting and studying helium clusters in molecular beams that are most closely related to the topic of this review. Among these are the time-of-flight method of detection and the method of studying cluster beams of helium, based on their interaction with transmission gratings. We will also examine the methods of studying cluster beams by their bombardment with electrons and excitation with photons. It is bombardment of particles with electrons that lies at the base of the most widespread mass-spectrometric method of detecting molecular and cluster beams. The spectroscopic methods of detecting and studying cluster beams are discussed in greater detail in Sections 3 and 4.

2.1 Formation of helium droplets during gas outflow from a nozzle

The first to observe helium droplets was Kamerlingh Onnes [36] in his experiments on helium liquefaction. Today, helium droplets of different sizes are being intensively studied. We will not touch on experiments in which large helium droplets are investigated. Instead, we limit ourselves mainly to a discussion of experiments in which droplets are generated through homogeneous formation of active centers in the course of helium expansion in the outflow from nozzle sources. The main interest today lies in studies of just such droplets. The number N of atoms in a cluster, which we call the cluster size, in this case varies between 10 and 10^7 (a micrometer diameter). Notice that it is these droplets that are most often called clusters. Hence, below, when referring to helium nanodroplets or clusters, we mean simply small-sized helium droplets.

The most widespread method of generating helium droplets is homogeneous condensation of a gas as it expands in its outflow from a nozzle [1-4]. The gas initially is above the nozzle at temperature T_0 and pressure p_0 , being at rest. It then expands when flowing from the outlet of the nozzle into a vacuum chamber. The gas accelerates in the process and cools down adiabatically. If the local thermodynamic state of the gas transforms into a region where the gas and liquid coexist before internal collisions cease to play an important role, phase separation occurs, with the result that the jet is a mixture of droplets and vapor. The jet is usually collimated by a skimmer, with the resulting formation of a beam of helium clusters.

2.2 Time-of-flight measurements involving condensed helium particles

The first experiments on the detection of condensed helium in its outflow from an expansion nozzle were conducted in 1961 by Becker et al. [37, 38]. The experimenters conducted timeof-flight experiments with a mechanically chopped beam. Helium outflowed from a divergent nozzle through an opening 150 µm in diameter. The temperature and pressure of the gas above the nozzle were $T_0 \approx 4.2$ K and $p_0 \approx 0.98$ atm, respectively. The researchers observed an extremely narrow velocity distribution of particles in the beam, and the average velocity of these particles was 165 m s⁻¹. The observed narrow velocity distribution could be attributed only to cluster formation [34]. Later on, many papers appeared that discussed measurements of the velocity distribution of particles in helium beams (e.g., see Ref. [23] and the literature cited therein).

Systematic research into the velocity distribution of condensed helium particles in beams within a broad range of the parameters of the gas above the nozzle began much later (e.g., see Refs [39-42]). The formation of helium clusters has received the most study in Refs [39, 42]. In the experiment by Buchenau et al. [39], a helium beam modulated by a mechanical chopper travelled for about 1 m before it crossed an electron beam. Here, He_N^+ ions were detected, which were then analyzed in a mass spectrometer. In most cases, a sonic nozzle with an opening diameter of 5 µm was used in the experiment. With so small an opening, one could raise gas pressures (8-20 atm) in the sources, compared to those used earlier. The temperature of the gas above the nozzle varied from 5 to 20 K. At a 20-atm gas pressure above the nozzle and a temperature of 20 K, only one peak, which corresponded to the atomic component, was present in the time-of-flight spectrum. However, as the temperature dropped, peaks corresponding to cluster components also emerged. At a fixed pressure of 20 atm, Buchenau et al. [39] found a temperature region within which only cluster peaks were observed.

Harms et al. [42] continued these measurements in the conditions in the gas above the nozzle, which were close to the critical point. The main goal of their work was to select the proper conditions for generating large slow droplets. The velocities observed were no higher than 45 m s⁻¹ at $p_0 \approx 1.5$ atm and $T_0 \approx 3.5$ K. Under such conditions in the gas above the nozzle, only one time-of-flight peak was present in the mass spectrum. As the temperature of the gas above the nozzle changed, anomalies were detected in the region near the critical point. In particular, a discontinuity in velocity and a minimum in the velocity ratio at the critical point were observed. It was found that with the helium pressure above the nozzle being constant and equal to 2.3 atm, the cluster size rapidly increased (with decreasing temperature T_0) from $\approx 10^3$ atoms at $T_0 = 6.5$ K to more than 10^5 atoms at $T_0 = 5.3$ K.

2.3 Interaction of cluster beams with transmission gratings The first to use nanostructure transmission gratings in their studies of the diffraction of helium cluster beams were Schöllkopf and Toennies [43, 44]. Since a cluster's de Broglie wavelength is inversely proportional to the number of atoms in the cluster, clusters of different sizes will undergo diffraction to different angles as they travel through a grating. In their studies of the diffraction of helium clusters by transmission gratings with a period of 200 nm, the researchers identified diffraction peaks belonging to He₂ and He₃ clusters. This was the first indication that there exists a low-bound cluster (or molecule) He₂. Luo et al. [45] studied the passage of beams containing helium atoms and clusters through various sieves with diameters from 98 to 410 nm. It was expected that helium clusters will break down at collisions with the sieve surface, and since their dimensions

were much larger than the atomic sizes they will traverse sieves with lower probability. By measuring the ratio of the transmission coefficients of atoms and dimers, the researchers found that the average distance between the atoms in a helium dimer amounts to 62 ± 10 Å. This value, however, is probably only the upper limit [46, 47]. In similar experiments, Grisenti et al. [48, 49] used transmission gratings with a 100-nm period and arrived at 52 ± 4 Å for the length of the bond in the ⁴He₂ dimer, and approximately 1.1 mK ($\approx 10^{-7}$ eV) for the binding energy.

The measurements described make it possible to find the optimal conditions needed for generating small clusters, as functions of the parameters of the gas above the nozzle. Schöllkopf et at. [50] revealed that by rotating the grating about an axis parallel to the grooves one can create filters for clusters of different sizes and select the large helium clusters containing from 10^4 to 10^6 atoms, while also being able to manipulate such clusters. Notice that the primary value of the methods considered in this section is that they all make possible a detailed study of the condensation threshold for the gas in nozzle sources, and thereby the researchers can bring forward experimental evidence for verifying the classical theories of homogeneous condensation.

2.4 Interaction between uncontaminated clusters and particles

Fundamentally, one of the most direct ways of uncovering the structure and composition of clusters is to study scattering of atoms from the clusters and then analyze the results. Actually, however, it is extremely difficult to extract the necessary information from such experiments. The problem is that the results are almost always presented in the form of a convolution that incorporates the *a priori* unknown size distribution of clusters and the unknown capture processes of particles and their detection. All these parameters and processes are studied simultaneously. Nevertheless, despite these difficulties, many interesting results have been obtained (e.g., see Ref. [23]).

The earliest research into the interaction between helium clusters and particles was done by Gspann et al. [51-55]. A detailed description of their work can be found in Gspann's review [34]. In the first experiments [51], the researchers measured the attenuation of a beam of cesium atoms as it crosses a beam of helium clusters. The advantage of using cesium in such experiments is that the presence of cesium is easily made evident with a detector whose operation is based on surface ionization. However, since the background atomic gas strongly affected the attenuation of the cesium beam, no detailed conclusions were drawn in this work. Later on, such experiments were repeated [53] with a better collimation of the atomic beams. The results led the researchers to a very interesting conclusion, namely, that the atoms do not pass through the clusters on which they impinge.

Gspann and Vollmar [52] (see also Ref. [54]) measured the deflection of helium clusters by a jet of Xe atoms or CO₂ molecules that crossed the cluster beam. First, comparative measurements with ${}^{4}\text{He}_{N}$ and ${}^{3}\text{He}_{N}$ clusters were done. It was found that for clusters of both types the momentum of the scattered atoms captured by the clusters is not transferred to the latter completely. The explanation was that the atoms penetrate deep into the cluster and then the cluster anisotropically emits helium atoms. The researchers also found that the small momentum transfer is an indication that the cluster viscosity disappears, and they related this fact to the

superfluidity of helium [54]. However, they were unable to observe the expected difference in momentum transfer for different helium isotopes [34]. Later on, Gspann and Ries [55] again studied the scattering of cesium atoms by helium clusters. The experimenters used two detectors to reveal the presence of the cesium atoms in the entire scattering plane. Cesium atoms were detected, in addition to the beam proper, only in the beam of helium clusters. They also found that the cesium atoms heading in the direction of the cluster beam had exactly the same velocity as the clusters. Thus, this research showed that cesium atoms are captured by clusters and reside either inside the clusters or on their surfaces.

The next series of experiments on the interaction of cluster beams with particles were conducted by Toennies and his co-workers (see Refs [42, 56-63]). Two approaches were employed in their experiments. In the first, the cluster beam passed through the scattering chamber in which the pressure of the scattering gas could be varied. In the second, the particles of a collimated atomic or molecular beam were utilized as scattering particles. The beam crossed the cluster beam at a certain angle at a point 60 cm from the nozzle. The detectors could be rotated about the crossing point. This approach made it possible to detect either the cluster beam via mass-spectrometric analysis of the fragments or the gas particles when a detector operated as a gas analyzer of the background gas. The experiments revealed (see Refs [58, 59]) that clusters capture several atoms or molecules. The researchers also studied the dependences of the capture process of a neon atom and the detection of this atom on the parameters of the gas above the nozzle.

Lewerenz et al. [56] examined the deflection of ${}^{4}\text{He}_{N}$ clusters caused by the capture of SF₆ molecules with welldefined momentum from the intersecting molecular beam. Their results made it possible to determine the size distribution of the clusters. The researchers used helium clusters of moderate size ($N \leq 2 \times 10^4$). The experiments were carried out in conditions of single collisions. Analyzing the detected signals from SF_5^+ ions, Lewerenz et al. [56] concluded that the momentum of a molecule is completely transferred to a helium droplet [34, 57]. From the angular distribution of the deflected clusters it was found that their size distribution is a log-linear one with a half-width comparable to the average cluster size. The second part of this work (see Ref. [57]) was devoted to a study of the multiple capture of impurity atoms (molecules) and their subsequent coagulation inside the clusters (see also Ref. [64]). The researchers found that ionization leads only to insignificant fragmentation of the clusters of implanted particles and that the size distribution of ions of these clusters agrees with the predicted Poisson distribution for multiple capture. Thus, the probability of formation of, say, an $(SF_6)_N$ cluster inside a helium droplet is determined by the probability of independent capture of N SF_6 molecules. The distribution of the capture probability has the form [57]

$$P(N) = N_0 \ \frac{(n\sigma L)^N}{N!} \exp(-n\sigma L) \,,$$

where N_0 is the amplitude factor, *n* is the gas particle number density, σ is the capture cross section, and *L* is the cell length. For example, for a droplet consisting of N = 4100 helium atoms, the capture cross section $\sigma \approx 3900$ Å² [56].

Harms et al. [60] used the results of scattering measurements to determine the average density of the ${}^{4}\text{He}_{N}$ clusters.

The value of the average density that they found proved to be much lower (by 20-30%) than the density of bulk liquid helium. The density defect emerged because of the diffusive nature of the surface's profile, and the size of the density deviation could be used as the measure of the thickness of the surface layer. The obtained values of the density deviation were found to be in good agreement with theoretical results and made it possible to predict the thickness of the surface layer as being within the range from 6 to 8 Å. A report of similar studies involving ³He clusters can be found in Ref. [63]. Harms and Toennies [61, 62] studied the transmission of fairly large $(N \approx 1.5 \times 10^9)$ ⁴He_N clusters slowly moving (≈ 75 m s^{-1}) through a scattering chamber filled with the ³He or ⁴He gas. The gas temperature in the scattering chamber was about 1.7 K. Here, the collision energy of ³He and ⁴He atoms with ${}^{4}\text{He}_{N}$ clusters amounted to (5–10) K. The researchers found that the ³He atoms transfer much less energy and momentum to ${}^{4}\text{He}_{N}$ clusters in the beam than the ${}^{4}\text{He}$ atoms. This agrees with the statement that low-energy ³He atoms do not satisfy the Landau criteria [65] for producing excitations in a superfluid ${}^{4}\text{He}_{N}$ droplet.

2.5 Ionization and excitation of uncontaminated clusters by electrons

As noted in Section 2.1, ionization of the cluster beam is employed in the detection of helium clusters in the overwhelming majority of experiments. In Sections 2.5.1-2.5.3and 2.6 we mainly discuss experiments in which ionization is used not only in detecting but also in studying the nature of the charged helium clusters. The bombardment of helium clusters by electrons may lead to the formation of positive and negative cluster ions and excited metastable ions [23].

2.5.1 Positive cluster ions. One of the earliest publications (that is by Gspann and Krieg [66]) devoted to the study of properties of positive cluster ions describes investigations into size distributions of helium droplets that become charged through electron bombardment. The researchers measured the ratio of the average cluster size $\langle N \rangle$ to the cluster charge Z by the time-of-flight method. Positive ions were produced when the clusters were bombarded with 190-eV electrons. The ratio value of $\langle N \rangle / Z \sim 1 \times 10^5$ was obtained for the following parameters of the gas above the nozzle: $T_0 \approx 4.2$ K, and $p_0 \approx 0.9$ atm. The experimenters used a cylindrical nozzle with an opening diameter of 100 µm. Gspann and Vollmar [67, 69] and Gspann [68] conducted experiments with large cluster ${}^{4}\text{He}_{N}^{+}$ and ${}^{3}\text{He}_{N}^{+}$ ions whose sizes N varied from 10⁵ to 10^7 and found that multiply charged clusters can also form. The phenomenon probably occurs because the electrons that form during ionization of helium atoms can easily leave the cluster, in contrast to the case of bulk helium. The researchers used a convergent-divergent nozzle with an opening diameter of 100 μ m. The temperature of the gas above the nozzle was 4.2 K in the case of ⁴He, and 3.2 K in the case of ³He. Similar research was done in conditions where the temperature of the gas above the nozzle passed the λ point (see Ref. [69]). In this case, the clusters are produced via direct condensation into the superfluid phase. Many properties of the cluster beam were found to be continuous at the transition point.

Stephens and King [70] examined the mass distribution in ⁴He_N and ³He_N cluster beams. Beams were formed in the gas expansion from a nozzle with an opening diameter of 5 μ m at $T_0 = 4.2$ K and $p_0 = 0.53$ atm for ⁴He, and $T_0 = 3.2$ K and

 $p_0 = 0.73$ atm for ³He and were ionized by electron impact. The mass distribution of the newly formed ions was studied by a mass spectrometer. The presence of a 'magic number' structure was discovered in the region up to N = 50 for locally stable ions of both isotopes at N = 7, 10, 14, and 30. An interesting feature relevant to the region where condensation begins was exposed, namely, the large difference in the threshold conditions of condensation for these isotopes. The researchers assumed that the difference is caused by the fact that ⁴He dimers are stable, while small ³He clusters are unstable.

The first to study large cluster ions produced by electron bombardment of fragmentation clusters were Jiang and Northby [71]. They applied the retarding potential method which, in conjunction with time-of-flight measurements, makes it possible to determine the mass distribution of clusters as a function of the parameters of the gas above the nozzle. The researchers found that the process of formation of large positively charged cluster ions exhibits a distinct threshold, the cluster size reaches $N \approx 10^6$, and the threshold values of the gas parameters above the nozzle correlate well with value of the entropy of the source, equal to 6.4 kJ kg⁻¹ K⁻¹. Henne and Toennies [72] and Knuth and Henne [73] made thorough measurements of the size distribution of positively charged cluster ions produced from fragmentation clusters. They found that the cluster ion size decreases exponentially in the large-size region, in contrast to the behavior of the size distribution of condensation clusters, which is a log-linear one [56].

2.5.2 Negative cluster ions. The first to report about the production of negatively charged ⁴He_N clusters was Gspann [74]. Using the time-of-flight method, he discovered negatively charged clusters with $N > 2 \times 10^6$. However, the mechanism by which an electron is bound to such a structure remained unclear, since there is no stable He⁻ ion. Gspann assumed that the formation of negative cluster ions of helium is a consequence of the multiparticle effect. From research on bulk helium it is known that an electron is weakly coupled with the flat surface of liquid helium. Gspann assumed that similar surface states also exist in the case of large helium clusters [75]. The results were interpreted within this model. Notice that later it was found (see below) that the structure of a negative ion in a helium cluster is in many respects similar to the structure of a negative ion in bulk liquid helium, according to which an electron in helium resides in a bubble state. The formation of a bubble around the electron requires a large number of helium atoms. It is possibly for this reason that the small helium clusters do not form negative ions.

Many experiments with negatively charged cluster ions were carried out by Northby and his colleagues [23, 71, 76– 79]. Jiang and Northby [71] measured the energy of large charged clusters by the retarding potential and beam deflection methods. These experiments showed that mainly large clusters form negative cluster ions. The beam deflection method made it possible to establish that the mass distribution falls off exponentially in the region of large masses and, which is most important, there is a threshold minimum size $N \approx 5 \times 10^5$, i.e., negatively charged clusters whose sizes are smaller than this do not exist (or, more precisely, were not observed). Basing their reasoning on these studies, Northby and Kim [80] supposed that the structure of a negative ion is that of an electron in a bubble state inside a cluster (the electron being bound by polarization forces). Such a structure is often called an electron balloon, by analogy with a bubblon in bulk helium. From the very beginning it was assumed (see Refs [76, 77]) that if such a model of the structure of a negative ion is valid, the ion is optically active and can easily be detected by electron detachment spectroscopy. Further studies [77-79] only corroborated the bubble model of an electron inside a helium droplet.

The most comprehensive studies of the capture of electrons by helium clusters were those carried out by Henne and Toennies [72]. Their experimental setup made it possible to investigate both positively and negatively charged cluster ions and metastable clusters. The measured distribution of negative cluster ions over sizes was found to be exponential in the large-size region. The researchers determined the threshold size for negative cluster ions as $N = 0.75 \times 10^5$ and discovered no ions of smaller sizes. These experiments also corroborated the bubble model of a negative cluster ion.

2.5.3 Excited metastable cluster ions. The excitation of metastable states of ⁴He and ³He cluster ions was first described by Gspann and Vollmar [67] and Gspann [68]. They studied the capacity of excited helium droplets to detach secondary electrons on the first dynode of the photomultiplier by using the time-of-flight method in their measurements. The researchers found that clusters that had been positively charged and simultaneously excited to a metastable state contain 2.4×10^6 atoms on the average. They also studied the dependence of the ion signal on the electron energy and, by extrapolating this dependence, found the threshold energy value of approximately 26 eV for the formation of such particles.

Toennies's group undertook a lot of research involving excited metastable helium droplets (e.g., see Refs [40, 41]). They also applied the time-of-flight method. The cluster beams were excited by electrons and then mass-spectrometric analysis was made on the small cluster ions. One of the most interesting results of this research consists in the following: it was discovered that the threshold value of the electron energy needed for charged clusters to emerge amounts to about 20 eV, which is in good agreement with the threshold energy needed for the formation of metastable helium atoms in the ${}^{3}S_{1}$ state. At the same time, clusters in a metastable state were not detected as the electron energy grew up to 26 eV, which is approximately the energy of ionization of free helium atoms. Martini et al. [81] explained the observed shift (to higher energies) of the threshold energy needed for exciting metastable states in large helium clusters, in relation to the threshold value of the energy needed for exciting free atoms, by the existence of a barrier in the process [82, 83] that depends on the particle density and is associated with the formation of a bubblon inside the helium droplet. The height of the barrier for large clusters is about 1.03 eV and decreases with cluster size. Martini et al. [81] believed that this fact indicates that the density of small clusters is lower than that of large clusters.

Jiang et al. [84], Kim et al. [85], and Yurgenson et al. [86] applied optical methods to study excited metastable clusters. These investigations have been described in detail in Northby's review [23]. Henne and Toennies [72] carried out high-resolution studies of the threshold energies needed for the formation of metastable clusters. The threshold values of the energy needed for the production of the excited ${}^{3}S_{1}$ state were found for the following cases:

(1) 19.82 eV, for free atomic helium;

(2) 20.07 eV, near the cluster surface (when the electron remains outside the cluster), and

(3) 21.22 eV, inside a cluster (when the electron is inside the cluster in a bubble state).

The third threshold value is in good agreement with the results of earlier measurements [81, 85]. The difference between the third and second values (1.15 eV) is considered the height of the energy barrier that the electron must overcome to find itself inside a helium cluster in the course of bubblon formation. The value of this energy difference is in very good agreement with measurements in bulk helium [82, 83], which implies that the density of large clusters is exactly the same as that of bulk liquid helium.

2.6 Excitation of doped clusters by electrons

The earliest experiments, in which the capture of impurity particles by helium clusters was studied and ion fragments were formed as a result of bombardment of clusters with electrons, were described in Refs [58, 59, 87]. A beam of neon atoms at room temperature crossed a chopped beam of helium clusters ($p_0 = 24$ atm, and $T_0 = 10$ K). The experiments demonstrated the presence of ions Ne⁺, Ne⁺₂, Ne⁺₃, $NeHe_N^+$, $Ne_2He_N^+$, $Ne_3He_N^+$, etc., in addition to the ions from the cluster beam. This was the first irrevocable proof of the stable capture of impurity atoms (including the multiple case) by helium droplets and of the clusterization of impurity atoms inside helium droplets. Scheidemann et al. [88] made the first attempt to investigate the ionization process in detail. The researchers studied the electron impact ionization of helium clusters doped with SF₆ molecules. What is most interesting here is that they detected SF_6^+ ions which are not observed in ordinary conditions on bombardment of free SF₆ molecules with electrons. They also found that the ionization mechanism amounts almost entirely to the transfer of charges from positive holes to the molecules. After a hole is created, it moves by hopping [89]. A hole and an impurity particle move toward each other and, at the same time, to the cluster's center due to polarization forces. According to estimates made by Scheidemann et al. [88], the hole may travel a distance of roughly 500 Å in 10⁴ hops before it becomes localized and a He_{2}^{+} ion is produced. The researchers also discussed the effect of the matrix on the ionization process, including the formation of an SF_6^+ ion. They supposed that the ionization process in helium clusters is especially 'soft'.

Later on, it was found (see Refs [90-92]) that the holes travel distances that are much shorter than assumed earlier (amounting to only several hops). The hole in the cluster is localized as a He⁺₂ ion, and the cluster emits a fragment of He⁺₂. If an impurity is met before this event, the probability of charge transfer and the distribution of fragments strongly depend on the properties of the impurity particle. For instance, charge transfer to neon atoms is most effective, but fragmentation always leads to formation of NeHe⁺_N ions rather than Ne⁺. Callicoatt et al. [90] also noted that the matrix effect, which in the early experiments of Scheidemann et al. [88] manifested itself in the formation of SF⁺₆ ions, is probably an artifact [93].

2.7 Excitation of uncontaminated clusters by photons

Electronic excitation of helium atoms requires radiation with a photon energy of about 20 eV. Hence, synchrotron radiation is perfect as a tool for studying the interaction of helium clusters with photons. Several researchers have studied the helium cluster fluorescence induced by 20-30-eV photons (see Refs [94-97]). Among these, Joppien et al. [94], von Haeften et al. [95], and Möller et al. [96] investigated the fluorescence excitation spectrum of ${}^{4}\text{He}_{N}$ clusters. In the experiments, the cluster beam crossed the synchrotron radiation line, and the integral luminescence signal was measured as a function of the energy of the incident photons. Broad peaks related to the transitions $1S \rightarrow 2P$ and $1S \rightarrow 2S$ (a forbidden transition) in the helium atom were recorded and identified. The peaks in the spectra of the clusters were found to be shifted with respect to these transitions in the atom. A broad peak at roughly 23 eV was also discovered, but its origin remained unknown. Von Haeften et al. [95] and Reho et al. [97] were the first to study the spectra of visible and IR luminescence induced by exciting photons. The researchers found that most emission lines correspond exactly to the atomic and molecular lines of helium, measured in the gaseous phase. Thus, it was established that these lines originate in atoms and molecules get detached from helium clusters as products of the relaxation process for electronic excitations.

Fröchtenicht et al. [93] were engaged in research on the process of cluster ionization by synchrotron radiation as a function of the photon energy and cluster size. In their experiments, the researchers measured the mass spectrum of small cluster ions that formed as a result of irradiation of a helium cluster beam by photons whose energy exceeded the threshold energy of helium atom photoionization. They found that the distribution of cluster ions was approximately the same as observed in electron bombardment of the cluster beam, including the magic numbers 7, 10, and 14. Small clusters were found to form even at photon energies below the ionization threshold energy. Finally, they established that fluorescence is the main mechanism of the relaxation of clusters after their excitation by photons has ceased, a fact that agrees well with earlier predictions made by Joppien et al. [94].

2.8 Summary

Research has shown that the formation of ${}^{4}\text{He}_{N}$ clusters during expansion of a gas from nozzle sources occurs because of the growth of small clusters, including He₂, which act as condensation centers. The most comprehensive information about the initial stage of cluster growth has been extracted through experiments with transmission gratings [49]. Clusters can be characterized according to their size and velocity distributions, the latter usually being very narrow. Cluster velocity is determined by the initial enthalpy of the gas in the source and the internal enthalpy of the system at the condensation point. Since the condensation point is determined by several parameters, including the geometrical characteristics of the expansion nozzle, there is a large distinction in the cluster distributions over size and velocity for different facilities, even for the similar conditions of the gas above the nozzle. The scaling parameters for the formation of clusters of a definite size in expansion nozzles of different sizes can be found in Ref. [98]. The best information about the size distribution of clusters has been extracted through experiments on the scattering of particles [56], and that about the velocity distribution through time-offlight measurements [39].

Studies involving charged clusters have revealed that a free electron produces a bubble (with a diameter of about 34 Å) in liquid helium in accordance with the principle of

Pauli's exchange repulsion from surrounding helium atoms. On the other hand, a positive ion is surrounded by a shell of helium atoms, which is compressed very strongly because of electrostriction. The rigid shell surrounding the ionic nucleus and containing from 30 to 50 helium atoms has a diameter of only about 12 Å. This shell is called a snowball [99, 100]. There is an energy barrier for the formation of a bubblon in a helium droplet, which is something like 1.15 eV for large droplets. In many respects, the structure of positive and negative ions in large helium clusters is similar to that of the same ions in bulk liquid helium.

There is a marked difference between ⁴He_N and ³He_N clusters. While the first is usually a bound complex for any value of *N*, calculations have shown that small ³He_N droplets (having fewer than 30 atoms) are unstable [101, 102]. The instability of small ³He_N droplets is due to the high energy of zero-point oscillations and the small mass of the ³He isotope. As a result, experimenters have observed a significant difference in the way the average cluster size $\langle N \rangle$ depends on the temperature of the gas above the nozzle for these two isotopes. While in the ⁴He_N droplet, the average size $\langle N \rangle$ increases gradually as the temperature decreases, the formation of ³He_N droplets being a threshold process.

When the entropy of the gas above the nozzle is equal to, or smaller than, the entropy of the gas at the λ point, a new mechanism of cluster formation may come into play, a mechanism for which fragmentation of the liquid phase is responsible. In this case, there is a high probability that clusters of 'another' type will form in the cluster beam because of condensation of the gas phase that is produced as a result of fragmentation of liquid clusters. The question of the identity of the properties of these two types of clusters remains open, however. It is likely that there could be a difference between condensation and fragmentation clusters. Or it is possible that not only their size and velocity distributions differ, but their internal states (including clusters of the same size) do as well, since their formation mechanisms are different. In particular, these two types of clusters may have very different angular momenta [23].

As a result of the various studies it has been established that there exists a process of capturing particles by helium clusters (including multiple capture) and the formation of impurity clusters inside or on the surface of helium droplets. The distribution of the impurity particles inside helium droplets agrees with the Poisson distribution predicted for multiple capture [57]. It is this possibility of impurity particles being captured by helium droplets that makes it possible to study the spectra of single molecules and clusters inside helium nanodroplets. The results of such investigations are discussed below in Sections 3 and 4.

3. Rovibrational spectroscopy of molecules and clusters inside helium nanodroplets

The last five or seven years have seen an avalanche of publications devoted to the vibrational–rotational spectroscopy of single molecules and clusters inside helium nanodroplets. Here, we discuss only the most characteristic results. Notice that, in contrast to electronic excitation, under vibrational and rotational excitations of molecules the helium state is preserved. The most distinctive feature of rovibrational spectroscopy of molecules inside ⁴He droplets is the manifestation of free molecular rotation in the spectra, which is a direct proof of the superfluid nature of helium nanodroplets. We will discuss the methods of the rovibrational spectroscopy of molecules inside helium droplets in Sections 3.1-3.5. Let us focus on a typical experimental facility used to produce helium nanodroplets doped with molecules or clusters, the sources of molecular excitations, and the methods utilized to detect signals and record the spectra. We examine some results obtained in the IR spectroscopy of molecules and clusters inside helium droplets, in double microwave (MW-MW) excitation and MW-IR excitation, and in Stark spectroscopy. We also explore the effect of the helium surroundings on the rotational constants of molecules and on the magnitude of the frequency shift and the shapes of spectral lines. In Section 3.6 we will discuss the experiments on the spectroscopy of molecules inside ³He droplets and mixed ${}^{3}\text{He}-{}^{4}\text{He}$ droplets that made it possible to establish the threshold nature of the formation of the superfluid state in ⁴He clusters.

3.1 Experimental methods

As noted in Section 1, the spectroscopy of molecules inside helium nanodroplets is based on two methods, namely, the molecular beam spectroscopy and the matrix isolation spectroscopy. This fact determines the advantages and drawbacks of the method under consideration. Obviously, not all methods of recording spectra can be applied in the case of molecular beams. For instance, when well-collimated beams are involved, it is almost impossible to take the absorption spectra of molecules by measuring the attenuation of the exciting radiation. In this case, only the laser-bolometric method [103, 104] or the pyroelectric method [105-107] of detecting the absorbed energy makes it possible to record the absorption spectra of molecules in the beam. The bolometric method presents a fairly widespread method of studies involving molecular beams [1, 2] and can also be successfully used to examine van der Waals complexes [9-12]. It should be emphasized that while in the event of molecular excitation in the beam a bolometer (or a pyroelectric detector) detects the increase in the energy of the molecular beam related to the absorption of energy from the laser beam [103-107], in the event of excitation of cluster beams these detectors most often are used to measure the decrease in the beam energy. The reason is that in most cases the absorption of laser light leads to cluster dissociation followed by the scattering of the fragments formed away from the beam [9-12]. The beam becomes depleted and, as a result, the total energy supplied to the bolometer decreases.

3.1.1 Facilities used to produce helium nanodroplet beams. The schematic of a typical experimental setup for studying the spectra of molecules and clusters inside helium nanodroplets is shown in Fig. 1. Because of the low binding energy of the atoms in small helium clusters (see Sections 2.3 and 6.3.2), cluster formation usually requires high densities and low temperatures of the gas in the expansion region [24] and, as a result, high gas fluxes. Hence, facilities used to generate liquid helium droplets must incorporate powerful pumps (high evacuation rates) and/or very small nozzle openings. The gas flux is proportional to $p_0 d^2 T_0^{-1/2}$, where d is the diameter of the nozzle opening. Usually, in experimental facilities for generating liquid helium nanodroplets, the diameter of the nozzle opening varies from 5 to 20 μ m, the pressure varies from 1 to 20 atm, and the temperature varies from 10 to 30 K. In experiments on generating fragmentation clusters, the nozzle is sometimes cooled to 3-4 K. If we apply



Figure 1. Schematic of the experimental facility used to study the spectra of molecules inside helium nanodroplets (clusters) [21]. Large helium clusters (droplets) are formed in the gas outflow from the nozzle. As they pass through the scattering chamber, they capture a 'guest' (investigated) molecule. In their further motion to the mass spectrometer, the clusters are irradiated by frequency-tuned laser radiation. When the laser radiation is in resonance with the guest molecule, the absorbed energy leads to evaporation of helium atoms from the cluster and a decrease in the amplitude of the mass-spectrometer signal.

the ideal gas approximation, a nozzle whose opening diameter is 10 µm at $T_0 \approx 20$ K and $p_0 \approx 15$ atm provides a gas flux equivalent to that produced with a nozzle opening of 40 µm in diameter at room temperature and $p_0 \approx 2$ atm [24]. This flux amounts to approximately 4 atm $cm^3 s^{-1}$ $(\approx 0.16 \text{ mmol s}^{-1})$. To ensure the evacuation of such a gas flux, one needs diffusion pumps with an evacuation rate of about 10,000 l s⁻¹ for helium (≈ 4000 l s⁻¹ for nitrogen) at the ultimate operating pressure of 3×10^{-4} Torr. Such facilities usually generate helium nanodroplets containing about several thousand atoms each. Notice that in the case of sources operating at temperatures below 10 K, which are employed to produce large helium clusters ($N \ge 10^5$), either refrigerators with low operating temperatures are used or the nozzle is directly cooled by liquid helium. At a distance of approximately 1-3 cm from the nozzle, the cluster (droplet) beam is collimated by a skimmer. To exclude the scattering of the beam by the skimmer, the front edges of the skimmer's walls must be made as thin as possible. This is usually done by employing skimmers fabricated by electrophoresis sputtering, which have an entrance opening diameter of about 0.5 - 1 mm.

3.1.2 Doping nanodroplets. After the skimmer has formed the helium cluster beam, the clusters are doped with the molecules or atoms selected for this purpose. As noted in Section 2, there are two most common ways of doping: (1) by sending the cluster beam through a low-pressure gas cell, and (2) by crossing the cluster beam with another molecular or atomic beam. The first method is used more often. The cell with the gas is usually about 10 cm long. A pressure is maintained in the cell so as to ensure the production of the required number of impurity particles per cluster. In the capture process, the kinetic and internal energy of the particles and the solvation energy become distributed over the droplet, which leads to evaporation of helium atoms from the droplet. Estimates made by Chin and Krotscheck [108] show that when a small molecule, such as HCN, is captured, then about 200-250 helium atoms are evaporated, with an energy of 5.5-7 K expended to evaporate a single atom. As a result, the microcanonical system in the case of a ⁴He cluster cools to a temperature of 0.38 K, and that in the case of a ³He cluster to 0.15 K [109]. These values are in rather good agreement with

theoretical estimates [110, 111]. In the process of atom evaporation, the angular momentum of the helium droplet also changes. As noted in Section 2.4, the number of doped molecules per cluster begins to obey the Poisson distribution as helium droplets capture the molecules [57]. To optimize the capture process in such a way that only one particle is captured by a droplet, the density of the column of gas must be about $330N^{2/3}$ Torr [24]. In typical conditions, the vapor pressure that is sufficient for effective doping of helium droplets is about $10^{-4} - 10^{-5}$ Torr, which is approximately 10,000 times lower than the pressure usually used to produce doped clusters in expanding jets with gas-carriers. Hence, many substances that cannot otherwise be studied in expanding jets may be studied by this method. The molecules captured by a single droplet form van der Waals complexes in it.

At a steady droplet temperature of 0.38 K, the width of the vibrational-rotational spectrum of a molecule amounts to no more than 1 cm⁻¹, which is smaller than the magnitude of the shift induced by the formation of complexes. Hence, the spectra of different small oligomers in helium droplets do not overlap, and the capture of more than one molecule by a droplet only reduces the intensity of the spectrum for an individual molecule but does not change the shape of the spectrum. On the other hand, the spectra of large oligomers tend to overlap, since the size of the shift of the spectrum tends to an asymptotic limit as the number of molecules in the cluster grows [31, 112]. Nevertheless, it has been possible to produce OCS-(H₂)_N complexes with up to N = 17 hydrogen molecules, and their spectra were successfully resolved [113].

3.1.3 Radiation sources for spectral studies. The spectroscopy of molecules inside helium clusters is a fairly new area of research. Hence, most often the existence of a suitable radiation source determines the choice of molecules for research. In their first experiments, Goyal et al. [19, 114] dealt with SF₆ molecules, in which the vibrational mode v_3 was excited. This molecule has a fairly large absorption cross section over the spectral region in which CO₂ lasers generate light. For cw frequency-tuned CO₂ lasers, the easily attainable output power may reach 10 W. To resolve the rotational structure, the v_3 transition in SF₆ was later studied by using a tunable diode laser [20]. Diode lasers have also been utilized

in experiments in which the spectra of the OCS molecules were investigated [30, 113, 115, 116].

The early experiments involving helium clusters doped with HF, H_2O , and NH_3 molecules [117–119] were carried out with pulsed lasers. The advantages of such lasers are the high output power and the large tuning range, while the drawbacks are the broad lasing line and the field-induced broadening of the transitions in the molecules being studied. This leads to a situation in which it is sometimes very difficult to understand the nature of spectral line broadening, i.e., whether this broadening is due to the interaction with the matrix or to the laser proper.

High-power line-tuned gas lasers (cw or pulsed) have also been used in such experiments (e.g., see Ref. [120). Due to the scarce set of lasing frequencies, these lasers are most suitable for studies of modest-sized molecules with a small moment of inertia and well-separated spectral lines. Because of their high output power, these lasers are widely employed in experiments on transition saturation [33].

Most of the experimental spectra in the $3-\mu m$ [31, 112, 120-122] and $1.5-\mu m$ [33] ranges have been obtained by using dye lasers which have a broad tuning range, a fairly high output power (30 and 250 mW, respectively), and a high spectral resolution. They can be stabilized with an accuracy no worse than 1 MHz. Since the $1.5-\mu m$ range is also applied in telecommunications, commercially available optical elements, such as optical fibers, connectors, and high-Q cavities, can be used in such measurements. With such radiation powers, saturation of strong, homogeneously broadened transitions in the $3-\mu m$ range with a transition width of about 10 MHz can be achieved.

3.1.4 Excitation schemes. IR excitation. The IR spectroscopy of molecules inside helium droplets has aroused the most interest probably because such a spectroscopy makes it possible to resolve a rotational structure in the spectra even in the case of relatively large molecules and clusters. We will discuss here several examples. Figure 2 shows the absorption spectrum for the v_3 vibration in an SF₆ molecule residing inside ⁴He droplets, and Fig. 3 displays the absorption spectra for the v_3 vibration in an OCS molecule residing inside ⁴He droplets and inside ³He droplets. Figures 2 and 3a clearly demonstrate well-resolved rotational structures. These spectra should be compared with similar spectra for the case of 'classical' solvents, in which the rotational structure is observed in the best of cases only for molecules with a small moment of inertia. It should be emphasized that the presence of a well-resolved rotational structure in the spectrum makes it possible to measure the cluster temperature. This is a very important fact, since before such experiments were conducted there was no way in which the cluster temperature could be measured, and no assumptions were even made as to how this temperature could be measured. However, soon the situation changed with the arrival of narrow-band tunable lasers, with which it became possible to resolve the rotational structure in the spectra of molecules inside helium clusters and thus measure the cluster temperature [20, 109, 123].

As years passed, the schemes of excitation and detection of helium cluster beams became more and more sophisticated. For instance, instead of bolometers, which were used in the first experiments, researchers employed mass-spectrometric detectors that were 'transparent' for the cluster beam. In the experiments, the cluster and laser beams propagate towards each other along parallel lines. This allows an increase in the



Figure 2. IR absorption spectrum for the v_3 vibration of an SF₆ molecule inside a ⁴He_N (N = 2700) droplet (solid curve). The results of calculations of the spectrum for a freely rotating molecule (dashed curve) [26] are given for the sake of comparison.

length of the interval on which the laser radiation interacts with the cluster beam to several dozen centimeters. With such a geometry, it became possible to employ lower-power diode lasers. An additional advantage in using pulsed lasers in such



Figure 3. IR absorption spectrum for the v_3 vibration of an OCS molecule inside a ⁴He_N (N = 6000) droplet (a) and inside a ³He_N (N = 12,000) droplet (b). On the horizontal axis, the variation of the wave number is given in relation to the beginning of the transition in Fig. 3a at $v_0 = 2061.64 \text{ cm}^{-1}$ [30].

setups is that the gating method can be utilized when measuring the signal. Multipass cells [31] and cavities amplifying the power [33] have been successfully used in conjunction with bolometers acting as detectors. While the employment of multipass cells can increase the signal strength by a factor of approximately 30-50 compared to the signal strength in the single-pass case, power-amplifying cavities make it possible to increase the signal strength by another factor of 10. One must bear in mind, however, that these approaches cannot always be applied [24]. The spectra of the molecules inside helium nanodroplets were studied by the beam depletion method with both the bolometers and mass spectrometers. Even at a droplet temperature of 0.38 K, the average angle by which the helium atoms are scattered in the course of evaporation amounts to about 10° in the laboratory system of coordinates. Thus, the evaporating helium atoms do not land in the detector, which reduces the flux on the beam axis, i.e., the beam is depleted.

Microwave excitation. When microwave radiation is used to excite molecules, the radiation is usually localized inside a waveguide, with a section of the waveguide being collinear to the cluster beam [24]. This results in a higher radiation power and also excludes the possibility of the radiation hitting the bolometer. Otherwise, the bolometer can markedly affect the signal to be measured.

Notice that the rotational spectroscopy of molecules inside helium droplets differs from the vibrational and electronic spectroscopies in that it is in essence multiphoton. The energies related to purely rotational transitions (0.5 -70 GHz) (see Table 1) are not high enough to evaporate even a single helium atom. The microwave spectroscopy of molecules inside helium droplets is based on the phenomenon that there is rotational relaxation inside an isolated droplet. Such relaxation makes it possible for the molecule inside the droplet to occasionally absorb photons whose energy transforms into that of the droplet. Experiments have demonstrated that when the molecules are excited by microwave radiation, the signal strength is approximately the same as the one in the case of vibrational excitation. This fact can be used to estimate the number of cycles of rotational excitation that each molecule undergoes over its residence time (for approximately 100 µs) in the microwave field. For instance, in this way an estimate of the relaxation time of the HCCCN molecule was made [124].

The existence of high-power sources of microwave radiation (> 10 W) and the large values of the dipole transition moments for molecules within this spectral region make it possible to conduct experiments on saturation spectroscopy [122, 124, 125]. By using the results of such experiments one can establish the nature of the inhomogeneous broadening of the spectra and determine the value of such broadening (see Section 3.2).

The double resonance method and Stark spectroscopy. The spectra of molecules inside helium clusters have been studied by the methods of double MW-MW and MW-IR resonance and by Stark spectroscopy. It is well known that the use of the double resonance method makes it possible to resolve the homogeneous line width against the background of inhomogeneous broadening. The first experiments on double resonance, precisely, on MW-MW resonances, were carried out by Reinhard et al. [124] and involved the HCCCN molecule. The researchers excited the rotational R(3) and R(4) transitions in the molecule. Measurements in conditions where the transitions are saturated showed that

Table 1. Rotational constants of some molecules, obtained from IR or microwave spectra with a well-resolved rotational structure. The absence of data in the 'Mode' column means that the rotational constants were obtained from purely rotational spectra.

Molecule	Mode	$B_{\rm gas},$ cm ⁻¹	$B_{\rm He},$ cm ⁻¹	$B_{\mathrm{He}}/B_{\mathrm{gas}},$	Refer- ences
DCH HCN HCN	 v ₁	1.208 1.478 1.478	0.999 1.204 1.175	82.7 81.5 79.5	[125] [125] [127]
HCCCN (HCCCN) ₂ (A)		0.1517	0.0525 0.0518 0.0168	34.0 34.1	[122] [33] [112]
(HCCCN) ₂ (B) CF ₃ CCH		0.0113 0.2851	0.0050 0.0717	42.2 25.15	[112] [33]
CF ₃ CCH HF	$2v_1$ (A) $2v_1$ (B) v_1	0.1908 0.0960 19.787	0.1004 0.0355 19.47	52.6 37 98.4	[33] [33] [140]
(HF) ₂ N ₂ -HF	$\begin{array}{c} v_1(v_2) \\ v_1 \end{array}$	0.2167 0.1066	0.0986 0.045	45.5 42.2	[133] [136]
CO-HF OC ³² S OC ³⁴ S	v_1 v_3 v_3	0.524 0.2029 0.1979	0.1022 0.0732 0.0706	19.5 36.1 35.7	[136] [139] [139]
CO_2 pH_2 - $OC^{34}S(A)$	v ₃ v ₃	0.39	0.154 0.0847	39.5	[32] [115]
pH_2 -OC ³⁴ S (B) pH_2 -OC ³⁴ S (C) SF ₆	v ₃ v ₃ v ₃	0.0911	0.0544 0.0422 0.034	37.3	[115] [115] [20]
HCOOH (A) HCOOH (B)	$v_2(v_1) v_2(v_1)$	2.5758 0.4020	1.3811 0.2970	53.6 73.9	[134] [134]
HCOOH (C) DCOOH (A) DCOOH (B)	$v_2(v_1) v_1 v_1$	0.3470	0.1996 1.16 0.24	57.5	[134] [134] [134]
DCOOH (C) NH ₃	v_1 v_2	9.96	0.21 7.5	75.3	[134] [120]
(CH) ₃ SiCCH (A) (CH) ₃ SiCCH (B) Mg-HCN	$2v_1$ $2v_1$	0.1056 0.0654	0.0275 0.0144 0.0285	26.04 22.02	[33] [33] [121]
Mg ₃ -HCN (A) Mg ₃ -HCN (B)	v_1 v_1		0.035 0.0167		[121] [121]

the typical line shape is preferably the inhomogeneously broadened one. It was anticipated that the double resonance spectra must reveal directly a homogeneous component of the spectral lines. However, the experimenters observed lines that were much broader than those expected. The line broadening was interpreted as an indication of spectral diffusion.

Later on, to clarify this situation, Callegari et al. [122] conducted experiments on double MW-IR resonance that involved the HCCCN molecule. But even before that Friedrich et al. [126] carried out experiments on double MW-IR resonance that involved OCS molecules. It should be emphasized that in the case of MW-IR resonance the experimenter can realize the advantage of this method: microwave radiation is useful in studying the entire set of rotational levels, namely, to equally probe the rotational states not related to the pump radiation. As a result of their experiments, Callegari et al. [122] and Friedrich et al. [126] found that all rotational states become populated, to a certain extent, as a result of pumping and that rapid rotational diffusion is the most probable cause of this. Indeed, the rotational relaxation times of molecules in helium droplets lie in the nanosecond range [124] (see Section 3.3).

Experiments on the Stark spectroscopy of molecules inside helium clusters have shown that this method carries great potential in studies of the interaction of impurity molecules and the helium surroundings and of the deformation of molecules and complexes by a soft helium solvent [31, 127]. Nauta and Miller [127] investigated the shape of the R(0) line of the HCN molecule in the IR region, observed line splitting, and found that the line strength distribution was similar to that expected of an isolated molecule. They attributed the line splitting to the splitting of the $|\mathbf{M}| = 0.1$ components. Such splitting was observed even in a zero field as a lowly resolved doublet structure of the R(0) line (Fig. 4).

It is notable that the mixing of rotational states is a manifestation of the Stark effect [128]. In the case of helium droplets, the attachment of helium atoms to the molecule inside a cluster can induce Q-branches (usually forbidden) in such linear molecules as HCN and HF, whose rotational constants are fairly large. Hence, their spectra in helium droplets contain only R(0) lines. The Stark spectroscopy method permits one to directly measure the beginning of the band (the zero line) and the rotational constant of the molecule [127]. Usually, the field employed in such experiments is rather weak, so as not to induce large line shifts. The size of such shifts is measured as a function of the field strength, and extrapolation to zero field strength yields the exact position of the Q-branch.

Notice that sometimes the rotational structure in the spectra is an unwelcome factor and measures are taken to suppress it. In some cases, the rotational structure not only does not yield new information but actually hinders one from obtaining such information. First, because of rotation the



Figure 4. Line R(0) of the DCN molecule $(v_1 = 0)$ and HCN molecule (v = 0, 1, 2) (the data of Refs [125, 125, 127], and [33], respectively). The presence of inhomogeneous broadening is evident. These results show that vibrational excitation has only a small effect on the structure of line broadening, while a change in the mass of the impurity molecule substantially alters the dynamics of the molecule inside the droplet. (From Ref. [24].)



Figure 5. Stark spectra of linear chains of HCCCN molecules [112]. Figures $2, \ldots, 9$ indicate the number of monomers in a chain. The spectra show that high resolution can be achieved through the spectroscopy of the pendular state. As helium droplets get smaller, the number of molecules in the chain decreases (transfer from Fig. 5a to 5c).

spectrum of the molecule is split into a set of lines, thus reducing the strength of the measured signal. Second, the typical width of the spectrum is comparable to $k_{\rm B}T$ (0.38 K or 0.25 cm⁻¹), where $k_{\rm B}$ is the Boltzmann constant. Rotational broadening of the spectrum leads to loss of resolution when we try to resolve closely spaced lines or bands. This factor is typical, say, for a cluster consisting of identical molecules.

An elegant solution for polar molecules in the gaseous phase is to resort to the method of spectroscopy of pendular states [126, 129], which amounts to using a fairly strong static field to convert the rotation of the molecule into oscillations (precession) of the dipole moment about the direction of the external field. In the limit of a strong static field (and in conditions where the permanent and induced molecular dipole moments are parallel to each other), the entire rotational contour collapses into a single line coinciding with the line of a purely vibrational transition. The integral strength of this line is three times the intensity in a zero field. This method has been applied in experiments with helium droplets, carried out by Nauta and Miller [31, 130]. It is an especially elegant method in the case of helium clusters, due to the very low temperature and the increase in the moment of inertia of the molecules. The specified factors make possible an easy implementation of the desired 'strong field' limit. The method has been in use at obtaining well-resolved spectra of linear chains containing up to eight HCN molecules [31] and up to twelve HCCCN molecules [112] (Fig. 5; see also Section 5.1).

The rotation of molecules inside helium droplets can also be suppressed by replacing ⁴He with ³He [30, 115]. This approach was employed by Grebenev et al. [113, 116], who induced a collapse of the absorption band of OCS- $(H_2)_N$ complexes to find the value of N from the measured band shifts. The method can also be applied to nonpolar molecules. However, in the case of ³He clusters the lines are not as narrow as in the case of ⁴He clusters.

3.2 Symmetry of molecules inside helium droplets

The first to observe a fine structure of rotational lines in rovibrational spectra of molecules inside ⁴He nanodroplets

were Hartmann et al. [20] in their experiments involving the SF₆ spectrum. Later on, such a structure was observed in the spectra of many unlike molecules (e.g., see Refs [131–136]). Table 1 lists some molecules whose rotational structure was resolved in IR spectra. In almost all the cases, the observed rovibrational structure is similar to that characteristic of the same molecules in the gaseous phase (conservation of linearity, symmetry, and selection rules), although the rotational constants often undergo dramatic changes (see column 5 in Table 1).

Volume excitations of a helium droplet should lower the droplet's symmetry. However, calculations based on the liquid-drop model have shown that at low droplet temperatures no thermally activated phonons exist [111] (see Section 6.3). Only surface modes of the droplet can get thermally activated, but such modes are only weakly coupled with solvated molecules, although in the final analysis exactly these modes can be responsible for the relaxation of molecules into a state that is in equilibrium with the droplet.

We emphasize that the rovibrational spectra of molecules in helium droplets exhibited no phonon wings. The wings are usually located on the high-frequency side in relation to molecular transitions and emerge because of the generation of one or several phonons in the solvent. Phonon wings have been observed and often dominate in electronic spectra of molecules [137] (see Section 4.8).

The symmetry of the rovibrational spectra of molecules inside helium droplets, observed in experiment, is similar to the symmetry of the spectra of molecules in the gaseous state. This is a strong argument in favor of the opinion that the molecules are in almost homogeneous surroundings. This suggests that there are no localized surface states, since the reduced symmetry of such states must lead to splitting of degenerate magnetic levels, as observed in the electronic spectrum of the He^{*}₂ excimer which is localized at the surface of the helium droplet [138]. We can assume that as soon as the molecule penetrates one or two subsurface layers, it finds itself in a region with a fairly homogeneous potential. Toennies, Vilesov and co-authors (see Ref. [139]) proposed interpreting the motion of a solvated molecule as the motion of a free particle in a spherical box. The total potential inside the droplet acts on the molecule in such a way that the molecule is localized at the droplet's center.

The relatively high density of the center-of-mass states related to the rotation of the molecule, which changes under vibrational – rotational excitation, is the source of inhomogeneous broadening in the spectrum. Initially, it was assumed that quantization of translational motion must lead to a potentially resolvable fine structure of the spectral lines. However, the spectra are usually taken in conditions where there is a fairly broad size distribution of the droplets, with the result that all the details of the fine structure become fuzzy, which ends up in the spectrum being inhomogeneously broadened.

We can assume that the interaction of the center-of-mass states and the rotational motion of the molecule provides a sizable contribution to the inhomogeneous broadening of spectral lines observed in rovibrational spectra [24]. However, the dependence of the helium-molecule interaction on vibrational excitation has always been ignored in calculations. In this case, the model predicts that the line shape is independent of vibrational transitions. When valid vibrationally averaged potentials for different vibrational states are proposed, it will become possible to predict the line shapes more accurately. Such a quantitative theory has yet to be developed.

3.3 Shapes of rotational lines

Only for a few molecules is there direct proof of the existence of inhomogeneous broadening of rotational lines [24]. Nevertheless, there are grounds to believe that this is a rule common for all molecules. One reason is that vibrational-rotational lines rarely correspond to Lorentzian line shapes predicted by simple models of line broadening assigned to the contribution of level lifetimes. This becomes especially evident in the case of the HCN molecule for which the R(0) transition $(J = 0 \rightarrow 1)$ has been studied in several vibrational states, as well as in the case of a deuterated molecule (see Fig. 4). In the spectrum of the OCS molecule, the lines in the P- and R-branches possess wings which may be harnessed to estimate the position of the beginning of the band and its width. The intensity of these wings increases with J. A possible explanation for this has been given by Stienkemeier et al. [137]. The experimental evidence suggests that inhomogeneous broadening contributes about 300 MHz or more to the line width, which corresponds to several nanoseconds in the level lifetime. However, often vibrational and rotational relaxation processes run much longer (with the possible exception of vibrationally excited HF molecules) [140], but still their duration is much shorter than 0.1 - 1 ms, which are characteristic values in the experiment (Tables 2 and 3).

Such slow relaxation can be explained by the fact that the frequencies of the molecular modes differ substantially from those of the helium 'bath' (helium is unable to react on the

Table 2. Vibrational state lifetimes calculated on the basis of the homogeneous values of the line widths of molecules inside helium droplets (by direct measurements in the case of Ar - HF). The causes of line broadening are given in the 'Notes' column. When relaxation is the cause, it is assumed that the chief cause of line broadening is vibrational relaxation. (Data taken from Ref. [24].)

Molecule	Mode	Lifetime, ns	Notes	References
HCOOH HCOOH d_1 -HCOOH H ¹² C ¹² CH H ¹³ C ¹³ CH (HCN) ₂ (HCN) ₂ (HFN) ₂ (HF) ₂ (HF) ₂ (HF) ₂ Ar-HF SF ₆ CU CCU	$ \begin{array}{c} v_1(\mathbf{A}) \\ v_1(\mathbf{B}) \\ v_1(\mathbf{C}) \\ v_1 \\ v_3 \\ v_3 \\ v_1 \\ v_2 \\ v_2 \\ v_2 \\ v_2 + v_5 \\ v_1 + v_4 \\ v_1 \\ v_3 \\ v_1 \\ v_2 \\ v_2 \\ v_2 + v_5 \\ v_1 + v_4 \\ v_1 \\ v_2 \\ v_2 \\ v_2 \\ v_3 \\ v_4 \\ v_1 \\ v_4 \\ v_1 \\ v_3 \\ v_4 \\ v_1 \\ v_2 \\ v_3 \\ v_4 \\ v_1 \\ v_2 \\ v_3 \\ v_4 \\ v_1 \\ v_2 \\ v_2 \\ v_2 \\ v_2 \\ v_2 \\ v_2 \\ v_3 \\ v_4 \\ v_1 \\ v_2 \\ v_3 \\ v_4 \\ v_1 \\ v_2 \\ v_3 \\ v_4 \\ v_1 \\ v_2 \\ v_3 \\ v_1 \\ v_2 \\ v_2 \\ v_2 \\ v_2 \\ v_2 \\ v_3 \\ v_1 \\ v_2 \\ v_2 \\ v_2 \\ v_2 \\ v_2 \\ v_3 \\ v_1 \\ v_2 \\ v_3 \\ v_1 \\ v_2 \\ v_2 \\ v_2 \\ v_3 \\ v_1 \\ v_2 \\ v_2 \\ v_2 \\ v_2 \\ v_3 \\ v_1 \\ v_2 \\ v_2 \\ v_3 \\ v_1 \\ v_2 \\ v_2 \\ v_2 \\ v_3 \\ v_1 \\ v_2 \\ v_2 \\ v_3 \\ v_1 \\ v_2 \\ v_2 \\ v_2 \\ v_3 \\ v_1 \\ v_2 \\ v_2 \\ v_3 \\ v_1 \\ v_2 \\ v_2 \\ v_2 \\ v_3 \\ v_1 \\ v_2 \\ v_2 \\ v_3 \\ v_1 \\ v_2 \\ v_2 \\ v_2 \\ v_3 \\ v_1 \\ v_2 \\ v_2 \\ v_3 \\ v_4 \\ v_1 \\ v_3 \\ v_2 \\ v_2 \\ v_3 \\ v_4 \\ v_1 \\ v_3 \\ v_3 \\ v_4 \\ v_1 \\ v_3 \\ v_4 \\ v_1 \\ v_2 \\ v_2 \\ v_3 \\ v_4 \\ v_1 \\ v_3 \\ v_4 \\ v_1 \\ v_2 \\ v_4 \\ v_1 \\ v_2 \\ v_2 \\ v_3 \\ v_4 \\ v_1 \\ v_3 \\ v_4 \\ v_1 \\ v_2 \\ v_4 \\ v_1 \\ v_2 \\ v_4 \\ v_1 \\ v_2 \\ v_2 \\ v_2 \\ v_3 \\ v_4 \\ v_1 \\ v_2 \\ v_2 \\ v_2 \\ v_3 \\ v_4 \\ v_1 \\ v_2 \\ v_2 \\ v_2 \\ v_4 \\ v_1 \\ v_2 \\ v_2 \\ v_4 \\ v_1 \\ v_2 \\ v_4 \\ v_1 \\ v_2 \\ v_2 \\ v_2 \\ v_2 \\ v_4 \\ v_1 \\ v_2 \\ v_4 \\ v_1 \\ v_2 \\ v_2 \\ v_2 \\ v_2 \\ v_2 \\ v_3 \\ v_4 \\ v_1 \\ v_1 \\ v_2 \\ v_2 \\ v_2 \\ v_2 \\ v_3 \\ v_4 \\ v_1 \\ v_2 \\ v_2 \\ v_2 \\ v_3 \\ v_4 \\ v_1 \\ v_2 \\ v_4 \\ v_1 \\ v_2 \\ v_2 \\ v_2 \\ v_3 \\ v_4 $	$\begin{array}{c} 0.12\\ 0.09\\ 0.05\\ 0.15\\ 0.12\\ \approx 1\\ > 0.64\\ 0.15\\ > 0.53\\ 7\times 10^{-3}\\ 3\times 10^{-3}\\ 1.5\times 10^{6}\\ 0.56\\ 0.16\\ 0$	Fermi resonance Fermi resonance Fermi resonance Fermi resonance Fermi resonance ? Dissociation Dissociation Relaxation ? Relaxation	[134] [134] [134] [132] [132] [133] [133] [133] [133] [133] [135] [131]
CH ₃ CCH	$2v_1$	0.16 - 1.5	Relaxation	[33]

Table 3. Rotational level lifetimes of molecules inside helium droplets. The droplet modes responsible for rotational relaxation are given in the 'Notes' column. (Data taken from Ref. [24].)

Molecule	Level or band	Lifetime, ns	Notes	Referen- ces
HCN-DCN	$J = 0J = 3, 4J = 2, 4v = 1, J = 1v_1, K = 1$	~ 10	Surface?	[125]
HCCCN		2-20	Surface?	[124]
HCCCN		10-100	Surface?	[122]
HF		12 × 10 ⁻³	Bulk	[140]
(HF) ₂		2.7 × 10 ⁻³	Bulk	[133]

time scale of the vibrational motion in the molecule). The maximum energy of the elementary excitation in the bulk of liquid ⁴He is about 20 K [141]. As a result, vibrational – translational (V–T) relaxation and even, in most cases, vibrational–vibrational (V–V) relaxation require that a large number (10–100) of phonons (rotons) be created simultaneously in helium. We can assume that the rate of such processes is low and decreases exponentially as the number of involved phonons grows.

The available experimental data show that the line profiles are determined by the relaxation times only if the energy of a single rotational quantum is sufficient for exciting the droplet's bulk modes. Since in this case the energy must not be smaller than the roton energy (≈ 8.6 K), only small molecules with large rotational constants manifest such behavior. The lines observed in experiments have a width of about 1 cm⁻¹, which corresponds to relaxation times of 1–10 ps (see Table 3).

3.4 Variation of rotational constants

An important characteristic of the rotational structure inherent in the spectrum of molecules injected into helium droplets is that in most cases the effective rotational constants are much smaller than their values in the gaseous phase. For molecules whose rotational constants are much larger than 1 cm⁻¹, these constants vary insignificantly, while for heavy molecules these values are smaller by a factor of three to four (see Table 1). Obviously, when the molecule rotates inside the droplet, at least a fraction of the helium must move and in this way contribute, at the expense of its kinetic energy, to the effective molecular moment of inertia. Several models that describe helium motion have been proposed.

The first, simple, model [20, 139] assumed that a certain number of helium atoms rigidly coupled with the molecule rotate together with it and directly contribute to the molecule's moment of inertia. It was found that this model operates well both for SF₆ and OCS molecules: the position and number of helium atoms rigidly coupled with the molecule agree with the experimentally established variations in the moments of inertia. There are drawbacks to this simple model, however. Firstly, according to estimates made when applying this model, for lighter molecules, such as NH₃ and HCN, even one helium atom rigidly coupled with the molecule has to increase the moment of inertia by a value that is 10 times greater than that exhibited in experiments. Secondly, it was found that the results obtained for the $OCS-H_2$ complex in helium [115] do not agree with the model entirely.

A more complicated model, which assumes that the first solvating layer consists of the normal fraction of helium, was posed in Ref. [30]. Basing their reasoning on the results of Andronikashvili's classic experiment [142], the authors of the model supposed that a fraction of normal liquid is rigidly coupled with the molecule and rotates with it, thus increasing the molecular moment of inertia. This model is incomplete, however, because the spatial dependence of the densities of the normal and superfluid liquids is not defined in it.

A quantum hydrodynamic model that describes the contribution of helium to the molecule's moment of inertia has also been developed. It is based on the fact that the linear motion of a rigid body through an ideal liquid makes the liquid move, too, and that this motion contributes to the effective mass for translational motion. For instance, for a ball the increase in effective mass is exactly half the mass of the displaced liquid [143]. Similarly, the rotation of an ellipsoid generates an amount of helium kinetic energy proportional to the square of the angular velocity, thus contributing to the effective moment of inertia. It turned out, however, that the contribution to the molecule's moment of inertia evaluated with this model amounts to only a small part of that established in experiments [31, 144]. On the other hand, the density of the helium surrounding the molecule is extremely nonuniform. Callegari et al. [145] have developed a quantum hydrodynamic model that allows for the density anisotropy in a meaningful manner. The moments of inertia of a number of molecules in helium droplets have been estimated by this model, and it has been found that they are in good agreement with the experimental data.

Another approach, known as the adiabatic following approximation, has been developed by Kwon et al. [22] and Callegari et al. [24]. It is based on the fact that the interaction potential between the molecule and helium atoms is anisotropic. Helium is considered a two-component liquid. It is assumed that some of the helium atoms belonging to the first solvating shell move together with the molecule in its rotation. It is also believed that the helium density in the coordinate system rotating together with the molecule is constant and equal to the density of helium surrounding an immobile molecule [145]. Physically, such an approach is admissible when the minimum separation between the rotational levels, 2B, is much smaller than the roton energy which determines the maximum energy of collective excitations [24]. This model provides a fairly good description of the motion in helium of molecules that are relatively heavy and possess a small rotational constant (e.g., SF_6 and OCS), while it is unsuitable for describing the motion of light molecules that have a large rotational constant (e.g., HCN and HCCH) (see papers [22, 24] and references cited therein).

Note that it has been established through experiments that when molecules inside helium droplets are excited vibrationally, the changes in the rotational constants are much larger than those related to the molecules excited in the gaseous phase [24, 33]. For instance, for a vibrationally excited HCCCN molecule the overall increase in the rotational moment of inertia varies from 0.35 amu $Å^2$ in the gaseous phase to 9.2 amu Å² in helium droplets, while for a CH₃CCH molecule it varies from 0.32 amu Å² to 8.5 amu Å² [33] (for the sake of comparison, see the data for these molecules in Table 1). These results show that the changes under consideration are caused basically by the change in the helium contribution to the effective moment of inertia of a molecule. As expected, excited vibrational states acquire higher contributions from helium surroundings than the ground state. This implies that when the molecule is excited, the density and/or anisotropy of an ambient helium tend to increase. At the same time, the absence of phonon wings in the rovibrational spectra indicates that these variations are insignificant. To calculate the solvate structure and the changes in moments of inertia as functions of the vibrational level, one must know the dependence of the interaction potential on the vibrational energy. Data of this kind do not exist, however.

3.5 Molecule – hydrogen clusters inside helium droplets

The study of the spectra of molecule-hydrogen clusters inside helium droplets is of special interest in connection with the purely quantum nature of the hydrogen molecule. The properties of this molecule have been studied through its effect on the spectra of the linear OCS molecule [113, 115, 116]. The first studies of van der Waals complexes $OCS-H_2$ (-HD, -D₂) [115] showed that the hydrogen molecule resides within a ringlike minimum of potential energy near the OCS molecule and is rather strongly delocalized with respect to the average position of the plane going through the OCS and H₂ molecules.

In the same year it was found (see Ref. [116]) that as parahydrogen molecules are added to the van der Waals complex OCS- $(pH_2)_N$ inside ⁴He droplets (0.38 K) or inside mixed droplets ³He-⁴He (0.15 K), the rovibrational spectrum of the complex very rapidly begins to resemble the spectrum of a symmetric top. However, the Q-branch disappears at N = 5 and N = 6, and the spectrum becomes similar to that of a linear molecule, i.e., becomes identical to the spectrum of a single OCS molecule inside a helium droplet. The reason probably lies in the fact that bosonic molecules (zero moment of inertia, I = 0) of parahydrogen pH_2 form a complete symmetry ring C_{Nv} (N = 5-6) around the OCS molecule, with the result that the Q-branch does not manifest itself in the molecular spectrum.

An interesting effect has been observed by Grebenev et al. [113]. The researchers found that for $OCS - (pH_2)_N$ clusters with N = 14 - 16, the Q-branch again disappears at 0.15 K but not at 0.38 K. They assumed that at the lower temperature (0.15 K) the greater delocalization of the pH_2 molecules leads to bosonic exchange and, hence, to a superfluid state of the hydrogen rings. This effectively induces the $C_{\infty v}$ symmetry group and forbids any states with $K \neq 0$. At the higher temperature (0.38 K), the pH_2 molecules are delocalized to a lesser extent and thermally populated states with |K| > 0 produce the Q-branch. Thus, the topic of Ref. [113] is the observation of a superfluid state of hydrogen.

Callegari et al. [24] gave a different explanation for this effect. They assumed that at the above values of N, the pH_2 molecules form several rings around the OCS molecule with a different number N_i of molecules in each ring. One can imagine a situation where two rings with $N_i = 6$ and $N_i = 8$ molecules of pH₂ with a C_{2v} symmetry group are formed. Using the data on the OCS-H₂ monomer, one can obtain the value of the moment of inertia of the given structure: $I_a \approx 370$ amu Å². This implies that the lowest state with a rotational angular momentum about the axis of the OCS molecule (K = 2) has an excitation energy of 0.26 K. Hence, this state can be populated to a large extent at 0.38 K and unpopulated at 0.15 K. The next two pH_2 molecules can then attach themselves to the two ends of the OCS molecule on the axis, thus preserving the C_{2v} symmetry and filling up the shell of 16 pH_2 molecules surrounding the OCS molecule. Such an explanation does not assume that molecular hydrogen can be in a superfluid state. The problem pertaining to pH_2 clusters requires further investigation to substantiate the hypothesis of the H₂ superfluidity.

3.6 Spectroscopy of molecules inside ³He and ³He-⁴He droplets

The IR spectra of molecules has also been studied for those cases where molecules are inside ³He droplets and mixed ³He⁻⁴He droplets (using the examples of SF₆ [109, 146] and OCS [30, 139] molecules). In mixed droplets, the ⁴He atoms due to their somewhat lower zero-oscillation energies are localized primarily around an impurity molecule [147]. Thus, a ⁴He cluster forms inside a ³He cluster. When the number of ⁴He atoms is small, the spectra of the molecules inside a ³He cluster are inhomogeneously broadened (Fig. 6). This broad-



Figure 6. Evolution of the IR spectrum of an OCS molecule inside a ${}^{3}\text{He}_{N}$ droplet (Fig. 3b) as the average number $\langle N \rangle$ of atoms in a ${}^{4}\text{He}_{N}$ droplet increases: $\langle N \rangle = 0$ (a), $\langle N \rangle = 7$ (b), $\langle N \rangle = 25$ (c), $\langle N \rangle = 35$ (d), $\langle N \rangle = 60$ (e), and $\langle N \rangle = 100$ (f). On the horizontal axis, the variation of the wave number is given in relation to $v_{0} = 2061.71$ cm⁻¹. (From Ref. [26].)

ening is related to the difference in the numbers of ⁴He atoms in the ³He clusters in the beam. In other respects the spectra resemble those for pure ⁴He clusters, except that the droplet temperature is much lower (≈ 0.15 K) due to the ³He cooling via evaporation. As the concentration of ⁴He atoms in an expanding medium increases from 0.1% to 4%, the temperature of the ⁴He droplets increases to its limiting value of 0.38 K [24].

The studies of the IR spectra of the OCS molecule in pure ³He droplets, done by Grebenev et al. [30, 139], showed that the spectrum collapses into a single broad band (Fig. 3b), as it does in the case of a classical liquid. On the other hand, the molecular spectra in ⁴He droplets exhibit a well-resolved rotational structure (Fig. 3a). Since the interaction potentials of the OCS molecule with ³He and ⁴He are approximately equal, this difference could be related to the different states of the droplets: superfluid for ⁴He, and that of a normal liquid for ³He.

Grebenev et al. [30] examined the threshold nature of the emergence of a superfluid state in ⁴He clusters with the use of the IR absorption spectrum for OCS. Into large ³He clusters with OCS molecules, the researchers gradually added a controllable number of ⁴He atoms (approximately up to a hundred atoms per cluster). They found that a rotational structure gradually emerged in the IR spectrum (see Fig. 6), which indicated that transition to the superfluid state was gradual, too. Superfluidity set in almost totally when the number N of ⁴He atoms in the cluster was about 60, which amounts to approximately two solvate layers. A further

increase in the number of ⁴He atoms in the cluster did not lead to a qualitative change in the molecular spectrum [30]. Notice that the transition to the helium superfluid state is, quite possibly, not smooth. The gradual nature of the observed threshold could be caused by the finite width of the size distribution of ³He clusters and the finite width of the concentration distribution of ⁴He atoms in ³He clusters in the conditions of the experiment.

3.7 Summary

The most amazing feature of rovibrational spectra of molecules inside helium nanodroplets is the manifestation of free molecular rotation in these spectra. For several molecules it was shown that the vibrational – rotational structure of the spectra of molecules inside helium nanodroplets is exactly the same as in the spectra of the identical molecules in the gaseous phase (conservation of linearity, symmetry, and selection rules), although the rotational constants undergo dramatic changes. It is the manifestation of the free rotation of molecules inside helium droplets that serves as direct spectroscopic confirmation of the superfluid nature of helium nanodroplets.

The symmetry of the rovibrational spectra of molecules inside helium droplets is similar to the symmetry of molecules in the gaseous phase, which is a strong argument in favor of the fact that the molecules are in almost homogeneous surroundings. This is an indication that there are no surface localized states, since the reduced symmetry of such states must lead to splitting of the degenerate magnetic levels.

It has been established that in most cases the spectral lines are inhomogeneously broadened. The source of the inhomogeneous line broadening is the relatively high density of center-of-mass states related to molecular rotation, which changes when the molecule is rovibrationally excited. No phonon wings have been detected in the rovibrational spectra of molecules inside helium droplets, which means that vibrational-rotational excitation of molecules has no effect on the state of helium.

An important characteristic of the rotational structure of the spectra of molecules implanted into helium droplets is that in most cases their effective rotational constants are much smaller than the corresponding gas-phase values. The changes in the rotational constants are much stronger when the molecules inside helium droplets are vibrationally excited than when they are excited in the gaseous phase. Profound theoretical models describe fairly well the data obtained from experiments. However, there is still no theory that explains the entire set of the results observed.

IR spectroscopy of OCS molecules inside mixed ${}^{3}\text{He} - {}^{4}\text{He}$ clusters has been used to establish the threshold number of atoms needed for the emergence of a superfluid state in ${}^{4}\text{He}_{N}$ clusters. The superfluidity of the ${}^{4}\text{He}_{N}$ cluster sets in almost completely at a number N of ${}^{4}\text{He}$ atoms per cluster equal to approximately 60.

An attractive property of the vibrational-rotational spectroscopy in helium droplets is the very small shift of zero vibrational lines, which is usually smaller than 0.1%. In contrast, the matrix isolation spectroscopy in ordinary Ne and Ar matrices yields much larger band shifts. For instance, in the case of HF, the band shift caused by the matrix amounts to 0.067, 0.24, and 1.1% for He, Ne, and Ar, respectively [148]. The small shifts for helium are due mostly to helium's low density and polarizability (even compared to those of other noble gases). However, the results of experi-

ments also show that often the effects mutually balance each other, and this leads to spectral shifts smaller than expected [24].

4. Electron spectroscopy of molecules and clusters inside helium droplets

The scientific literature devoted to the spectroscopy of electronically excited molecules and clusters inside helium nanodroplets is vast (see a recent review in Ref. [25] and earlier reviews in Refs [149-151]). Here, we consider only the most general properties and the characteristic features of the electron spectroscopy of molecules inside helium droplets and examine several specific examples. Notice that in many respects electron spectroscopy is similar to vibrational spectroscopy, but there are also marked differences between the two. For instance, the helium state is usually preserved under rotational and vibrational excitations of the molecules injected into the cluster, while under electronic excitation the degrees of freedom of helium may become excited. The reason is the larger change in the interaction potential between the molecule and the helium atoms under electronic excitation, which is the cause of a large change in the equilibrium configuration of the helium solvating shell. Being very soft, liquid helium is extremely sensitive to the interaction with the impurity particle. Electronic excitation may substantially change both the strength and the anisotropy of the interaction, and in some limiting cases it can even change attractive interaction to repulsive, which causes excited particles to be ejected from the droplet. In less violent cases, electronic excitation may cause a large change in the rotational constants and even lead to the appearance of phonon wings (PWs) in the spectra. Thus, the electronic spectra of molecules and clusters inside helium droplets contain a lot of information about the structure and the dynamics of the helium surroundings.

4.1 Experiment and method

In the case of electron spectroscopy inside helium droplets, molecular excitation is achieved in the wavelength range that extends approximately from 1.5 µm to vacuum ultraviolet (VUV). The common sources of light for such excitation are commercially available lasers and synchrotron radiation. Experimenters have successfully used cw diode lasers [85, 86], Ti-Sa lasers [152-155], as well as nanosecond [45, 156-161], picosecond [162-164], and femtosecond [165-169] pulsed lasers. As in the case of IR spectroscopy, in experiments involving electronic excitation of molecules one can use detection methods based on measuring the signal with a mass spectrometer [20, 21, 149, 157, 159, 161]. However, in these experiments it was found that the employment of other detection techniques is preferable when electronic excitation is involved. For instance, surface-ionization detectors have been successfully employed in experiments on the spectroscopy of alkali metal atoms [155] and He^{*}₂ excimers [85, 86] (such detectors are known to have a high quantum yield). When electronic excitation is introduced, the specified particles separate from the droplets, which leads to a decrease in the ion current when detection is done in the beam plane. Another widely used method is that of laserinduced fluorescence (LIF) [61, 101, 137, 152, 154, 158, 159, 170, 171]. For atoms and molecules with a fluorescence quantum yield of about 10%, this method ensures a signalto-noise ratio 10-100 times greater than that ensured by the method in which the decrease in signal strength as a result of beam depletion is measured by a mass spectrometer. The LIF method is also more sensitive compared to the abovementioned method in the case of large droplets, i.e., droplets with more than 10^4 helium atoms [172]. It should be emphasized that in experiments with helium clusters the method of multiphoton ionization [165, 167, 168, 173–175] has also been successfully used in conjunction with a quadrupole mass filter or the time-of-flight method.

4.2 Atoms of metals on the surface of helium droplets

The van der Waals attraction between helium and metal atoms is very weak. The binding energy of alkali metal atoms and helium atoms is the weakest in nature. For instance, the depth of the potential well for the following pairs is: Li-He, 1.5 cm⁻¹; Na-He, 1.2 cm⁻¹; K-He, 0.9 cm^{-1} ; Rb-He, 0.8 cm^{-1} , and Cs-He, 0.7 cm^{-1} (see Ref. 176]). Hence, the size and shape of the helium solvating shell surrounding a metal atom are determined mainly by the repulsive part of the interaction potential, which is caused by Pauli repulsion between the parallel spins of the electrons in the helium atom and the metal atom. Thus, the region in the helium droplet occupied by the solvated metal atom is to a certain degree similar to a bubble surrounding a free electron in liquid helium. However, the radius of this bubble (5-10 Å)is smaller because the electrons in this case are not free: they are bound (true, not very strongly) to the ion core [150, 151, 177 - 180], with the result that their zero-oscillation energy is lower.

The spectra of metal atoms in liquid helium have been thoroughly studied (e.g., see the reviews in Refs [150, 151]). Since the equilibrium radii of the bubble surrounding an excited atom are larger than in the case where the atom resides in the ground state, so as a result of electronic excitation the system acquires a sizable amount of potential energy due to strong repulsion, and the solvate bound to the atom becomes excited. Hence, the absorption lines of the atoms are broadened ($\delta v \approx 50 - 300 \text{ cm}^{-1}$) and are strongly shifted $(\Delta v \approx 500 - 1500 \text{ cm}^{-1})$ to the blue part of the spectrum in relation to the lines of a free atom [150, 151, 179-183]. The emission of radiation that follows excitation usually happens after the bubble relaxation, with the result that the corresponding spectral lines are shifted not so strongly into the blue region and sometimes even have a small red shift $(\Delta v \approx \pm 30 \text{ cm}^{-1})$ and are narrower $(\delta v \approx 30 \text{ cm}^{-1})$ [150, 151, 180, 184, 185]. A distinctive feature of helium droplets is that here we cannot ignore the surface effects, in contrast to the case of bulk helium. If the attractive interaction between the metal and helium atoms is fairly weak, as in the case of alkali metal atoms, at equilibrium a metal atom will most likely form a surface state rather than be pulled into the bulk of the helium. In the case of a helium droplet with a radius of 10-50 Å, it takes about $10^{-3}-10^{-4}$ s for the equilibrium position to be reached [25].

The corresponding absorption spectra show whether the metal atom resides at the surface or inside the helium droplet. It has been found (see the review [25] and the references cited therein) that the spectra of metal atoms (Ag, Al, Eu, and Mg) attached to helium clusters strongly resemble the spectra obtained for the bulk liquid, which means that the metal atoms are inside the helium droplets. The size of the blue shift and the width of the spectra ordinarily amount to about $300-500 \text{ cm}^{-1}$. This agrees with the predictions of the model that allows for bubble formation [150]. As noted at the beginning

of Section 4, electronic excitation of an atom may lead to a situation in which its attractive interaction with the droplet is replaced by repulsive interaction, with the result that the excited metal atom may be ejected by the droplet. For example, the multiphoton ionization spectrum of silver atoms inside helium droplets exhibits the progression of Rydberg levels characteristic of a free Ag atom [173, 174]. This is an indication that such atoms leave the droplets in the course of approximately 10 ns after excitation, and are then ionized in a vacuum. But it is not quite clear whether this process is the predominant one. The time-resolved fluorescence spectra of Mg atoms show that even upon cessation of electron excitation the atoms remain primarily inside the droplet [186] (Fig. 7c).

Experimenters have established that all alkali metal atoms (Li, Na, and K [152], as well as Rb and Cs [175]) are on the surface of helium droplets rather than inside these droplets. This irrevocably follows from the fact that the spectra are much narrower and are slightly shifted (e.g., see Fig. 7a) in



Figure 7. LIF spectra of Li (a) [152], Sr (b) [153, 154], and Mg (c) [154] in helium droplets. The vertical lines indicate the transition frequencies in the gaseous phase. The LIF spectra of Sr [181] and Mg [182] in bulk helium (light curves) are given for the sake of comparison. The spectra are presented as functions of the difference of frequencies with respect to transitions in the gaseous phase: 14903.83 cm⁻¹ for Li, 21698.43 cm⁻¹ for Sr, and 35051.36 cm⁻¹ for Mg. (From Ref. [25].)

relation to those observed for bulk liquid helium [180, 184, 185]. For instance, the peaks in the spectra of atomic transitions $({}^{2}P \leftarrow {}^{2}S)$ are only slightly shifted toward the blue side of the spectrum (by approximately 10 cm⁻¹ for Na, K, and Cs) or are even shifted toward the red side of the spectrum (by approximately 4 cm^{-1} for Li) in relation to the transition frequencies typical of the gaseous phase. The profiles of the spectral lines have a width ranging from 10 to 50 cm^{-1} , and are accompanied by wings that extend toward the high-frequency region. Theoretical evaluations have shown that alkali metal atoms are located approximately at a depth of 5-6 Å from the surface of the droplet [187] (where the helium density is roughly half the bulk density) and that the droplet surface near the atom is deformed due to formation of a kind of the 'dimple'. Calculations predict that the binding energy of the surface is approximately 15 cm⁻¹ [187], which agrees well with the results of measurements of the threshold energy needed to detach the atoms from the surface, done from data on the emission of free Na* and K* atoms [162]. The shape of the absorption spectra of alkali metal atoms at the droplet surface may be described satisfactorily by the bubble model in which the calculated shape of the helium droplet surface is used [152].

The situation is quite different with alkaline-earth atoms. Even knowing the interaction potential between such atoms and helium is not sufficient for deciding whether the atoms are localized at the surface of the helium droplet or inside such a droplet. Only in the case of Mg have Reho et al. [186] shown that the atoms are inside the droplets. Ca, Sr, and Ba atoms attached to helium droplets produce a much larger blue shift of the spectra than alkali metal atoms do [181] (Fig. 7b), which implies that they are immersed in liquid helium and form bubble states. However, the size of this shift is much smaller than that of a similar shift in spectra taken in bulk helium [153, 154] (Fig. 7c), which can be explained, obviously, by the localization of the atoms near the droplet surface, where the helium density is low. This is corroborated by calculations [188] which show that Ca atoms are localized in a deep 'cavern' and are covered by a thin layer of helium whose density amounts to only 1% of the bulk density. Since the results of theoretical predictions are highly dependent on the details of the interaction between an atom and helium, the experimentally established spectra serve as initial data for selecting the correct interaction potential.

4.3 Formation of molecules on the surface of helium droplets

The production of dimers or clusters of alkali metal atoms has been a pressing experimental problem for a long time. The formation of molecules and alkali metal clusters on the surface of helium droplets ensures an elegant solution to this problem. Moreover, several additional and very interesting features manifest themselves in the process of formation. Dimers of alkali metals can form either in the singlet state or in the triplet state. The pairing of electron spins in the singlet state corresponds to formation of a covalent bond (5943 cm⁻¹ for Na₂). On the other hand, the configuration of parallel spins of valence electrons brings about Pauli repulsion. For instance, a triplet state being formed has a very shallow van der Waals minimum (174 cm $^{-1}$ for Na₂). In experiments with the gaseous phase in a heated tube, dimer formation occurs at high temperatures, so that the equilibrium concentration of triplet states is negligible. Only the use of molecular beams with appropriate carriers makes it possible to produce

molecules in the triplet state and conduct experiments in which such states are excited [189, 190].

Helium droplets may solve this problem. Two or more metal atoms can place themselves on a droplet in succession in the trapping cell. These atoms move freely inside the droplet or on its surface until they meet one another and form a molecule or a large cluster. The newly formed particles rapidly cool off to the droplet's temperature ($T \approx 380$ mK), a fact confirmed by studies of spectra in the IR region with a well-resolved rotational structure [20, 24, 149] (see Section 3). Since dimers and trimers of alkali metal atoms are coupled very weakly to the surface of a helium droplet (the binding energy is less than 1 cm⁻¹), it is not surprising that the relaxation of an amount of energy equal to almost 6000 cm⁻¹ leads to effective detachment of singlet molecules from the droplet [191]. On the other hand, the weakly coupled triplet molecules accumulate at the surface of the droplet. Figure 8 displays an LIF spectrum of sodium-doped helium droplets in the 12900-16500-cm⁻¹ range. The spectrum contains mostly strong triplet bands $(1^{3}\Sigma_{g}^{+}-1^{3}\Sigma_{u}^{+})$, while singlet transitions are hardly visible. This suggests that the concentration of the weakly coupled triplet molecules on the droplet surface increases [137, 191]. Similar results have been obtained for Li2 and K2 molecules.

It should be remarked that both triplet and singlet molecules localize at the droplet surface. This fact is corroborated by the very small spectral shift of the electron transition frequencies (less than 5 cm^{-1}). On the other hand, large spectral shifts of about 700 cm⁻¹ have been observed for Na₂ singlet–singlet transitions in bulk liquid helium [185]. The fact that alkali metal molecules localize at the droplet surface is also corroborated by computations based on the density functional [192] and by semiempirical calculations [193]. According to these evaluations, Na₂ and Li₂ molecules occupy dimples on the droplet surface, just as atoms do.

Vibrational progressions $v' \leftarrow v'' = 0$ in the electronic transitions $1^{3}\Sigma_{g}^{+} - 1^{3}\Sigma_{u}^{+}$ clearly manifest themselves in the excitation spectra of dimers of alkali metal atoms (see Fig. 8). The width of the vibrational bands was found to be about 30 cm⁻¹. No rotational structure was resolved in the spectra. Higgins et al. [170] and Stienkemeier et al. [191] used such spectra to determine the vibrational constants of molecules in excited electronic states. The results of measurements in the



Figure 8. LIF spectrum of sodium-doped helium droplets in the 12900 - 16500-cm⁻¹ range [137, 191]. The transition bands were identified. Bands pertaining to quartet transitions in Na₃ molecules emerge on the high-frequency side of the spectrum. (Data taken from Ref. [25].)

gaseous phase were found to be in good agreement with theoretical predictions. In addition, bound-bound transitions and transitions into the repulsive dimer states $1^{3}\Pi_{g}$ have also been studied by Higgins et al. [170]. Vibrationally allowed emission spectra caused by laser excitation of the ${}^{3}\Sigma_{g}^{+}$ state exhibit strong vibrational relaxation which is related to the proximity of the helium surface, as well as rapid triplet-singlet internal conversion [170].

Each electronic – vibrational band of the singlet transition in Na₂ (A¹ Σ_u^+ – X¹ Σ_g^+) has a relatively sharp ($\delta v \approx 0.5 \text{ cm}^{-1}$) zero phonon line (ZPL) accompanied by a phonon wing on the blue side (see Fig. 8). The width of the phonon wing decreases approximately from 110 to 30 cm⁻¹ as the number of helium atoms in the droplet decreases respectively from approximately several thousand to several hundred [170]. Such a behavior shows that the electron transitions are strongly dependent on the surface modes of the helium droplet. Some spectral features of the photon wing were studied by Higgins et al. [170] at excitation energies on the order of the roton energies in liquid helium. The researchers found that despite surface localization the molecules are coupled fairly strongly to the bulk modes of the droplet.

4.4 Time-resolution studies

The results discussed in Sections 3.1-3.6, 4.2, and 4.3 show that the absorption molecular spectra provide a fairly full picture of the dynamics of molecules inside helium droplets. For instance, the rotational and vibrational relaxation times of molecules implanted into the droplets and excited by laser light can be estimated by the widths of the spectral lines and from measurements on absorption saturation [20, 24, 122, 125, 140]. Direct time-resolved spectral measurements constitute another approach to studying molecular dynamics. A fairly large number of investigations have been carried out in this area of research (e.g., see the review [25]), including research done with picosecond and femtosecond lasers and with the excitation-probing method. Among the problems studied were the formation of the Na*-He and K*-He exciplexes [162-164] and KHe_N [175], the time evolution of the excited state $1\,{}^3\Pi_g$ in the K_2 molecule coupled with a helium droplet [163], and the dynamics of the detachment of K atoms from helium droplets [175].

Not so long ago, the excitation-probing method aided with femtosecond lasers was used by Diederich et al. [167] to study the Coulomb explosion of magnesium clusters inside helium droplets. The researchers found that at high laser-light intensities the magnesium clusters decompose into atomic ions. With moderate intensities (about $5 \times 10^{12} \text{ W cm}^{-2}$), the experimenters observed the formation of helium snowballs around magnesium ions (MgH e_N^+), with the number of helium atoms being up to N = 150. As the delay time between the excitation and probe pulses increased, an increase in the number of snowballs in the first 4 ps was observed. A further increase in the pulse delay time resulted in an exponential decrease in the number of helium atoms coupled with the magnesium ions. Thus, the evolution of the system was studied within a fairly broad time interval (longer than 50 ps) after laser excitation had ceased, which clarified the picture of the dynamics of the interaction between a heavily fragmented metallic cluster and a helium droplet.

4.5 Excitation of organic molecules inside helium droplets

Experiments on electronic excitation of organic molecules inside helium droplets have involved electron transitions into the lowest excited singlet states. Among these molecules were glyoxal [157, 172, 194], polyaromatic molecules [158–160], indoles [101, 171], and porphyrins [195, 196]. Most often the spectra were obtained by the LIF method, and sometimes the beam depletion method was used. Usually, the spectra comprised a sharp line corresponding to the beginning of the transition, accompanied by well-resolved vibrational bands on the high-frequency side. The zero transition and the transitions in each vibrational band have sharp phononless lines followed by PWs. The strength of these wings rapidly increases near zero phonon lines. Phonon wings extend over $\approx 20-50$ cm⁻¹ in the direction of high frequencies [25].

Zero electron transitions for some molecules in helium droplets and the corresponding gas-phase frequencies are listed in Table 4. For all the molecules listed in this table the frequency shifts are fairly small. For some molecules, the shift proceeds toward the red region of the spectrum in relation to the corresponding gas-phase frequencies, which is an indication that the coupling of the molecule with the droplet increases under electronic excitation. Such a phenomenon is usually observed in other matrices, where the coupling is caused primarily by the van der Waals interaction. The above-mentioned small line shifts differ markedly from the large shifts of absorption lines of metal atoms in liquid helium (see Fig. 7c), for which the repulsive part of the potential plays the leading role in the bubble model. The sizes of the shifts of the zero spectral lines, caused by the interaction with the helium matrix, range from 10 to 100 cm⁻¹, which is approximately a hundred times larger than in the case of vibrational transitions [24] (see Section 4.8), due to the strong coupling of the helium matrix with excited electronic states. It must be noted, however, that the energy of electronic excitation is approximately 10 times higher than the energy

Table 4. Frequencies of the zero phonon lines for $S_1 \leftarrow S_0$ transitions in some molecules inside helium droplets. (Data taken from Ref. [25].)

Molecule	Frequen- cy *, cm ⁻¹	Frequency shift, cm ⁻¹	Number of ZPLs	References
Glyoxal	21942.8	-30.6	1	[157]
Indole	35282	+43	3	[101]
3-methylindole	34943	+61	3	[101]
NATA **	35014	+59	4	[101]
Tryptophan	34960.8	+ 55	1	[171]
Tryptamine	34959.6	+44.1	3	[101]
Tyrosine	35538.0	+47.8	1	[171]
Tetracene	22293.4	-103	2	[158]
Pentacene	18545.0	-104	1	[158, 159]
Porphin	16310	-10	1	[195]
Phthalocyanine	15088.9	-46	1	[195]
C ₆₀	15666	-14 ± 4	1	[161]
BaO (A ¹ Σ^+ – X ¹ Σ^+)	16722.3	+40.3	1	[220]

* Typical errors caused mainly by uncertainties in the calibration of lasers amount to about 1 cm^{-1} .

** NATA stands for N-acetyl-L-tryptophanamide, C13H15N3O2.

of vibrational transitions.

4.6 Zero phonon lines

Zero phonon lines comprise sharp spectral bands with a width of about $0.2-1 \text{ cm}^{-1}$, often limited by the width of the laser lines when pulsed lasers are used for excitation. Thus, the inhomogeneous line broadening is very small in helium

droplets, in contrast to other matrices. Usually, the spectral lines for the same transitions in other matrices are wider (up to a factor of 1000) [16, 17]. The large inhomogeneous line broadening in solid matrices is usually caused by the fact that chromophore molecules may occupy many metastable places, each of which is characterized by a slightly different interaction with the matrix. The recorded spectra show that such places either do not form entirely in helium droplets or their number is negligible.

The interaction between a chromophore molecule and helium atoms is much stronger than between helium atoms proper, with the result that the helium surroundings take the shape of the molecule even in the case of highly asymmetric particles, such as amino acids [171]. This makes it possible to use sharp zero phonon lines to investigate small changes in molecular structure, usually related to small spectral shifts. The most interesting demonstration of the possibilities of helium droplets as perspective cryogenic matrices is presented by the spectra of the $S_1 \leftarrow S_0$ transitions in the amino acids, tryptophan, and tyrosine [171]. These spectra, which were first studied in molecular beams with carriers, cooled to $T \approx 10$ K [197, 198], constitute important probes in the case of proteins and peptides.

Like IR spectra, electronic-vibrational spectra of molecules make it possible to extract information about the vibrational frequencies of molecules, but only in the excited S_1 state. Notice that these two methods can be applied to study different groups of vibrations. Not totally symmetrical vibrational modes are usually excited in the IR region, while totally symmetrical fundamental and combinational vibrations are excited in electron transitions to the S_1 state [199]. One can assume that at $T \approx 380$ mK all molecules in helium droplets are in the ground vibrational state. This excludes the possibility of the emergence of 'hot' bands whose presence considerably complicates the interpretation of molecular spectra. Experiments have shown that the vibrational frequencies extracted from the electronic-vibrational spectra of molecules inside helium droplets are in good agreement $(\pm 5 \text{ cm}^{-1})$ with those obtained for the gaseous phase. This result agrees well with the fact that the frequency shifts in vibrational spectra in the IR region are small [24, 149] (see Section 3).

It should be remarked that a rotational structure in the electronic spectra of molecules inside helium droplets may show itself as well. Indeed, Pörtner et al. [172] observed such a structure in the 0–0 band ($\approx 21930 \text{ cm}^{-1}$) of the glyoxal molecule (CHOCHO). It has been established that, in accordance with the results of IR spectroscopy for other molecules [20, 21, 30, 33, 109, 118, 127, 131, 139, 145, 146], the ground-state rotational constants ($A = 0.643 \text{ cm}^{-1}$ and $B = 0.0728 \text{ cm}^{-1}$) of glyoxal in helium droplets are smaller than in the gaseous phase by a factor of 2.75 and 2.35, respectively. This points to the large contribution of helium, ΔI_{He} , to the effective moment of inertia I_{eff} :

$$I_{\rm eff} = I_{\rm mol} + \Delta I_{\rm He} \,. \tag{4.1}$$

What is new here is the large change ΔI_{He} introduced by electronic excitation. In the event of vibrational excitation, ΔI_{He} is almost 10 times smaller. This large difference shows that due to the large change in electron density, caused by electronic excitation, the helium surroundings undergo substantial transformation. Thus, the rotational constants of excited electronic states are a sort of sensitive probe of the electron density in molecules.

4.7 Line widths

Despite the fact that narrow-band ($\delta v \approx 1$ MHz) cw lasers were used in measurements of the spectra of the glyoxal molecule in helium droplets, Pörtner et al. [172] found in their experiments that the rotational lines have a width (at half-height) greater than 1 GHz. The researchers established that the lines broaden as the number N of helium atoms in the droplet increases, approximately from 1 GHz at N = 2600 to 3 GHz at N = 20,000. The same dependence on N was corroborated in studies of well-resolved spectra of the tetracene molecule in helium droplets by the LIF method [172]. At the same time, when certain molecules were vibrationally excited, a slight decrease in the line width was detected as the droplet became bigger [33, 131, 139]. The reason for such behavior of the broadening of molecular transitions in helium remains unclear.

In the case of vibrational excitation there is obviously a dependence of line broadening on the lifetime of the level involved in vibrational relaxation. Indeed, experimenters (see Refs [157, 159]) found that the lines for nonzero vibrational bands were broader than those of the zero band. The reason for inhomogeneous line broadening could also be the finiteness of the droplet sizes and the peculiarities of the size distribution of droplets (see Ref. [25] and the literature cited therein). Another reason for line broadening could be the excitation of the dense spectrum ($\Delta v \leq 0.1 \text{ cm}^{-1}$) relevant to the translational degrees of freedom in helium, which are similar to those degrees of freedom of a particle residing in a three-dimensional potential well [172, 200, 201]. Electronic excitation may dramatically alter the effective mass of the molecule in helium and the force constant for the molecule in the effective potential of the droplet, thus increasing the Franck-Condon activity. Since line broadening hinders the recording of well-resolved spectra (places a theoretical limit on resolution), it is obvious that the nature of this effect requires further investigation.

4.8 Phonon wings

Each zero phonon line of molecules is accompanied by a phonon wing from the blue side of the spectrum [101, 157-160, 195]. Phonon wings are an indication that the compressed volume of the helium surroundings vibrates and that these vibrations are caused by the electronic excitation of the molecule. Hartmann et al. [157] found that the PWs of the glyoxal molecule in a ⁴He droplet (Fig. 9a) is separated from the zero phonon line by a distinct dip (gap), whose width is about 5 cm⁻¹. Pryce [202] developed a theory of PWs for impurities in solids. The theory predicts that the strength of a PW is proportional to the density of phonon states [157, 202]. Applying this theory to glyoxal, the phonon line can be described fairly well by using the dispersion curve of elementary excitations in bulk superfluid helium [203-207] (the light line in Fig. 9a). The theory predicts that the width of the gap between the zero phonon line and the peak in the phonon wing spectrum equals the roton energy. The discrepancy between the observed energy (7.8 K) and the roton energy (8.65 K) in bulk liquid can be attributed to the fact that the helium density near the molecule increases substantially. Since the distinct phonon-roton curve is a characteristic of the superfluid state of helium, this result is one more experimental confirmation of the superfluidity of ⁴He droplets.

The recorded spectrum of glyoxal in uncontaminated normal (i.e., nonsuperfluid) ³He droplets [156, 172, 194] (Fig. 9b) has no gap between the zero phonon line and the



Figure 9. Spectrum of the band origin for the $S_1 \leftarrow S_0$ transition of a glyoxal molecule (C₂H₂O₂) inside ⁴He_N (a) and ³He_N (b) droplets with $N \approx 5000$ helium atoms [194]. The light line in Fig. 9a represents the results of calculations done in Ref. [157]. (From Ref. [25].)

phonon wing, which agrees with the above statement and also corroborates the fact that elementary excitations in ⁴He and ³He are of different natures. Pi et al. [147] studied the evolution of the roton dip as a known number of ⁴He atoms are added to an uncontaminated ³He droplet with a glyoxal molecule inside it. Because of the low zero-oscillation energies, the ⁴He atoms form a shell surrounding the glyoxal molecule [204]. The investigations done by Lugovoj et al. [156], Pörtner et al. [172], and Pörtner [208] suggested that a distinct dip (gap) between the zero phonon line and the phonon wing appears again when the number N of ${}^{4}\text{He}$ atoms becomes ≥ 120 . Theoretical evaluations for an uncontaminated ${}^{4}\text{He}_{N}$ cluster [108, 209, 210] showed a gradual emergence of a roton minimum for clusters with $N \ge 100$, which was interpreted as the onset of superfluidity, in full compliance with the experimental results. However, establishing the details of the transition to the superfluid state and the role of the attractive interaction between helium atoms and a chromophore molecule will require further investigation.

4.9 Localization of helium atoms near a molecule and the splitting of zero phonon lines

Large aromatic molecules whose interaction with helium atoms is strong (a binding energy of approximately 100 cm^{-1} per helium atom) are the cause of distinct localization of helium atoms in the first solvating shell. This leads to the following changes in the spectra:

(1) a dense helium shell may serve as a base for the formation of structural isomers, resulting in a splitting of zero phonon lines;

(2) the shape of the phonon spectrum transforms, thus reflecting the more localized excitations of the compressed shell, and

(3) a dense helium shell surrounding a molecule may alter the probability of formation of various van der Waals complexes with atoms.

The spectra of some molecules, such as indole [101] (Fig. 10) and tetracene [159], in helium exhibit multiplets of zero phonon lines separated by approximately $1-2 \text{ cm}^{-1}$. Since these molecules possess no isomers, the splitting can be related only to some of the nonequivalent configurations of the helium surroundings. These results show that the initial idea that liquid helium constitutes a completely homogeneous matrix must be modified. The nature of line splitting has been studied in greatest detail for the tetracene molecule. The experiments on burning dips in the spectra and on measuring the radiative lifetime, conducted by Hartmann et al. [159] and Lindinger et al. [160], corroborated the fact that both the ground and excited states of tetracene molecule inside helium droplets are split into two components. This excludes the possibility of assuming that some low-energy vibrations are the reason for such splitting. The researchers found that the dip burnt in the spectra exists longer than 1 µs. This sets a lower limit on the lifetime of helium excited states in a droplet [159]. The most plausible explanation of such splitting is that several helium atoms are localized at the surface of the planar molecule, and because of this the topology of the appropriate interaction potential determines the number and structure of the isomers. It is worth noting that the distance between helium atoms in the liquid is about 3.6 Å, which is much larger than the characteristic distance between the potential minima of polyaromatic molecules, i.e., the distance between



Figure 10. Spectra of the band origins of indole $(v_0 = 35282 \text{ cm}^{-1})$ (a) and 3-methylindole $(v_0 = 34943 \text{ cm}^{-1})$ (b) molecules in a helium droplet $(N = 8 \times 10^5)$ [101]. The absolute transition frequencies were listed in Table 4. (From Ref. [25].)

the centers of adjacent aromatic rings, which amounts to ≈ 2.5 Å. Thus, helium atoms are probably unable to occupy all the minima at the same time. The resulting combinations of the occupied positions create isomers of the helium solvating shell, which leads to line splitting in the spectrum of the chromophore molecule. Since the attractive potential rapidly decreases as the interparticle distance becomes greater, we can assume that only atoms of the first solvating shell play an important role in the formation of isomers, with the result that only a small number of isomers are produced. More distant helium atoms probably belong to the quantum liquid and do not participate in the formation of isomers. On the other hand, in solid matrices the defects induced by the impurity molecule may propagate through a larger number of external shells, which leads to formation of a great number of isomers. The spectra of the isomers usually overlap, which explains their inhomogeneous broadening. It has been established through experiments that the structure of the splitting depends significantly on the surroundings of the chromophore. For instance, the addition of an Ar atom to the tetracene molecule inside a helium cluster completely eliminates splitting of zero phonon lines [158, 159]. The reason is that the addition of the atom leads to a rise in the inner temperature of the cluster, with the result that the structure of the helium surroundings changes.

Notice that the shapes of phonon wings for large molecules differs dramatically from that of the glyoxal molecule (see Fig. 9). Usually one can observe additional low-frequency modes with energies lower than the roton energy, and the phonon wings are less intense. These special features have yet to be explained (see the review [25] and the references cited therein).

4.10 Summary

The studies covered in this section have made it possible to establish and understand many properties of molecules and atoms that are on the surface of, and inside, liquid superfluid helium droplets and the nature of their interaction with helium atoms. What is more, spectroscopic methods provided new information about small liquid helium droplets themselves. Direct experimental substantiation of the superfluidity of helium nanodroplets was provided by detection of a gap between the zero phonon line and the phonon wing in electronic spectra. This property, which was first observed in the glyoxal molecule, is directly related to the well-known phonon – roton dispersion curve characteristic of a superfluid liquid.

The spectra of large molecules inside helium clusters (indole, porphyrins) exhibit additional features, such as the splitting of zero phonon lines and bands on phonon wings that are similar to molecular spectra. These features are related to the localization of helium atoms near a molecule. Future studies on the dependence of these characteristics on the cluster size will probably help in understanding the properties of the quantum liquid itself in systems of a limited size.

The line widths relevant to electron transitions are about 0.1 cm^{-1} , which is approximately a thousand times smaller than those observed for the same transitions in ordinary solid matrices. The effect of helium droplets on the transition frequency is negligible. For electronic spectra, the line shifts caused by the interaction with the matrix vary from, say, $\approx 30-50 \text{ cm}^{-1}$ in the case of organic molecules inside helium droplets to $\approx 5-6 \text{ cm}^{-1}$ in the case of dimers and trimers of alkali metal atoms on the droplet surface. Just compare this to

ordinary solid matrices, where the shift ranges from $\approx 200-300 \text{ cm}^{-1}$ to $\approx 1000 \text{ cm}^{-1}$. The electronic spectroscopy of molecules in helium droplets presents an additional approach to studying vibrational frequencies in excited electronic states. We can expect that such studies will soon extend to molecules that are of importance from the viewpoint of biology (proteins and nucleotides).

Time-resolution measurements constitute a unique way of studying the real-time dynamics in helium droplets. This has been vividly demonstrated by research involving pico- and femtosecond lasers in which metal atoms and their complexes with helium atoms are detached from droplets, as well as by nanosecond-resolved research on the reconstruction of the helium shell surrounding a tetracene molecule experiencing electronic excitation.

5. Other applications of helium nanodroplets

5.1 Synthesis of nonequilibrium structures

A promising application of helium droplets has been recently demonstrated by Nauta and Miller [31, 211] and Nauta et al. [112]. The researchers showed how it is possible to employ very cold helium droplets in synthesizing highly nonequilibrium structures which are impossible to produce in any other way.

Here, we take the example of producing a linear chain of HCN molecules [31]. First, however, it is pertinent to note that the formation of complexes with this molecule has also been intensively studied during gas expansion in a free jet. These experiments demonstrated that in stated conditions there is a tendency to form most stable isomers of the complex. Hence, the geometry of the complex that was detected in experiments usually corresponded to the structure predicted by calculations based on allowing for a global minimum. Only when the complex has several isomers with approximately equal energies can we expect the formation of more than one such isomer [212, 213]. This can be understood if we allow for the fact that clusters form in a very dense and relatively hot expansion region, where they still have sufficient energy to overcome the existing potential barriers on the energy surface and to land in the global minimum. Subsequent pair collisions with the carrier gas results in cooling to a very low temperature ($\sim 1 \text{ K}$) typical of an expanding gas in a free jet, so that the complex finds itself in the global minimum. The HCN trimer forms both linear and cyclic isomers in the course of expansion in a free jet [214, 215], which implies that these isomers have comparable energies, as predicted by the preliminary calculations done by Kurnig et al. [216]. The experimenters found that all larger HCN clusters that form during expansion in a free jet are nonpolar. This suggests that the resulting structures are disordered (cyclic or antiparallel), which agrees with the results of the calculations done in Refs [216-218].

In experiments with an HCN molecule inside a helium droplet, a bolometer was used as the detector of the cluster beam. The molecules were excited by the light from a tunable IR F-center laser. The vibrational spectra of the C–H bond were investigated. Figure 11 shows the spectrum taken in the region of the C–H bond of a linear chain of HCN molecules inside helium droplets. The origin of the vibrational transition for this vibration in helium falls at 3311.20 cm⁻¹. To remove the rotational structure from the transition spectra, Nauta and Miller [31] used a Stark cell and a strong static electric



Figure 11. Vibrational spectrum in the region of the C-H bond for a chain of HCN molecules. The absorption lines are observed up to heptamer clusters. The linear heptamer chain is shown at the top of the figure. The spectrum was recorded in the presence of an intense electric field used to align the polar chains inside the helium droplets. The intense field induced a collapse of the rotational bands into a single line for clusters of all sizes [31].

field (30 kV cm⁻¹). As noted in Section 3.1.4, a strong electric field effectively induces a collapse of the rotational band by orienting the dipoles [219], thus guaranteeing a spectral resolution needed to observe the separate lines that belong to large clusters (see Fig. 11). The researchers found that all observed bands exhibit a strong dependence on the applied electric field, which indicates that they are related to polar complexes. So far no nonpolar complexes, including cyclic trimers which were observed in an expanding jet, have been detected inside helium droplets.

Such chains with more than three monomers are not produced even in cold surroundings during supersonic gas expansion, where usually cyclic and other nonpolar structures may be formed. When an HCN molecule collides with a cluster inside which there is already another molecule, the long-range dipole-dipole forces orient (align along a line) two dipoles at distances at which other forces between two molecules do not act. The rapid rotational relaxation needed for such aligning to take place is probably caused by multiple collisions with the droplet surface, where the coupling with ripplons is rather strong. After the two dipoles are aligned, the molecules move closer to each other because of mutual attraction. What is important is that, as shown by Nauta and Miller, this process continues up to the point where the linear chain has been stretched over the entire diameter of the cluster. In view of this, it must be noted that the cluster diameter represents the theoretical limit in synthesizing the long chains of molecules inside helium droplets. For instance, the length of a chain consisting of 10 HCN molecules $(\sim 4 \text{ nm})$ is almost equal to the diameter of superfluid helium droplets produced in nozzle beams.

5.2 Chemical reactions in helium droplets

Intensive research into the problem of helium droplets has shown that such droplets constitute tiny isothermal reactors. It would be interesting to extend such experiments to chemical reactions which change the electronic structure of the initial particles substantially. In contrast to chemical reactions proceeding at high temperatures, reactions that are often activated by the thermal energy of the surrounding particles, at low temperatures (≤ 1 K) quantum effects, such as tunneling, could play the leading role. Thus, with helium droplets one can study reactions that occur because of tunneling with the lowest possible perturbations of the solvent. At very low temperatures of liquid helium, the orientation effect produced by the weak van der Waals forces may determine the extent to which reagents move closer to each other and, therefore, increase the yield of the products via a special channel. This channel may differ from the one determined by the coordinates of the reaction in the region where the chemical bonds are stronger [31, 211]. Note, for the sake of comparison, that at ordinary temperatures the effect of the van der Waals forces is negligible because of intensive thermal averaging. Thus, reactions at low temperatures may serve as a new approach to selective chemistry and possibly lead to the formation of unusual products.

In Section 4.3 we noted that the recombination of alkali metal atoms on the surface of helium droplets leads to selective formation of high-multiplicity spin states of dimers and trimers, since singlets are ejected by the droplet due to their high energy. This supports the above assumptions. The following bimolecular reaction in a droplet, accompanied by strong chemiluminescence of the products, has been recently observed by Lugovoj et al. [220] in their studies of the reaction between Ba atoms and N₂O molecules:

$$Ba + N_2 O \rightarrow BaO^* + N_2 \quad (\Delta H = 4.1 \text{ eV}), \qquad (5.1)$$

$$\operatorname{BaO}^*(\operatorname{A}^1\Sigma^+, \operatorname{v}') \to \operatorname{BaO}(\operatorname{X}^1\Sigma^+, \operatorname{v}'') + hv.$$
(5.2)

Figure 12 shows the chemiluminescence spectra recorded in helium droplets and in an Ar_N cluster [221]. The spectrum for the argon cluster (Fig. 12a) has two components. One component in the 400–600-nm range is structureless and corresponds to the emission of radiation by highly vibrationally and rotationally excited BaO molecules in the excited electronic state A, which leave the cluster immediately after the reaction on the cluster's surface has terminated. The other component in the 600–700-nm range consists of pronounced peaks that correspond to the emission of radiation by BaO (A, v' = 0) molecules that have relaxed to the ground state and are already in thermal equilibrium with the cluster. In the case of a helium cluster (Fig. 12b), these peaks are much narrower than for the argon cluster, because of the lower temperature and small inhomogeneous broadening.

Lugovoj et al. [220] exposed the following interesting effect. If approximately 15 xenon atoms are added to a droplet in which the reactions (5.1), (5.2) are taking place, the first component of the spectrum, the one related to the emission of radiation by highly vibrationally and rotationally excited BaO molecules in the upper electronic state, is suppressed. All radiation is emitted in the form of a vibrational progression of sharp spectral lines (Fig. 12c), which implies that the products are in equilibrium with the droplet, i.e., all the products were produced inside the droplets rather than on the droplet's surface. Thus, Lugovoj et al. [220] demonstrated how reactions inside helium droplets can be 'catalyzed'. Hence, ultracold helium droplets can be utilized as tiny reactors with catalytic activity to investigate multistage reactions. One would expect that such experiments will extend to many reactions involving atoms and molecular radicals, and to photochemical reactions.

5.3 Orientational effects

The electronic absorption spectra of tetracene molecules inside helium droplets in conditions where excitation is achieved by using laser light of two different directions of



Figure 12. Emission spectra of BaO in the $A^{1}\Sigma^{+}$, $v' = 0 \rightarrow X^{1}\Sigma^{+}$, v'' transition. The spectra were recorded for Ba atoms (a) initially adsorbed on Ar clusters [221], (b) adsorbed on uncontaminated helium clusters $(N = 2 \times 10^{5})$ [189], and (c) adsorbed on helium clusters doped with approximately 15 xenon atoms [220]. (From Ref. [25].)

polarization, namely, parallel to and perpendicular to the cluster beam, have recently been studied by Pörtner et al. [222]. Both the LIF method and the beam depletion method demonstrated a 15% increase in signal strength in the case of parallel polarization. This suggests that the molecules are polarized in the laboratory system of coordinates. The $S_0 \rightarrow S_1$ transition in tetracene is a b-type transition, with the result that its dipole moment is aligned with the short axis in the molecular plane. Thus, the long axis of the molecule is primarily aligned with the direction perpendicular to the axis of the helium droplet beam. Pörtner et al. [222] assume that this effect is related to the capture process: the droplets become oriented in space because of the preferable orientation of the collisional angular momentum in the direction perpendicular to the beam axis. These experiments pose the question of the need to investigate the possible effect of the processes of capture and evaporation of a droplet on the droplet's shape and the influence of this shape on the spectra of the molecules. A thorough study of the capture process by Harms et al. [60] showed that in the case of uncontaminated ⁴He clusters there is no deviation from the spherical droplet's shape.

5.4 Small doped helium-4 droplets

To establish the origin of the various spectral phenomena in helium droplets, such as ZPL splitting and modification of the

phonon wing structure in the case of large molecules, it is advisable to extend the research to clusters containing a molecule with the number N of helium atoms ranging from 1 to 100. Several researchers (see Refs [223-226]) applied spectroscopic methods to studying the complexes of several molecules with $N \leq 3$, produced in pulsed molecular beams. The vibrational-rotational structure present in the $B \leftarrow X$ transition of the He₂Cl₂ cluster has been investigated in detail by Sands et al. [224] and Hernández et al. [225, 226]. The He₂Cl₂ cluster is the smallest helium-containing cluster for which there are data on the allowed rotational states and for which Bose statistics is important. The helium atoms in the cluster are localized in a plane that is at right angles to the axis of the Cl₂ molecule and display a very large amplitude of vibrations of the He-He bond which has an energy of about 0.5 cm^{-1} . However, the number of helium atoms is possibly too small to observe the onset of the manifestation of the collective phenomena, which, apparently, requires that at least one shell (≈ 20 atoms) around the molecule be filled.

The generation of clusters of the size just mentioned is hindered by the weak interaction of the helium atoms and the insufficient cooling in ordinary conditions of gas expansion. These limitations have been successfully overcome by Even et al. [227], who used a newly designed source of the pulsed beam which operates at high gas pressures above the nozzle. The experimenters generated clusters of aromatic molecules (naphthalene, anthracene, and tetracene) with up to 20 helium atoms. The two-photon ionization technique was used to record the excitation spectra of the clusters and to study the cluster evolution as the number of helium atoms in the cluster increased.

5.5 Summary

The research discussed in this section demonstrated the possibility of using helium nanodroplets to synthesize highly nonequilibrium structures which are impossible to produce in any other way. When linear chains of molecules are synthesized inside helium nanodroplets, the diameter of the cluster is the theoretical limit imposed on the length of the chains.

Helium nanodroplets constitute tiny isothermal reactors. Quantum effects, such as tunneling, play the leading role at low temperatures. The employment of helium droplets opens up the possibility of studying chemical reactions that take place due to tunneling with the smallest possible perturbations of the solvent. Reactions at low temperatures may open up new avenues in the development of selective chemistry, which could lead to the creation of new products.

The possibility of utilizing ultracold helium droplets as small reactors with catalytic activity for studying multistage reactions has also been demonstrated. One can expect that in the future experiments of this type will be extended to many reactions with atoms and molecular radicals [24], and to photochemical reactions. It is also obvious that this method has great potential in synthesizing exotic and high-energydensity materials.

Another useful method of nonequilibrium synthesis, whose potential was recently demonstrated by Nauta et al. [121], must be mentioned in connection with the problems discussed in Sections 5.2-5.4. A cluster of chemically responsive metal atoms (Mg) was attached to a molecule (HCN) that is active in the IR region of the spectrum, and the rotational spectrum of this complex was recorded with a high resolution. It is usually very difficult to study metallic clusters,

since their UV spectra are broad lines and their IR spectra, if they exist, lie in the low-frequency range, where no lasers operate. The vibrational – rotational structure of the complex (rotational constants and line shifts) make it possible to gain information useful in studying the properties of the metallic cluster.

6. Helium nanodroplets and the Bose – Einstein condensate in traps

In the context of the problems related to helium nanodroplets and discussed in Section 2, we believe that a comparison of the properties of helium nanodroplets and Bose-Einstein condensates in traps would be very advantageous. As noted in Section 2, helium clusters have become the subject of intensive studies in the last 10-15 years. The first observation of Bose-Einstein condensation (BEC) in ultracold vapors of alkali metal atoms took place in 1995 [228-230]. These observations opened a new area of research, for which E A Cornell, W Ketterle, and C E Wieman were awarded the 2001 Nobel Prize in physics [231, 232]. The area in which BEC was first studied is at the interface between atomic physics and quantum optics. At first glance it would seem that these studies have no relation to helium clusters, since helium clusters are a typical subject of interest for the physics of condensed media and chemical physics. However, there exists a profound analogy between Bose-Einstein condensates in traps and helium clusters [27, 28]. The physics on which these two systems are based is closely related to the physics of superfluid substances. One could even say that helium droplets and atomic gases in traps correspond to limiting cases of a common system, since they are examples of, respectively, very dense and dilute quantum liquids occupying a confined space [27].

A quantum liquid constitutes a system of many interacting particles, which exhibits such quantum effects as zeropoint motion and motion with nondissipative and nonrotating velocity, which means that the system is superfluid. These and other features of a quantum liquid may be related to the existence of an *order parameter*. As soon as the particles cool off to a fairly low temperature, the length of their de Broglie wave becomes larger than the average distance between them, and the particles lose their individual properties. In the case of bosons they can be interpreted as components of a single 'macroscopic wave function'. The concept of an order parameter is a suitable instrument for describing this idea [27, 28].

The temperature at which these quantum effects manifest themselves is generally very low, so that the liquid usually freezes before this temperature is reached. In the case of ⁴He, the system becomes a quantum liquid at temperatures below ≈ 2.2 K and remains such down to absolute zero of temperature. In the case of condensates in traps, the vapors of alkali metal atoms are kept in a metastable gaseous state down to 30-50 nK, at which quantum effects become predominant. The existence of a metastable state agrees with the existence of kinetic equilibrium which is ensured by two-particle elastic collisions. On the other hand, the transition to thermodynamic equilibrium, at which the crystalline phase sets in, occurs because of three-particle collisions which are quite infrequent in highly dilute cold gases and take place on a long time scale.

Notice that there are well-developed theoretical models used in describing Bose-Einstein condensates (e.g., see

Refs [27, 28] and the literature cited therein). In order to describe such a system, one must solve an exact multiparticle Schrödinger equation or, which amounts to the same thing, find the eigenvalues of the operator for the interaction between many particles in the system [27, 28]. Generally, this is an extremely difficult problem, to put it mildly. Many properties of a Bose – Einstein condensate can be described by employing an approach that utilizes the density matrix and the Gross – Pitaevskiĭ equations [233, 234] for the order parameter. Several microscopic approaches have been developed in an attempt to describe dense quantum liquids, to which helium droplets belong. Some of them are based on the density matrix concept, while others rely on phenomenological theories [27] (say, the liquid-drop model).

6.1 Bose – Einstein condensation

The features of Bose-Einstein condensation have been thoroughly established for the case of noninteracting (free) particles. The system is represented by a set of single-particle states with energy ε_i , and each such state is populated by a certain number n_i of particles. At a given temperature T, the average number of particles populating a level is determined by the Bose statistics, given by the well-known formula

$$\langle n_i \rangle = \frac{1}{\exp\left[\beta\left(\varepsilon_i - \mu\right)\right] - 1},$$

where $\beta = (k_B T)^{-1}$, and μ is the chemical potential, with the total number of particles $N = \Sigma_i \langle n_i \rangle$. At fairly high temperatures, many states are thermally populated, and in each $\langle n_i \rangle$ is on the order of unity. Since for bosons there is no Pauli exclusion principle, a large number of bosons can occupy the same state at low temperatures. As the temperature is lowered and the chemical potential becomes comparable to the energy ε_0 of the lowest single-particle state, the population of this state becomes determined by a macroscopic number $N_0 = \langle n_0 \rangle \sim N$. This phenomenon is known as Bose–Einstein condensation. The critical temperature at which Bose–Einstein condensation sets in can be calculated on the basis of the single-particle Hamiltonian, with the corresponding thermodynamic limit $N \to \infty$ retained [27, 28].

In the simplest case of a homogeneous system of free bosons of mass *m*, with the volume *V* increasing but the particle number density n = N/V remaining constant, the critical temperature T_c is given by the formula [235]

$$k_{\rm B}T_{\rm c} = \frac{2\pi\hbar^2}{m} \left[\frac{n}{\zeta(3/2)}\right]^{2/3},\tag{6.1}$$

where \hbar is the Planck constant, ζ is the Riemann zeta function, with $\zeta(3/2) \approx 2.61$, which can be written as $n\lambda_T^3 \approx 2.61$, where λ_T is the thermal de Broglie wavelength: $\lambda_T = \left[2\pi\hbar^2/(mk_BT)\right]^{1/2}$.

Quantum effects become predominant at temperatures at which the de Broglie wavelength becomes larger than the average distance between the particles. The fraction of the condensate is then determined by the following formula [27]: $N_0/N = 1 - (T/T_c)^{2/3}$. All particles reside in the state $\varepsilon_0 = 0$ at T = 0, i.e., the system becomes fully condensed. This state has a homogeneous density and zero momentum, so that often one speaks of condensation in the momentum space. What is important is that in the case of helium-4 equation (6.1) yields a transition temperature that is quite close to T_{λ} , i.e., the temperature at which helium transforms into a superfluid [236].

The critical temperature for N bosons that are trapped by the spherical harmonic potential $V_{\text{ext}} = (1/2) m\omega_{\text{ho}}^2 r^2$, where $\omega_{\rm ho}$ is the frequency of the confining field, and r is the radial coordinate, is determined by the formula [237]

$$k_{\rm B}T_{\rm c} = \hbar\omega_{\rm ho} \left[\frac{N}{\zeta(3)}\right]^{1/3} \simeq 0.94\hbar\omega_{\rm ho} N^{1/3},$$
 (6.2)

and the condensate fraction amounts to $N_0/N =$ $1 - (T/T_c)^{1/3}$ [27]. A different temperature dependence of the condensate fraction in the inhomogeneous case, as compared to the homogeneous one, is caused by the higher density of states characterizing the Hamiltonian of the harmonic potential [27, 28]. All particles at T = 0 reside in the lowest eigenstate of the harmonic oscillator, namely, $\mu \rightarrow \epsilon_0 = (3/2) \hbar \omega_{ho}$. Thus, the distribution of the particle density is Gaussian, and the same is true of the momentum distribution. In contrast to the case of a uniform gas, condensation takes place both in the real space and in the momentum space. It was the formation of a sharp peak in the velocity distribution in the cloud of 87Rb atoms freed from a magnetic trap that provided the first experimental proof of the existence of a Bose-Einstein condensate in cold gases [228]. The transition temperature proved to be very close to the value predicted by equation (6.2).

6.2 Dilute cooled gases and dense liquids

In a dilute cooled gas of weakly interacting particles, the fraction of uncondensed particles is small. When the gas is homogeneous, the condensate's wave function is a constant quantity [27, 28], while in the case of an inhomogeneous gas the relevant wave function varies in space. Hence, a theory that describes a condensate in traps must allow for this spatial variation of the condensate. The average-field theory is applied to describe the system [27, 28], and many properties of the system are satisfactorily governed by the Gross-Pitaevskiĭ equation for the order parameter [233, 234]. This equation is derived for large values of N under the assumption that the fraction of uncondensed atoms is small. First, this means [27, 28] that the quantum fluctuations of the field operators must be small, so that $na^3 \ll 1$, where n is the particle number density, and a is the scattering length. Huang [235] has shown that the depletion of the condensate at T = 0is proportional to $(na^3)^{1/2}$. Second, thermal fluctuations must also be negligible, which places a limit on the temperature: $T \ll T_{\rm c}$. Only in such conditions can one assume that the total density *n* is approximately equal to the condensate density n_0 .

When the system is not dilute and does not consist of weakly interacting particles, as is the case with a helium droplet, the average-field theory breaks down. The quantum fluctuations outside the average field become essential. They may, for instance, lead to a considerable decrease in the condensate fraction even at T = 0, so that perturbative methods cease to work. In this case, to describe the system we must use either microscopic approaches so as to obtain more accurate solutions of the many-particle problem or phenomenological theories in which the liquid is examined from the macroscopic viewpoint (see Ref. [27] and the literature cited therein).

What is important here is to decide whether we can establish a relationship between dilute gases and dense liquids within a common theoretical approach. In a recent article, DuBois and Glyde [238] obtained encouraging results. The researchers applied the Monte Carlo variational method Physics-Uspekhi 47 (3)

to calculate the condensate fraction and found that it decreases approximately from unity to 10%, when na^3 increases from zero to its value in liquid helium, which is approximately 0.2-0.3 (the size of the interaction region was $a \approx 2-3$ Å, and $n \approx 0.022$ Å⁻³). They also noted an interesting feature related to the spatial dependence of the condensate, namely, that dense liquids usually have a higher fraction of the condensate at their surface, where the density is lower. Such an increase in the condensate fraction in helium droplets was first detected by variational calculations with the Monte Carlo method by Lewart et al. [239].

The simplest phenomenological model for liquids residing in a confined space is the liquid-drop model. The model examines a drop of radius R with a constant density and a pronounced surface. Many properties of droplets of a quantum liquid are described fairly well by this model [240]. However, it is unable to exactly predict the structure and excitations on the microscopic scale, i.e., on the scale of atomic distances. The next step in this approach was the use of the density functional concept (see the paper [27] and the references cited therein).

A direct consequence of the very large difference in the values of na^3 for condensates in traps and for helium droplets is that only in the first case can the total density be assumed approximately equal to the condensate density, since the uncondensed fraction counts for less than 1%. In helium droplets, the condensate density is equal to about 10% of the total density and reaches its maximum at the surface, where the system is more dilute [239, 241].

Notice that an important parameter of superfluid systems is the healing length $\xi = [8\pi na]^{-1/2}$ [27, 28]. The meaning of this parameter amounts to the following. Suppose that as a result of a certain factor the order parameter vanishes at a certain point, say, near an impurity or at a wall. Then the healing length is the distance at which the order parameter retains its value equal to the bulk value. The order of magnitude of the healing length for helium droplets and condensates in traps is listed in Table 5.

Table 5. Approximate scales of length (in meters) for a typical helium droplet and a Bose-Einstein condensate in a spherical trap: a, the size of the interaction region (in the case of helium) and the scattering length (in the BEC case); d, the average interatomic distance; ξ , the healing length; R, the system's radius, and a_{ho} , the size of the condensate (see Section 6.3.2). The corresponding density profiles are shown in Fig. 13. The energy per particle is about 6 K in the case of helium droplets, and about 60 nK in the case of a condensate. (Data taken from Ref. [27].)

	а	d	ξ	R
${}^{4}\text{He}_{N} \text{ droplets}$ $N = 10^{4}$	$\sim 3 \times 10^{-10}$	$\sim 3 \times 10^{-10}$	$\sim 10^{-10}$	$\sim 5 \times 10^{-9}$
87 Rb BEC $N = 10^5$ $\omega_{ho} = 2\pi (100 \text{ Hz})$ $a_{ho} = 10^{-6} \text{ m}$	$\sim 5 \times 10^{-9}$	$\sim 10^{-7}$	$\sim 10^{-7}$	$\sim 5 \times 10^{-6}$

6.3 Similarities and differences in features of helium nanodroplets and condensates in traps

6.3.1 Temperature. ⁴He droplets have a temperature of about 0.38 K [20], which is determined by the process of evaporation of the hottest atoms from the droplet after it has formed in the helium expansion process. This temperature is much lower than the temperature of the transition to the superfluid state in bulk helium, $T_{\lambda} = 2.17$ K. Calculations done with the Monte Carlo method for path integrals [242] have shown that even small droplets containing several dozen atoms are superfluid at such a temperature (see Sections 3 and 4 and Ref. [243]). In addition, the droplets are cold enough, so that we can ignore thermal activation of excited states. The lowest excited states are discretized modes (bulk and surface oscillations), which are scarcely populated at $T \approx 0.4$ K. Thus, helium droplets in many cases can be thought of as systems with T = 0 [27, 28].

Condensates in traps can be cooled to $\approx 30-50$ nK. As in the first case, this is the result of evaporation. But here the cooling via evaporation is induced and controlled by an external high-frequency field which affects the shape and depth of the confining potential, and because of this the hottest atoms escape from the trap. The cooling can be continued up to the point where most thermally excited atoms have left the condensate. Hence, the system can be interpreted as a condensate at T = 0. In contrast to helium droplets, the properties of gases in traps can be studied as functions of the temperature T, and the cooling processes can be stopped at any temperature. In this case, the gas has two components, namely, the condensate and the thermally heated cloud.

6.3.2 The ground state. In its ground state, a typical helium cluster consisting of $10^3 - 10^4$ atoms is a self-bonded liquid droplet with a fairly flat density distribution. The density at the droplet's center is close to that of a homogeneous liquid in the zero-pressure limit, i.e., n = 0.022 Å⁻³ (Fig. 13). If we assume that the droplet has a constant density and a pronounced surface, then its radius $R = r_0 N^{1/3}$, where $r_0 = 2.2$ Å, must be approximately 20 to 50 Å, which is much larger than the average interatomic distance. Actually, the real density profile varies smoothly because of the large zero-point motion of the atoms. The density decreases from the bulk value to zero over distances of approximately twice the average interatomic distance, i.e., over distances ranging from 6 to 9 Å, depending on the accuracy with which the thickness of the surface is determined (see Ref. [60] and the literature cited therein). The thickness of the surface region becomes comparable to the droplet's radius when the number of helium atoms is $N \leq 100$. But even for large droplets, the

diffusive nature of surfaces may play an important role. In particular, it is because of the diffusive surface that the average droplet density is lower than the density of bulk liquid helium. Hence, the atoms in a droplet are coupled more weakly than in a homogeneous liquid.

The liquid-drop model can be used to express the binding energy per particle in a droplet as a function of N [27]:

$$\frac{E}{N} = a_V + a_s N^{-1/3} + a_c N^{-2/3} + \dots,$$
(6.3)

where a_V is the bulk coefficient, i.e., the energy per particle in bulk liquid (in the limit of zero temperature and zero pressure), $a_V \cong 7.2$ K, and the second and third terms on the right-hand side are the surface and bending energies, respectively. Notice that Chin and Krotscheck [108] devised the following formula for the binding energy per atom in a helium cluster (in kelvins): $E/N = -7.21 + 17.71N^{-1/3} - 5.95N^{-2/3}$.

The density distribution in an uncontaminated helium droplet is determined by the balance between the kinetic energy related to the zero-point oscillations of the atoms and the potential energy of the interatomic interaction. One can also induce density modulations in the droplets due to the capture process of an impurity atom or molecule (see Section 3.4), as if applying an external potential to which the helium atoms adapt. This, however, has a local effect in the sense that the main changes in the density distribution are limited to a few first layers of atoms surrounding the captured particle.

In contrast to helium droplets, condensates in traps are not self-bonded. They are formed and preserved by an external confining harmonic potential of the type $V_{\text{ext}} = (1/2) m\omega_{\text{ho}}^2 r^2$ (in the case of an isotropic potential). If this potential is switched off, the condensate freely expands. The density distribution is governed by the balance between three energies, namely, the external energy the internal energy, and the quantum kinetic energy which emerges because of the uncertainty principle (this energy is usually called the *quantum pressure* and vanishes in the case of homogeneous systems) [27, 28].

If the atoms were not to interact (a = 0), the condensate would have the shape of the lowest single-particle state in a harmonic potential, i.e., the Gaussian shape with a width



Figure 13. Density profile of a ⁴He droplet at T = 0 (left half of the figure) and the density profile of ⁸⁷Rb Bose – Einstein condensate in a spherical trap at T = 0 and $a_{ho} = 1.08 \times 10^{-6}$ m [27].

 $a_{\rm ho} = [\hbar/(m\omega_{\rm ho})]^{1/2}$. In real condensates (a > 0), the repulsion between the atoms reduces the density at the center and because of this the condensate becomes bigger. Under the condition that $Na/a_{\rm ho} \ge 1$, which is met in a real experiment (see below), the Gross – Pitaevskiĭ equation makes it possible to derive (see Refs [27, 28]) an expression for the condensate's density: $n(r) = g^{-1}[\mu - V_{\rm ext}(r)]$, where g is the coupling constant: $g = 4\pi\hbar^2 a/m$. The density distribution has the shape of an inverted parabola. In the same limit, the binding energy per particle, which has the form [27, 28]

$$\frac{E}{N} = \frac{5\hbar\omega_{\rm ho}}{14} \left(\frac{15Na}{a_{\rm ho}}\right)^{2/5},\tag{6.4}$$

depends both on the harmonic-potential parameter and the scattering length. Only within a narrow region near the surface, where the density and interaction between the atoms are small and the surface profile is determined by the balance between the quantum pressure and the external potential, does the shape of the density distribution differ from that of an inverted parabola and the density gradually tend to zero [27] (see Fig. 13).

By now, several condensates of various geometries and different particles have been produced. Let us examine the most general situation, when the condensate consists of $10^5 - 10^6$ sodium or rubidium atoms in a trap with a confining field with a frequency $\omega_{\rm ho}/(2\pi) \sim 10-100$ Hz. The characteristic size of the condensate, $a_{\rm ho}$, is usually no greater than 10 µm, although in anisotropic traps condensates with dimensions up to 300 µm have been observed. Since the scattering length a < 10 nm, we have $a/a_{\rm ho} \approx 10^{-3}$, with the result that $Na/a_{\rm ho} \gg 1$. Thus, the density profile is described fairly well by an inverted parabola, and the surface region is thin.

Table 5 lists [27] the characteristic parameters for a ${}^{4}\text{He}_{N}$ droplet consisting of 10⁴ rubidium atoms and a condensate in a trap, with 10⁵ rubidium atoms in the condensate. It should be mentioned that the ratios of *d*, ξ , and *R* (see Table 5) for these two systems are approximately the same. The values of the quantities proper are in the nanometer range for helium droplets, and in the micrometer range for condensates in traps. The situation with *a* is quite different: this quantity is of the same order of magnitude as *d* in the dense liquid, and is much smaller than *d* in the dilute gas.

6.3.3 Elementary excitations. A distinctive feature of superfluid Bose liquids is that their excitation at a low energy corresponds to collective modes which can be described as fluctuations of the order parameter [27, 28]. Such a description is adequate when the excitation wavelength is larger than the healing length. Helium droplets and Bose – Einstein condensates in traps possess a limited radius *R*. As a consequence, their spectra are discrete [27, 28] and the excited states must be classified according to the number $n_{\rm r}$ of radial nodes and quantum values of angular momenta (*l* and *m* if the system is spherical). Discretization becomes especially important in the case of the lowest-energy excitations, whose wavelength is comparable to *R* and which correspond to oscillations of the system as a whole.

Another important class of excitations is comprised of excitations with $n_r = 0$ and $l \ge 2$. These modes correspond to shape oscillations, or surface excitations. In this case, the motion is concentrated primarily near the surface. The abovementioned collective states can be observed in experiments that either employ modulation of the external potential in the case of Bose – Einstein condensates in traps [244-246] or rely on the spectroscopic methods described in Sections 3 and 4 in the case of helium droplets.

Rotations and quantized vortices comprise an extremely interesting class of excitations in superfluid systems [247– 249]. Descriptions of their manifestations in helium droplets and condensates in traps, as well as the possibility of observing them in experiments, including those that use spectroscopic methods, can be found, say, in Refs [27, 28] (see also the references cited therein).

Thus, the results presented show that despite the diversity of properties of helium nanodroplets and condensates in traps there is a profound analogy between the two systems. They are also related through a common theoretical basis for describing Bose – Einstein condensates and helium droplets. Notice that the theory of weakly interacting Bose gases was developed long before Bose – Einstein condensates in traps were observed. It was developed in order to explain the behavior of superfluid helium. However, in helium droplets the value of na^3 is on the order of unity, which markedly limits the application of this theory.

7. Conclusions

The study of helium nanodroplets is one of the most interesting and rapidly developing areas of research at the interface between physics and chemistry. The scale and depth of experimental and theoretical work and the results obtained constitute a breakthrough in chemistry and physics, in particular, in spectroscopy and in the area of condensed media. In a relatively short time, many new effects were discovered, their nature was explained, and the laws governing them were established. These laws were found to be related to the helium nanodroplets proper and to the spectroscopy of molecules and clusters inside helium droplets at ultimately low temperatures. The parameters and properties of helium nanodroplets (clusters), including charged droplets, were studied, and the superfluid nature of the droplets was established. The experimental and theoretical work with helium nanodroplets made it possible to understand the similarities and differences in the properties of helium droplets and Bose-Einstein condensates in traps. Helium droplets and condensates in traps can be interpreted as the limiting cases of a common system, since they are examples of, respectively, extremely dense and dilute quantum systems with limited dimensions.

The experimental results clearly show that liquid helium is a very soft and practically unperturbed ultracold matrix. The advantage of this matrix is that at the temperature of a liquid droplet almost all 'hot' vibrational states and most rotational states become 'frozen'. Due to its softness, the structure of the helium matrix near a molecule adapts to that of the molecule. These properties of the quantum liquid of helium droplets make them a unique medium for high-resolution spectroscopy.

Spectroscopic methods made it possible to establish and understand many properties of the molecules and atoms that are at the surface and inside liquid superfluid helium droplets, as well as the nature of their interaction with helium atoms. What is more, these methods allowed researchers to establish many facts about the properties of small liquid helium droplets. Spectroscopic measurements have been taken to study elementary excitations in helium droplets, and the temperature of such droplets has been established. The spectroscopic approach to the study of metallic clusters inside or at the surface of helium droplets may become the basis for studying the problem that has long awaited a solution: How do metallic properties change with the size of the cluster? Perhaps this approach will also make it possible to establish the threshold cluster size needed for superconductivity to set in. The helium droplet method allows the production of various atomic and atomic-molecular complexes. For instance, in helium droplets one can synthesize mixed metallic clusters or clusters containing atoms of metals and organic molecules, which opens up the possibility of creating new nanomaterials.

Further research into the problem of helium nanodroplets will certainly lead to discoveries of many interesting effects and will reveal new possibilities for studying the physicochemical processes at the atomic-molecular level and at extremely low temperatures.

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